



รายงานวิจัยฉบับสมบูรณ์

เรื่อง

การสังเคราะห์สารประกอบชนิดใหม่ของอนุพันธ์ Aryl-ethenylpyridinium และ Aryl-ethenylquinolinium เพื่อหาสารที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้น

Synthesis of New Aryl-ethenylpyridinium and
Aryl-ethenylquinolinium derivatives Toward the Non-Linear Optic

โดย

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ได้รับทุนอุดหนุนการวิจัยจากงบประมาณแผ่นดิน ปีงบประมาณ 2551 และ

เงินรายได้มหาวิทยาลัย ประจำปีงบประมาณ 2552

มหาวิทยาลัยสงขลานครินทร์ วิทยาเขตหาดใหญ่ สงขลา

กิตติกรรมประกาศ

ผู้วิจัยขอขอบคุณ มหาวิทยาลัยสงขลานครินทร์ ที่ได้ให้ทุนอุดหนุนการวิจัยจากเงินงบประมาณแผ่นดิน ประจำปีงบประมาณ 2551 และเงินรายได้มหาวิทยาลัย ประจำปีงบประมาณ 2552 ทำให้สามารถดำเนินงานวิจัยได้ตามความมุ่งหมาย

ผู้วิจัยขอขอบคุณ ศาสตราจารย์ ดร. สูง คุณ พัน มหาวิทยาลัยไซน์ มาเลเซีย ที่ได้ให้ความอนุเคราะห์ในการเก็บข้อมูลการเลี้ยงเบนของรังสีเอกซ์บนผลึกเดี่ยว

ผู้วิจัยขอขอบคุณภาควิชาเคมี ในการสนับสนุนอุปกรณ์และสถานที่ในการทำวิจัย ขอขอบคุณ นายภูมิศักดิ์ เรือนवास นักศึกษาปริญญาเอก นางสาวกุลภา ชนะวรร โณ และ นางสาววัลรัตน์ กอบเกียรติถวิล นักศึกษาปริญญาโท สาขาเคมีอินทรีย์ ภาควิชาเคมี คณะวิทยาศาสตร์ สำหรับการช่วยวิจัย ขอขอบคุณ นายธีรศักดิ์ อนันตพงศ์ ในการช่วยทดสอบฤทธิ์ทางชีวภาพ และขอขอบคุณผู้บริหาร และเจ้าหน้าที่ของมหาวิทยาลัยสงขลานครินทร์ ที่ได้ให้การสนับสนุนทำให้งานวิจัยดำเนินไปได้ด้วยดี

สุชาดา จันทร์พรหมมา

ฉัตรชนก กะราลัย

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(Reprint 1)

1-Methyl-4-[(E)-2-(2-thienyl)ethenyl]pyridinium 4-chlorobenzenesulfonate

(Reprint 2)

(E)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methoxybenzenesulfonate
monohydrate

(Reprint 3)

(E)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium iodide sesquihydrate

(Reprint 4)

1-Methyl-2-[(E)-2-(2-thienyl)ethenyl]quinolinium iodide

(Reprint 5)

1-Methyl-4-[(E)-2-(2-thienyl)ethenyl]pyridinium 4-methylbenzenesulfonate

(Reprint 6)

(E)-4-[4-(Dimethylamino)styryl]-1-methylpyridinium 4-bromobenzenesulfonate

(Reprint 7)

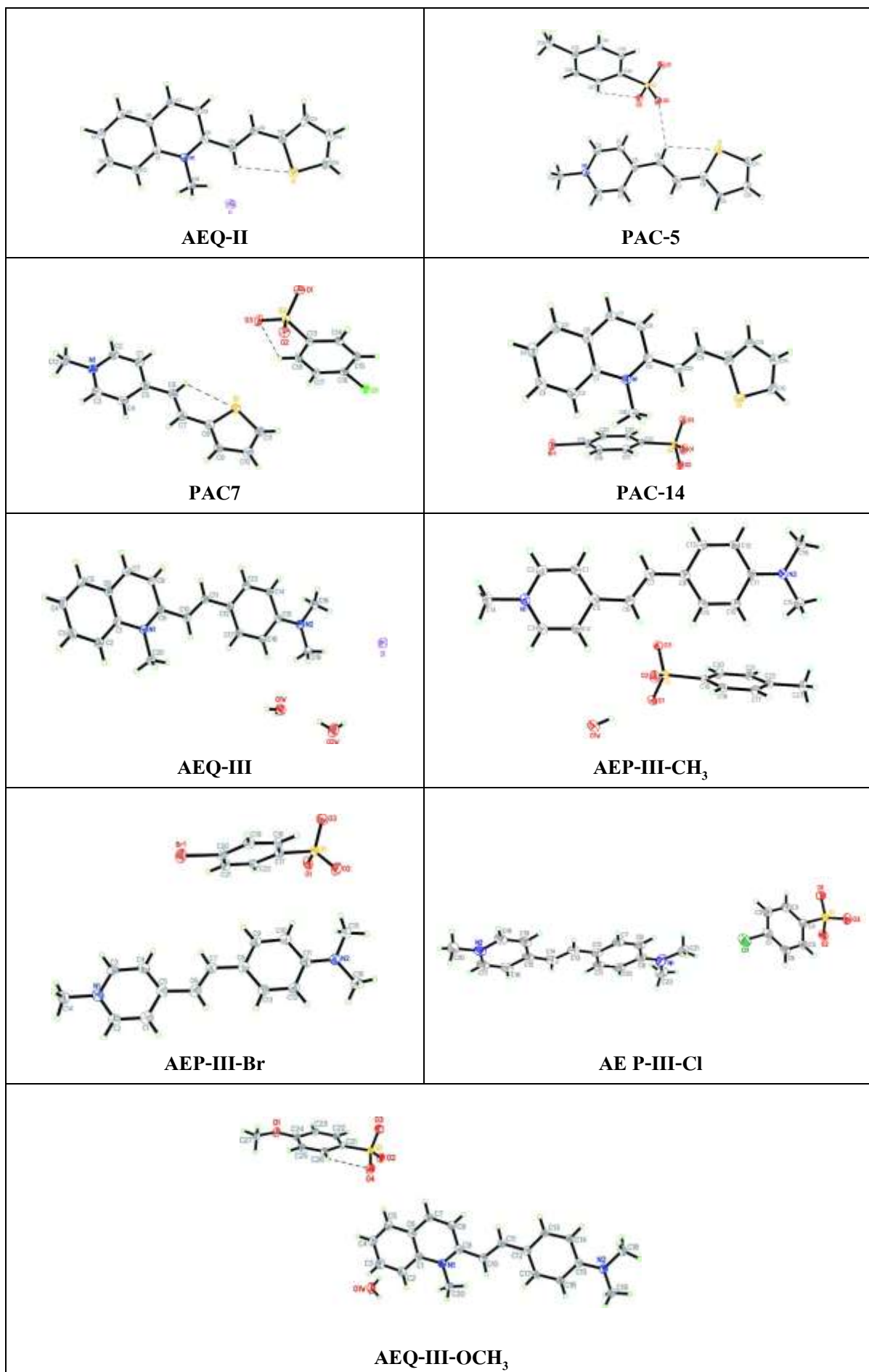
1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]quinolinium 4-bromobenzenesulfonate

(Reprint 8)

Synthesis, structure and in vitro antibacterial activities of new hybrid disinfectants
quaternary ammonium compounds: Pyridinium and quinolinium stilbene
benzenesulfonates

บทคัดย่อ

ทำการสังเคราะห์สารอนุพันธ์ของ pyridinium และ quinolinium จำนวน 20 สาร คือ **AEP-II**, **AEQ-II**, **PAC-5**, **PAC-6**, **PAC-7**, **PAC-8**, **PAC-13**, **PAC-14**, **PAC-15**, **PAC-16**, **AEP-III**, **AEP-III-CH₃**, **AEP-III-Br**, **AEP-III-Cl**, **AEP-III-OCH₃**, **AEQ-III**, **AEQ-III-CH₃**, **AEQ-III-Br**, **AEQ-III-Cl** และ **AEQ-III-OCH₃** เพื่อหาสารที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้น ทำการหาโครงสร้างสารสังเคราะห์ด้วยเทคนิคทางสเปกโทรสโกปี และได้ทำการตกผลึกและหาโครงสร้างด้วยเทคนิคการเลี้ยวเบนของรังสีเอ็กซ์บนผลึกเดี่ยวของสารได้ 9 สาร คือ **AEQ-II**, **PAC-5**, **PAC-7**, **PAC-14**, **AEQ-III**, **AEP-III-CH₃**, **AEP-III-Br**, **AEP-III-Cl** และ **AEQ-III-OCH₃** และ พบว่าสาร **AEQ-II**, **PAC-5** และ **AEP-III-CH₃** ตกผลึกใน centrosymmetric $P\bar{1}$ space group **PAC-7**, **PAC-14** และ **AEQ-III-OCH₃** ตกผลึกใน centrosymmetric $P2_1/c$ space group **AEQ-III** ตกผลึกใน centrosymmetric $C2/c$ space group **AEP-III-Br** และ **AEP-III-Cl** ตกผลึกใน centrosymmetric Cc space group และสารทั้งเก้าชนิดไม่แสดงสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้นอันดับสอง (second-order nonlinear optic) และได้ทำการทดสอบฤทธิ์ต้านเชื้อแบคทีเรียของสาร 8 ชนิด คือ **AEP-III-CH₃**, **AEP-III-Br**, **AEP-III-Cl**, **AEP-III-OCH₃**, **AEQ-III-CH₃**, **AEQ-III-Br**, **AEQ-III-Cl** และ **AEQ-III-OCH₃** พบว่าสารดังกล่าวออกฤทธิ์ต้านเชื้อแบคทีเรียแบบจำเพาะเจาะจงต่อเชื้อแบคทีเรียชนิด MRSA



1. บทนำ

ในการทำวิจัยทางด้านสารสังเคราะห์หัวข้อหนึ่งที่ได้รับคามสนใจกันอย่างแพร่หลายจวบจนปัจจุบันคือ การสังเคราะห์สารเพื่อหาสารประกอบที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้น(Non Linear Optic, NLO) เนื่องจากสารประกอบที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้นนั้นสามารถนำมาประยุกต์ใช้ทางด้านอิเล็กทรอนิกส์ การเก็บข้อมูล ทางด้านวัสดุศาสตร์ ทางด้านการสื่อสาร (telecommunications) และ electro-optics เช่น สามารถใช้เปลี่ยนความถี่ของแสงให้มีพลังงานสูงขึ้น เป็นต้น และเป็นเรื่องที่น่าสนใจมากในการที่จะหาสารที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้นที่มีสมบัติเป็น higher order NLO และมีความคงตัวสูงด้วย โดยทั่วไปสารประกอบที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้นนั้นจะต้องเป็นสารที่มีขั้วสูง (hyperpolarizability) สารอินทรีย์หลายชนิดที่เป็นระบบ π -conjugated จึงได้รับความสนใจที่จะศึกษามาก และจากทฤษฎีสารที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้นต้องเป็นสารที่ตกผลึกใน space group แบบ noncentrosymmetric space group กล่าวคือ ไม่มี inversion center ด้วย ซึ่งหากสามารถสังเคราะห์สารและได้สารที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้นนั้นก็จะเป็ประโยชน์ต่อการพัฒนาเพื่อการประยุกต์ใช้ต่อไป

จากรายงานการวิจัยเกี่ยวกับการสังเคราะห์สารที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้น (1-10, 12-14, 16) พบว่าสารกลุ่มหนึ่งที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้นนั้น ได้แก่ สารอนุพันธ์ของสารประกอบ stilbazolium *p*-toluenesulfonate เช่น N'-(4-dimethylaminophenyl)ethenylpyridinium *p*-toluenesulfonate, 1-methyl-4-(2-(4-(dimethylamino)-phenyl)ethenyl)pyridinium *p*-toluenesulfonate (DAST), N'-(4-hydroxyphenyl)ethenylpyridinium *p*-toluenesulfonate (HOST), 1-methyl-4-(2-(4-(dimethylamino) phenyl)ethenyl)pyridinium *p*-toluenesulfonate, 4-Methoxy benzaldehyde-N-methyl-4-stilbazolium tosylate (MBST) และ 4-Hydroxy benzaldehyde-N-methyl-4-stilbazolium tosylate (HBST) เป็นต้น นอกจากนี้จากรายงานการวิจัยยังพบว่า ผลึกของสารอินทรีย์ที่เป็น ionic salts แสดงสมบัติทางทัศนศาสตร์ดีกว่าสารที่เป็น non-ionic (3)

จากสมบัติที่น่าสนใจและเป็นประโยชน์ในการประยุกต์ของสาร NLO ทำให้ผู้วิจัยสนใจออกแบบสารที่คาดว่าน่าจะมีสมบัติ NLO และทำการสังเคราะห์และหาโครงสร้างสารประกอบที่เป็น organic-inorganic salts เพื่อหาสารที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้นเพื่อพัฒนาหรือประยุกต์ใช้ในด้านวัสดุศาสตร์ และวัสดุทางแสง (optical materials) ต่อไป และจากรายงานการวิจัยที่เกี่ยวข้องพบว่า สารที่มีระบบ π conjugated และสารอนุพันธ์ของ benzenesulfonate และ pyridinium ได้รับการสนใจในการศึกษา ผู้วิจัยจึงต้องการศึกษาการเตรียมสารกลุ่มนี้โดยการเพิ่มความเป็น π conjugated และเปลี่ยนหมู่ donor เพื่อให้ได้สารที่มีความเป็น polarity ที่แตกต่างกัน

ในการออกแบบสารสังเคราะห์เพื่อหาสารประกอบที่มีสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้น นั้นโดยทั่วไปต้องคำนึงคุณสมบัติพื้นฐาน 2 ข้อ คือ สารต้องมีค่า hyperpolarizability สูง ซึ่งสารที่มีระบบ π -conjugated จะสอดคล้องกับสมบัติข้อนี้ และสมบัติอีกข้อคือ สารสังเคราะห์นั้นต้องตกผลึกใน noncentrosymmetric space group กล่าวคือ การจัดเรียงตัวในโครงสร้างผลึกไม่มี inversion center ซึ่งจะต้องทำการตกผลึกสารที่สังเคราะห์ได้และทำการหาโครงสร้างผลึกด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยว (single crystals X-ray structure determination) เพื่อให้ได้ข้อมูล space group ของผลึกดังกล่าว และผลึกที่ได้ต้องมีขนาดใหญ่พอที่จะศึกษาสมบัติทางทัศนศาสตร์ด้วย และโดยทั่วไปสารที่มีลักษณะการ packing ของโมเลกุลในของแข็งเป็นแบบ parallel ก็จะมีสมบัติเป็น NLO ที่ดีด้วย และหากผลึกของสารสังเคราะห์นั้นมีลักษณะ transparent ในช่วง visible light ก็จะมีดีมากในการใช้เป็นสาร NLO ดังนั้นผู้วิจัยจึงเลือกระบบของสารอินทรีย์ที่มี π -conjugated ที่ไม่มีหมู่ chromophores มากจนเกินไป และเลือกโลหะไอออน Zn(II) เนื่องจากมีแนวโน้มการเกิดสารประกอบแบบไม่มีสี ซึ่งจะไม่ดูดกลืนแสงในช่วง visible light จากทฤษฎีและสมมติฐานดังกล่าวจึงมีแนวคิดในการออกแบบสารสังเคราะห์ PAC1-PAC20 ดังเสนอในโครงการวิจัยนี้

2. วัตถุประสงค์ของโครงการ

- 2.1 เพื่อสังเคราะห์และหาโครงสร้างของสารประกอบอนุพันธ์ของ Aryl-ethenylpyridinium และ Aryl-ethenylquinolinium โดยเทคนิคทางสเปกโทรสโกปี
- 2.2 เพื่อหาโครงสร้างผลึกของสารประกอบ Aryl-ethenylpyridinium และ Aryl-ethenylquinolinium ที่สังเคราะห์และตกผลึกได้
- 2.3 เพื่อหาสมบัติทางทัศนศาสตร์ของสารที่ได้จากข้อ 2
- 2.4 เพื่อให้ได้ข้อมูลความสัมพันธ์ของ crystal packing และสมบัติทางทัศนศาสตร์
- 2.5 เพื่อหาสมบัติที่น่าสนใจทางด้านอื่นในกรณีที่สารไม่แสดงสมบัติทางทัศนศาสตร์
- 2.6 เพื่อสร้างผลงานทางวิชาการตีพิมพ์ในวารสารวิชาการระดับนานาชาติ
- 2.7 เพื่อสร้างความร่วมมือกับนักวิจัยชาวต่างชาติ (อินเดีย) ในส่วนของการศึกษาสมบัติทางทัศนศาสตร์

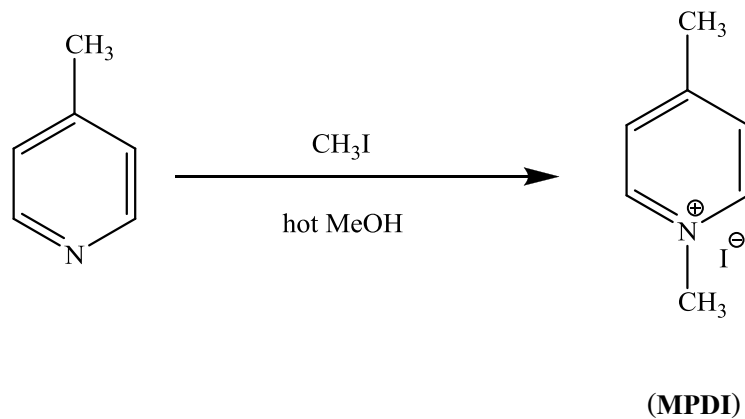
3. ขั้นตอนการวิจัย

- 3.1 ค้นคว้าเอกสาร เตรียมสารเคมี และอุปกรณ์ห้องปฏิบัติการ
- 3.2 สังเคราะห์สารประกอบ 1,4-Dimethylpyridinium iodide และ 1,2-Dimethylquinolinium iodide ดังแผนการสังเคราะห์ที่ 3.1-3.2 พร้อมหาโครงสร้างสารด้วยเทคนิคทางสเปกโทรสโกปี (UV-Vis, FT-IR และ NMR)
- 3.3 สังเคราะห์สารประกอบ Aryl ethenylpyridinium และ Aryl-ethenylquinolinium ดังแผนการสังเคราะห์ที่ 3.3-3.4 พร้อมหาโครงสร้างสารด้วยเทคนิคทางสเปกโทรสโกปี (UV-Vis, FT-IR และ NMR)

- 3.4 สังเคราะห์ Benzenesulfonate salts ดังแผนการสังเคราะห์ที่ 3.5
พร้อมหาโครงสร้างสารด้วยเทคนิคทางสเปกโทรสโกปี (UV-Vis, FT-IR และ NMR)
- 3.5 สังเคราะห์สารประกอบ Aryl-ethenylpyridinium benzenesulfonates และ
Aryl-ethenylquinolinium benzenesulfonates ดังแผนการสังเคราะห์ที่ 3.6–3.7
พร้อมหาโครงสร้างสารด้วยเทคนิคทางสเปกโทรสโกปี (UV-Vis, FT-IR และ NMR)
- 3.6 สังเคราะห์ Aryl-ethenylpyridinium zinc iodide และ Aryl-ethenylquinolinium zinc iodide
ดังแผนการสังเคราะห์ที่ 3.8-3.9 พร้อมหาโครงสร้างสารด้วยเทคนิคทางสเปกโทรสโกปี
(UV-Vis, FT-IR และ NMR)
- 3.7 ทำการตกผลึกสารที่สังเคราะห์ได้จากข้อ 3.5-3.6 เพื่อให้ได้ผลึกที่ดีและมีขนาดเหมาะสม
เพื่อการหาโครงสร้างด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยว โดยใช้ตัวทำละลาย
ชนิดต่างๆ เพื่อให้ได้ตัวทำละลายที่เหมาะสมในการตกผลึก
- 3.8 ทำการเก็บข้อมูลการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยวของผลึกที่ได้ ด้วยเทคนิค
Single crystal X-ray Diffractions ด้วยเครื่อง APEX II CCD
- 3.9 หาโครงสร้างผลึกของสารประกอบที่ได้จากข้อมูลการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยว
- 3.10 วิเคราะห์โครงสร้างสามมิติของสารประกอบและการ packing ของโมเลกุลในหน่วยเซลล์
- 3.11 หาสมบัติทางทัศนศาสตร์ของสารที่สังเคราะห์ได้และตกผลึกใน non-centrosymmetric
space group ด้วยเทคนิค classical powder SHG measurements เทียบกับ urea ซึ่งพัฒนาโดย
Kurtz and Perry
- 3.12 พิจารณาความสัมพันธ์ของโครงสร้างสามมิติ และ crystal packing กับ สมบัติ NLO ที่ได้
- 3.13 สรุป เขียนรายงานการวิจัย และ manuscripts เพื่อตีพิมพ์ผลงานในวารสารวิชาการ
ระดับนานาชาติ

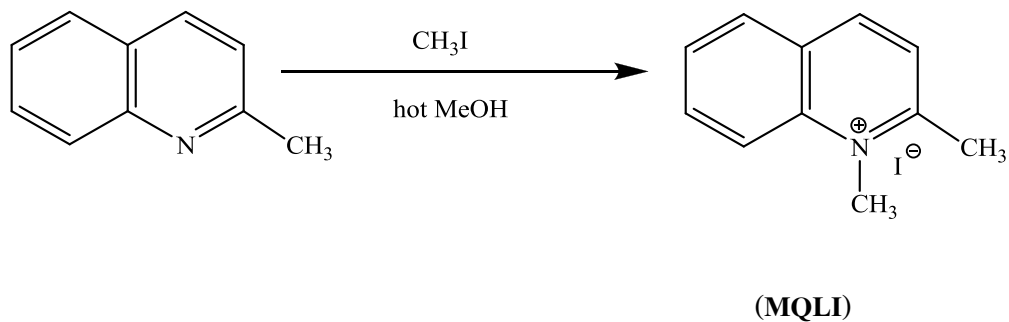
Scheme 3.1 การเตรียม 1,4-Dimethylpyridinium iodide (MPDI) เพื่อใช้ในการสังเคราะห์

Aryl-ethenylpyridinium

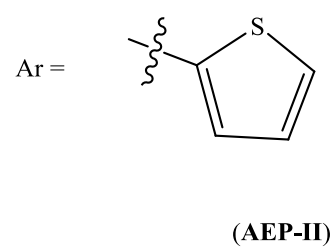
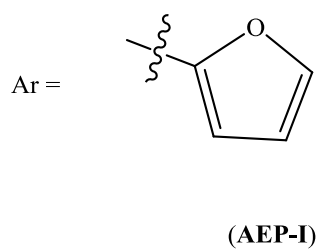
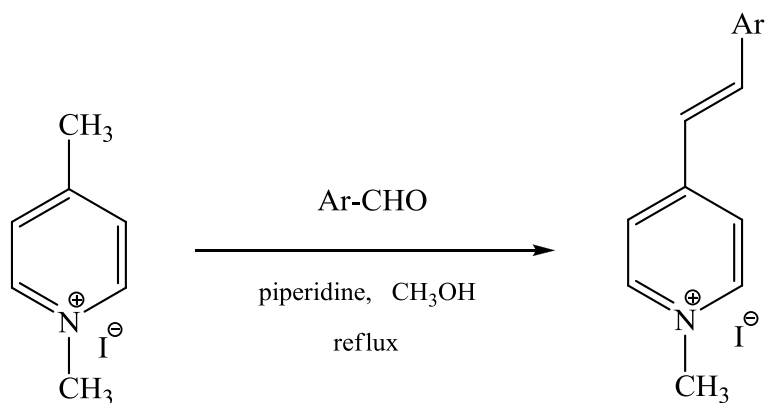


Scheme 3.2 การเตรียม 1,2-Dimethylquinolinium iodide (MQLI) เพื่อใช้ในการสังเคราะห์

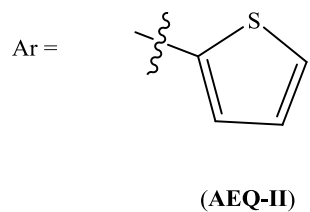
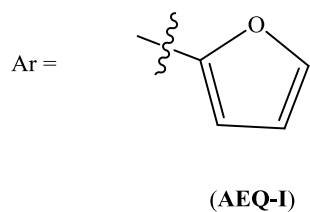
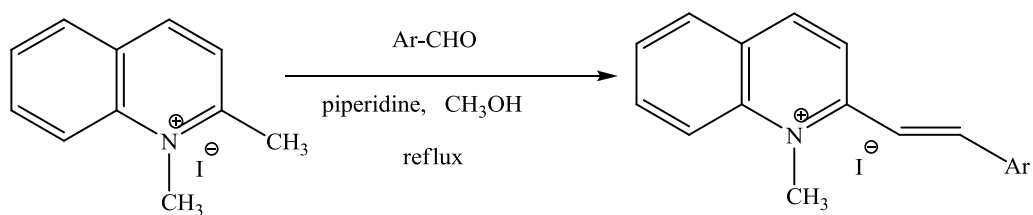
Aryl-ethynylquinolinium



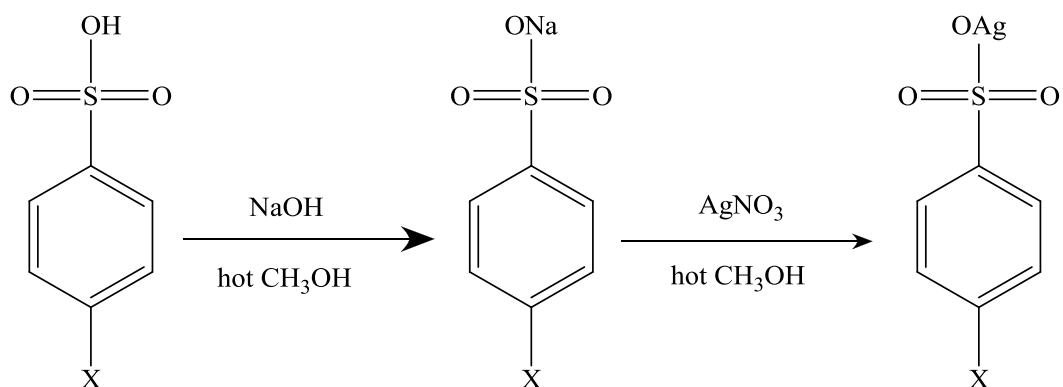
Scheme 3.3 การสังเคราะห์ Aryl ethenylpyridinium (AEP)



Scheme 3.4 การสังเคราะห์ Aryl ethenylquinolinium (AEQ)

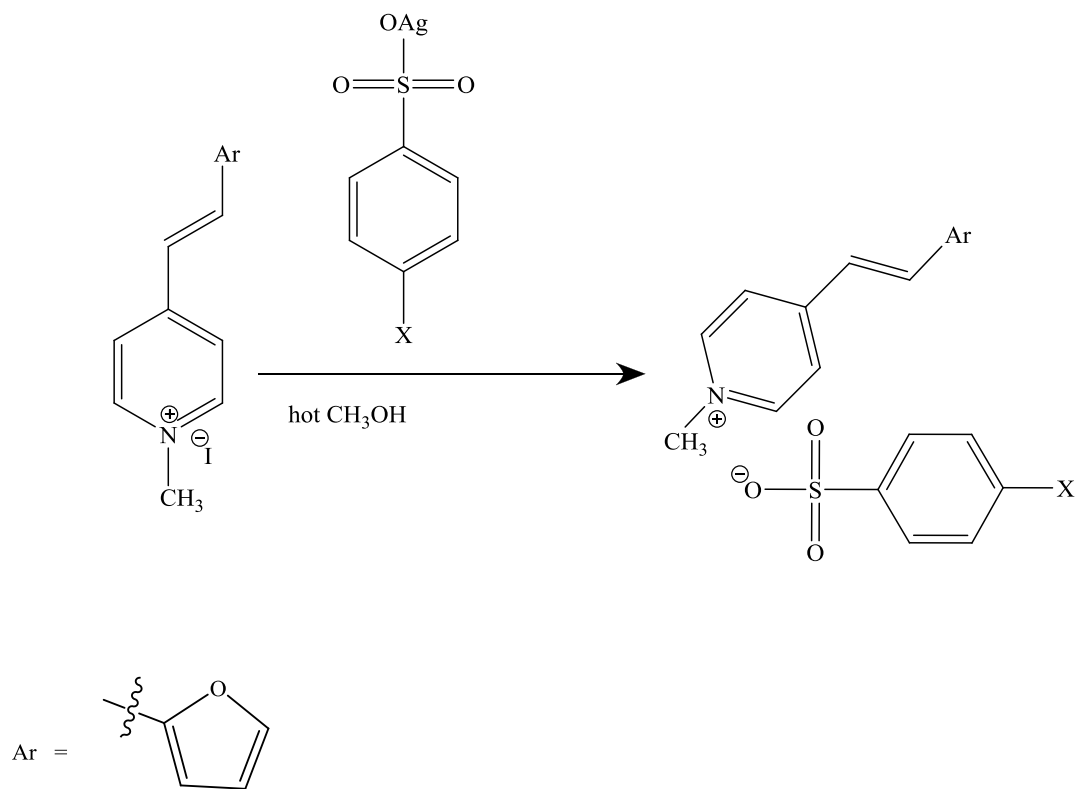


Scheme 3.5 การสังเคราะห์ Benzenesulfonate salts (An-X)

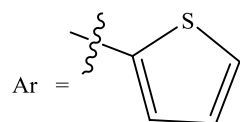


เมื่อ $\text{X} = \text{CH}_3$ (An-Me), OCH_3 (An-OMe), Cl (An-Cl) and Br (An-Br)

Scheme 3.6 การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (AEP-An)

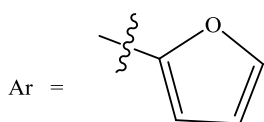
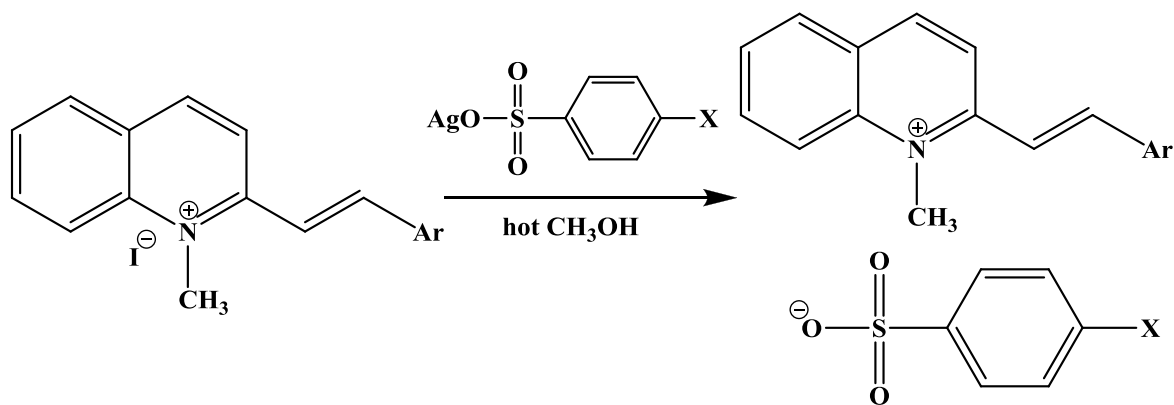


และ X = CH₃ (AEP-I-An-Me) หรือ PAC-1
 Br (AEP-I-An-Br) หรือ PAC-2
 Cl (AEP-I-An-Cl) หรือ PAC-3
 และ OCH₃ (AEP-I-An-OMe) หรือ PAC-4

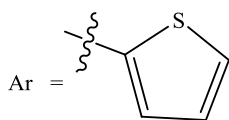


และ X = CH₃ (AEP-II-An-Me) หรือ PAC-5
 Br (AEP-II-An-Br) หรือ PAC-6
 Cl (AEP-II-An-Cl) หรือ PAC-7
 และ OCH₃ (AEP-II-An-OMe) หรือ PAC-8

Scheme 3.7 การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (AEQ-An)

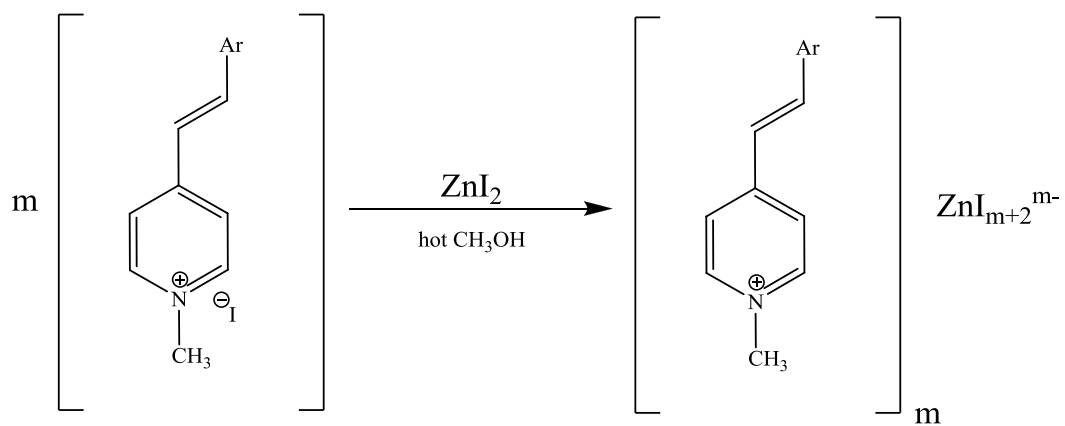


และ X = CH₃ (AEQ-I-An-Me) หรือ PAC-9
 Br (AEQ-I-An-Br) หรือ PAC-10
 Cl (AEQ-I-An-Cl) หรือ PAC-11
 และ OCH₃ (AEQ-I-An-OMe) หรือ PAC-12

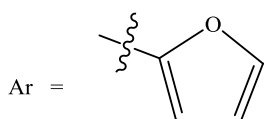


และ X = CH₃ (AEQ-II-An-Me) หรือ PAC-13
 Br (AEQ-II-An-Br) หรือ PAC-14
 Cl (AEQ-II-An-Cl) หรือ PAC-15
 และ OCH₃ (AEQ-II-An-OMe) หรือ PAC-16

Scheme 3.8 การสังเคราะห์ Aryl ethenylpyridinium zinc iodide (AEP-ZnI)

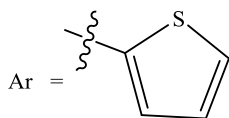


เมื่อ



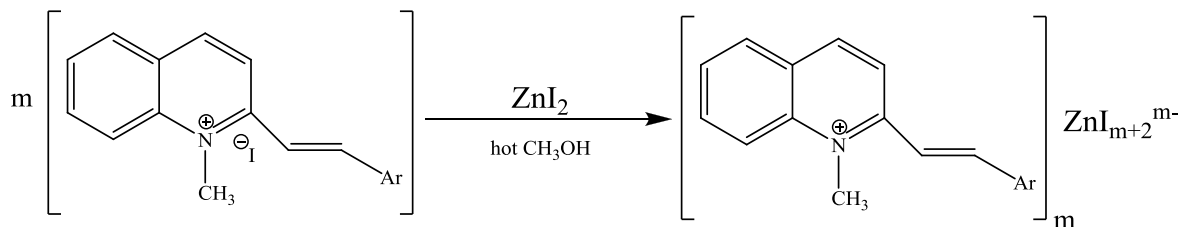
AEP-I-ZnI หรือ PAC-17

และ

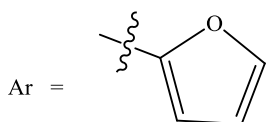


AEP-II-ZnI หรือ PAC-18

Scheme 3.9 การสังเคราะห์ Aryl ethenylquinolinium zinc iodide (AEQ-ZnI)

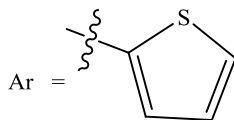


เมื่อ



(AEQ-I-ZnI) หรือ PAC-19

และ

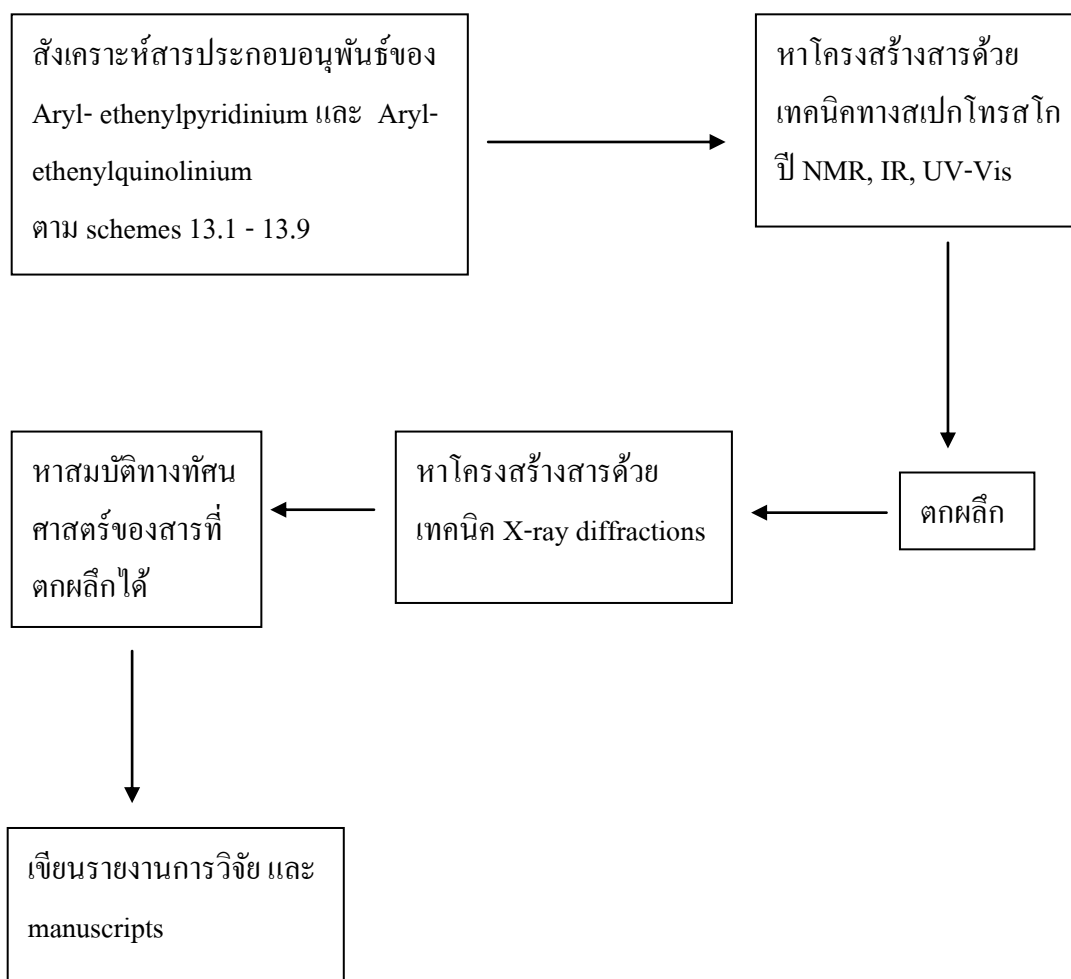


(AEQ-II-ZnI) หรือ PAC-20

สถานที่ทำการวิจัยหรือเก็บข้อมูล

- ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ วิทยาเขตหาดใหญ่ จังหวัดสงขลา
- X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, Penang, Malaysia

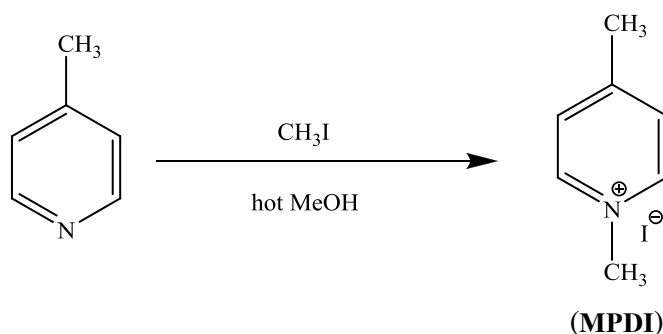
แผนการดำเนินงานตลอดโครงการวิจัย



4. วิธีการทดลอง และ ผลการทดลอง

ทำการสังเคราะห์สารและหาโครงสร้างสารด้วยเทคนิคทางสเปกโทรสโกปีได้ผลดังนี้

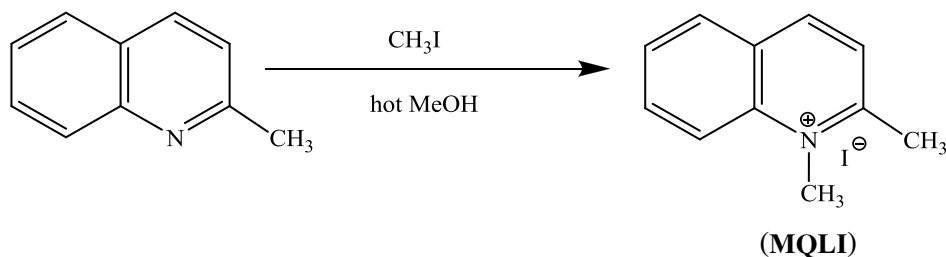
การเตรียม 1,4-Dimethylpyridinium iodide (MPDI) ตาม Scheme 3.1 เพื่อใช้ในการสังเคราะห์ Aryl-ethenylpyridinium



ละลาย 4-picoline (1) (0.05 โมล) ในเมทานอลเย็น 5 มิลลิลิตร พร้อมคนสารละลายที่อุณหภูมิห้อง 5 °C ค่อยๆเติม methyl iodide (CH₃I) 3.2 มิลลิลิตร (0.05 โมล) ลงในสารละลายอย่างช้าๆ คนของผสมที่อุณหภูมิ 5 °C เป็นเวลา 1 ชั่วโมง จากนั้นรีฟลักภายใต้บรรยากาศก๊าซไนโตรเจนที่อุณหภูมิ 60 °C เป็นเวลา 5 ชั่วโมง มีของแข็งสีขาวเกิดขึ้น นำขวดปฏิกิริยาไปตั้งในตู้เย็นเป็นเวลา 1 วัน สารในขวดปฏิกิริยาเกิดเป็นของแข็งหมด กรองตะกอนแบบลดความดันไปทำให้แห้งโดยใช้ vacuum ได้ของแข็งสีเหลืองอ่อนของ 1,4-dimethylpyridinium iodide (MPDI) (17.00 กรัม 72% mp. 140-142 °C)

ผลิตภัณฑ์เป็นของแข็งสีเหลืองอ่อน (17.00 g, 72%) จุดหลอมเหลว 140-142 °C, UV-Vis (CH₃OH) λ_{\max} (nm) (log ϵ): 219.7 (3.78), 255.3 (3.16), FT-IR (KBr) $\nu(\text{cm}^{-1})$: 1600-1500 (C=C stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 9.13 (2H, *d*, *J* = 6.3 Hz), 7.88 (2H, *d*, *J* = 6.3 Hz), 4.62 (3H, *s*), 2.69 (3H, *s*)

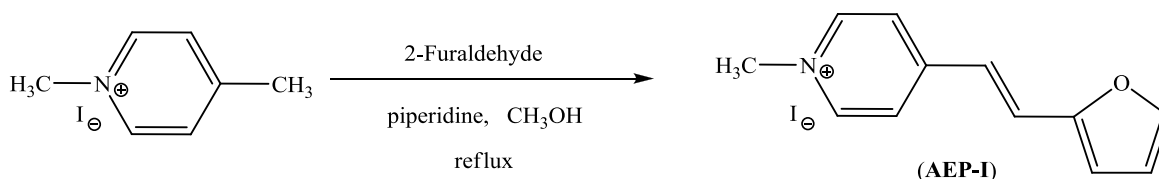
การเตรียม 1,2-Dimethylquinolinium iodide (MQLI) ตาม Scheme 3.2 เพื่อใช้ในการสังเคราะห์ Aryl-ethynylquinolinium



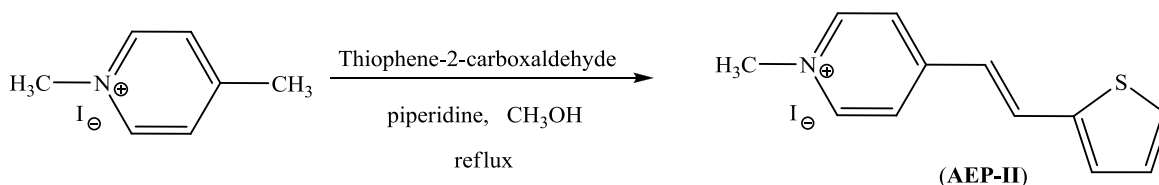
ละลาย quinaldine (0.07 โมล) ในเมทานอลเย็น 10 มิลลิลิตร คนสารละลายที่อุณหภูมิ 5 °C ค่อยๆ เติม methyl iodide (CH₃I) 4.65 มิลลิลิตร (0.07 โมล) ลงในสารละลายช้าๆ คนของผสมที่อุณหภูมิ 5 °C เป็นเวลา 1 ชั่วโมง จากนั้นรีฟลักซ์ภายใต้บรรยากาศก๊าซไนโตรเจนที่อุณหภูมิ 60 °C เป็นเวลา 3 ชั่วโมง เกิดของแข็งสีเหลืองนำขวดปฏิกิริยาไปทำให้เย็นในตู้เย็นเป็นเวลา 1 วัน สารในขวดปฏิกิริยาเกิดเป็นของแข็งหมด กรองตะกอนแบบลดความดันได้ของแข็งสีเหลืองนำไปทำให้แห้งโดยใช้ vacuum ได้ของแข็งสีเหลืองของ 1,2-dimethylquinolinium iodide (MQLI)

ผลิตภัณฑ์เป็นของแข็งสีเหลือง (14.00 กรัม, 66%) จุดหลอมเหลว 182-184 °C, UV-Vis (CH₃OH) λ_{\max} (nm) (log ϵ): 234.5 (3.47), 316.7 (2.90), FT-IR (KBr) ν (cm⁻¹): 1600-1500 (C=C stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 9.07 (1H, *d*, *J* = 8.7 Hz), 8.55 (1H, *d*, *J* = 8.1 Hz), 8.39 (1H, *dd*, *J* = 1.5, 8.1 Hz), 8.23 (1H, *dt*, *J* = 1.5, 8.1 Hz), 8.09 (1H, *d*, *J* = 8.7 Hz), 7.98 (1H, *t*, *J* = 8.1 Hz), 4.57 (3H, *s*), 3.20 (3H, *s*)

การสังเคราะห์ Aryl ethenylpyridinium (AEP-I และ AEP-II) ตาม Scheme 3.3



สำหรับการเตรียมสารประกอบ AEP-I ไม่ได้ผลิตภัณฑ์ตามต้องการ โดยได้เปลี่ยนแปลงเงื่อนไขปฏิกิริยาในการสังเคราะห์หลายเงื่อนไข แต่ได้ผลิตภัณฑ์เป็นของเหลวหนืดสีน้ำตาล จึงคาดว่าสารน่าจะเกิดการ polymerization และไม่สามารถทำการแยกสารได้

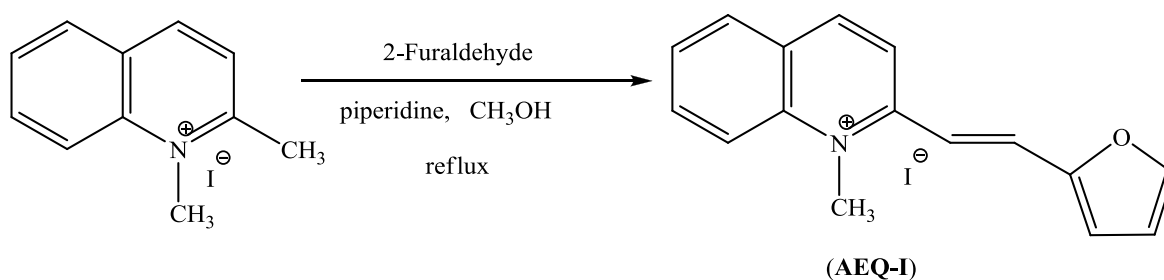


ละลาย 1,4-dimethylpyridinium iodide 2.0 กรัม (8.51 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลายหมดเติมสารละลายของ Thiophene-2-carboxaldehyde 0.78 มิลลิลิตร (8.51 มิลลิโมล) และ piperidine 0.84 มิลลิลิตร (8.51 มิลลิโมล) ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกันได้สารละลายสีเหลืองน้ำตาล ทำการรีฟลักซ์สารผสมภายใต้บรรยากาศก๊าซไนโตรเจนที่

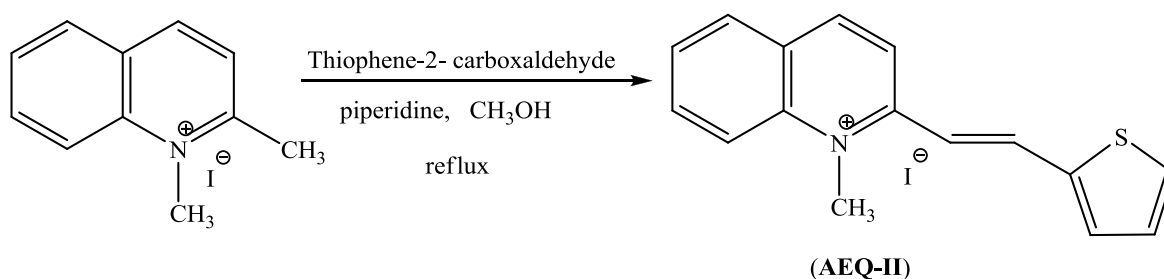
อุณหภูมิ 55-60 °C หลังจากรีฟลักซ์ไปได้ 30 นาที สารละลายเปลี่ยนเป็นสีน้ำตาล รีฟลักซ์ต่อเป็นเวลา 4 ชั่วโมง นำขบวนการปฏิกิริยาไปทำต่อให้เย็นในตู้เย็นเป็นเวลา 1 วัน กรองตะกอนแบบลดความดัน ล้างตะกอนด้วยคลอโรฟอร์ม นำตะกอนไปทำให้แห้งโดยใช้ vacuum ใต้ของแข็งสีเขียวเหลืองของ (AEP-II) (17 กรัม 75%)

ผลิตภัณฑ์เป็นของแข็งสีเหลืองอมเขียว (3.17 กรัม, 75%) จุดหลอมเหลว 219-221 °C, UV (CH₃OH) λ_{\max} (nm) (log ϵ): 218.6 (4.12), 250.6 (2.51), 389.7 (4.16), IR (KBr) ν (cm⁻¹): 1607 (C=C stretching), 1168 (C-O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.89 (2H, *d*, *J* = 6.9 Hz), 8.10 (2H, *d*, *J* = 6.9 Hz), 8.08 (1H, *d*, *J* = 15.6 Hz), 7.57 (1H, *d*, *J* = 5.1 Hz), 7.49 (1H, *d*, *J* = 5.1 Hz), 7.16 (1H, *t*, *J* = 5.1 Hz), 7.04 (1H, *d*, *J* = 15.6 Hz), 4.40 (3H, *s*)

การสังเคราะห์ Aryl ethenylquinolinium (AEQ-I และ AEQ-II) ตาม Scheme 3.4



สำหรับการเตรียมสารประกอบ AEQ-I ไม่ได้ผลิตภัณฑ์ตามต้องการ โดยได้เปลี่ยนแปลงเงื่อนไขปฏิกิริยาในการสังเคราะห์หลายเงื่อนไข แต่ได้ผลิตภัณฑ์เป็นของเหลวหนืดสีน้ำตาลดำ เช่นเดียวกับกรณีของการสังเคราะห์ AEP-I และไม่สามารถทำการแยกสารได้

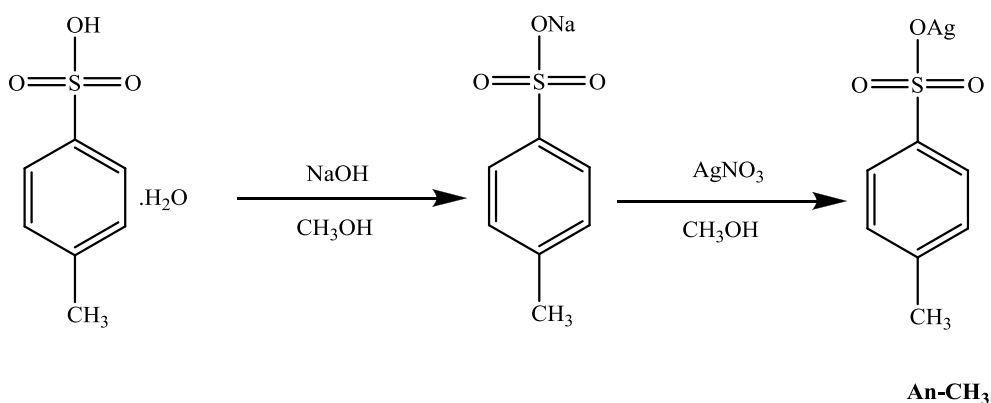


ละลาย 1,2-dimethylquinolinium iodide 2.0 กรัม (7.01 มิลลิโมล) ด้วยเมทานอลร้อน 40 มิลลิลิตร คนจนสารละลายหมดเติมสารละลายของ thiophene-2-carboxaldehyde 0.64 มิลลิลิตร (7.01

มิลลิโมล) และ piperidine 0.69 มิลลิลิตร (7.01 มิลลิโมล) ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกันได้สารละลายสีเหลืองน้ำตาล ทำการรีฟลักซ์สารผสมภายใต้บรรยากาศก๊าซไนโตรเจนที่อุณหภูมิ 55-60 °C หลังจากรีฟลักซ์ไปได้ 30 นาที สารละลายเปลี่ยนเป็นสีน้ำตาล รีฟลักซ์ต่อเป็นเวลา 5 ชั่วโมง นำขวดปฏิกิริยาไปทำต่อให้เย็นในตู้เย็นเป็นเวลา 1 วัน กรองตะกอนแบบลดความดันล้างตะกอนด้วยไดเอทิลอีเทอร์ นำตะกอนไปทำให้แห้งโดยใช้ vacuum ได้ของแข็งสีน้ำตาลดำของ (AEQ-II) (1.99 กรัม 75 % mp. 191-192 °C)

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาลดำ (1.99 กรัม, 75%) จุดหลอมเหลว 191-192 °C, ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.93 (1H, *d*, *J* = 9.0 Hz), 8.49 (1H, *d*, *J* = 9.0 Hz), 8.43 (1H, *d*, *J* = 9.0 Hz), 8.38 (1H, *d*, *J* = 15.6 Hz), 8.28 (1H, *d*, *J* = 9.0 Hz), 8.19 (1H, *t*, *J* = 9.0 Hz), 7.93 (1H, *t*, *J* = 7.5 Hz), 7.77 (1H, *d*, *J* = 3.3 Hz), 7.74 (1H, *d*, *J* = 5.1 Hz), 7.52 (1H, *d*, *J* = 15.6 Hz), 7.24 (1H, *d*, *J* = 3.9 Hz), 4.63 (3H, *s*)

การสังเคราะห์ Benzenesulfonate salts (An-X) ตาม Scheme 3.5



flask A : ละลาย p-toluenesulfonic acid monohydrate 2 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน

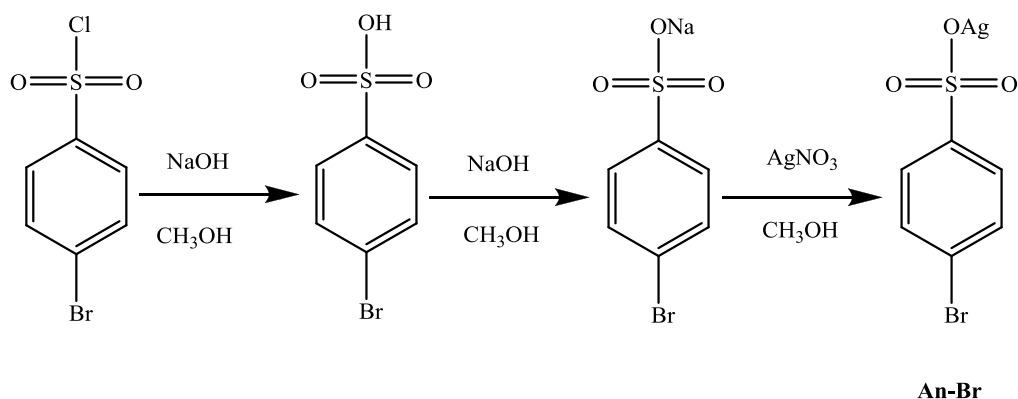
15 มิลลิลิตร คนจนสารละลายหมด

flask B : ละลาย NaOH 0.42 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด

flask C : ละลาย AgNO₃ 1.78 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน 100 มิลลิลิตร คนจนสารละลายหมด

นำสารละลายใน flask A และ B ผสมกันได้ของเหลวใสไม่มีสี จากนั้นเติมสารละลายใน flask C ลงไป มีตะกอนสีดำเกิดขึ้น ทำการกรองตะกอนออกโดยใช้กรวยกรอง ได้สารละลายใสไม่มีสี วางสารละลายไว้ที่อุณหภูมิห้องเป็นเวลา 4 วัน มีผลึกสีขาวของ An-CH₃ เกิดขึ้น กรองผลึกแบบลดความดันและนำผลึกไปทำให้แห้งโดยใช้ vacuum ได้ผลึกสีขาวของ Silver (I) 4-methylbenzenesulfonate (An-CH₃) (3.07 กรัม 70% mp. 260-262 °C)

ผลิตภัณฑ์เป็นของแข็งสีขาว (3.07 กรัม, 70%) จุดหลอมเหลว 260-262 °C (decomp.), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 7.74 (2H, *d*, *J* = 8.1 Hz), 7.17 (2H, *d*, *J* = 8.1 Hz), 2.38 (3H, *s*)



flask A : ละลาย 4-bromobenzenesulfonyl chloride 2 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน

15 มิลลิลิตร คนจนสารละลายหมด

flask B1 : ละลาย NaOH 0.312 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน 15 มิลลิลิตร คนจนสารละลายหมด

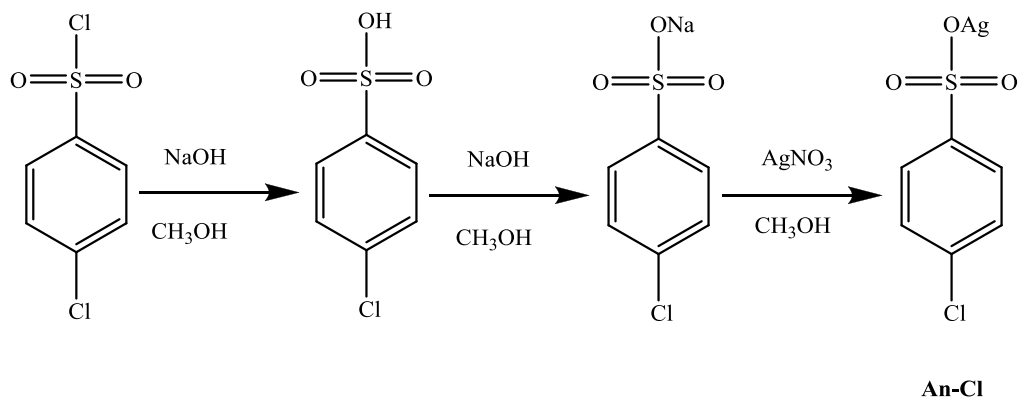
flask B2 : ละลาย NaOH 0.312 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน 15 มิลลิลิตร คนจนสารละลายหมด

flask C : ละลาย AgNO₃ 1.324 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน 15 มิลลิลิตร คนจนสารละลายหมด

นำสารละลายใน flask A และ B1 ผสมกันมีตะกอนสีขาวเกิดขึ้น เติมน้ำกลั่น 10 มิลลิลิตร จำนวน 2 ครั้ง ตะกอนจะละลายหมด จากนั้นนำไปสกัดด้วย CH₂Cl₂ 3 ครั้ง ครั้งละ 15 มิลลิลิตร นำส่วนที่สกัดด้วย CH₂Cl₂ ไปเติม Na₂SO₄ anhydrous เพื่อดูดน้ำออกและกรอง Na₂SO₄ anhydrous ออกโดยใช้กรวยกรอง นำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ตะกอนสีขาวของสาร (1)

ละลายสาร (1) ด้วยเมทานอลร้อน 25 มิลลิลิตร เติมน้ำกลั่นใน flask B2 และ C ลงในสารละลายตามลำดับมีตะกอนสีดำเกิดขึ้น ทำการกรองตะกอนออกโดยใช้กรวยกรองได้สารละลายใสไม่มีสี วางสารละลายไว้ที่อุณหภูมิห้องเป็นเวลา 4 วันมีผลึกสีขาวของ **An-Br** เกิดขึ้น กรองผลึกแบบลดความดันและนำผลึกไปทำให้แห้งโดยใช้ vacuum ได้ผลึกสีขาวของ Silver (I) 4-bromobenzenesulfonate (**An-Br**) (0.71 กรัม 18% mp. 219-221 °C)

ผลิตภัณฑ์เป็นของแข็งสีขาว (0.71 กรัม, 18%) จุดหลอมเหลว 219-221 °C decomposed, ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 7.81 (2H, *d*, *J* = 8.4), 7.34 (2H, *d*, *J* = 8.4 Hz)



flask A : ละลาย 4-chlorobenzenesulfonyl chloride 2 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด

flask B1 : ละลาย NaOH 0.388 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด

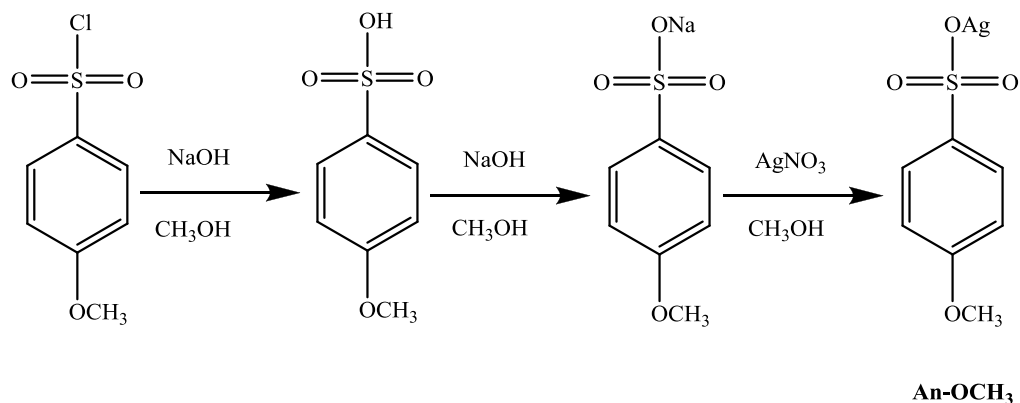
flask B2 : ละลาย NaOH 0.388 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด

flask C : ละลาย AgNO₃ 1.613 กรัม (2.0 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด

นำสารละลายใน flask A และ B1 ผสมกันมีตะกอนสีขาวเกิดขึ้น เติมน้ำกลั่น 10 มิลลิลิตร จำนวน 2 ครั้ง ตะกอนจะละลายหมด จากนั้นนำไปสกัดด้วย CH₂Cl₂ 3 ครั้ง ครั้งละ 15 มิลลิลิตร นำส่วนที่สกัดด้วย CH₂Cl₂ ไปเติม Na₂SO₄ anhydrous เพื่อดูดน้ำออกและกรอง Na₂SO₄ anhydrous ออกโดยใช้กรวยกรอง นำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ตะกอนสีขาวของสาร (1)

ละลายสาร (1) ด้วยเมทานอลร้อน 25 มิลลิลิตร เติมน้ำกลั่นใน flask B2 และ C ลงในสารละลายตามลำดับมีตะกอนสีดำเกิดขึ้น ทำการกรองตะกอนออกโดยใช้กรวยกรองได้สารละลายใสไม่มีสี วางสารละลายไว้ที่อุณหภูมิห้องเป็นเวลา 4 วันมีผลึกสีขาวของ **An-Cl** เกิดขึ้น กรองผลึกแบบลดความดันและนำผลึกไปทำให้แห้งโดยใช้ vacuum ได้ผลึกสีขาวของ Silver (I) 4-chlorobenzenesulfonate (**An-Cl**) (1.40 กรัม 33% mp.220-222 °C)

ผลิตภัณฑ์เป็นของแข็งสีขาว (1.40 กรัม, 33%) จุดหลอมเหลว 220-222 °C (decomp.), ¹H NMR (CDCl₃ + DMSO-d₆) (δ ppm) (300 MHz): 7.76 (2H, d, J = 7.8), 7.50 (2H, d, J = 7.8 Hz)



flask A : ละลาย 4-methoxybenzenesulfonyl chloride 2 กรัม (9.7 มิลลิโมล) ด้วยเมทานอลร้อน 15 มิลลิลิตร คนจนสารละลายหมด

flask B1 : ละลาย NaOH 0.388 กรัม (9.7 มิลลิโมล) ด้วยเมทานอลร้อน 15 มิลลิลิตร คนจนสารละลายหมด

flask B2 : ละลาย NaOH 0.388 กรัม (9.7 มิลลิโมล) ด้วยเมทานอลร้อน 15 มิลลิลิตร คนจนสารละลายหมด

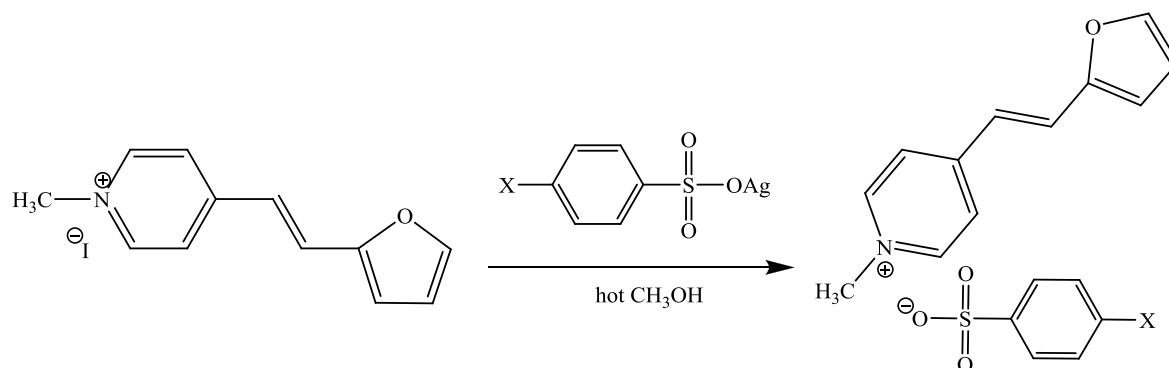
flask C : ละลาย AgNO₃ 1.648 กรัม (9.7 มิลลิโมล) ด้วยเมทานอลร้อน 75 มิลลิลิตร คนจนสารละลายหมด

นำสารละลายใน flask A และ B1 ผสมกันมีตะกอนสีขาวเกิดขึ้น เติมน้ำกลั่น 10 มิลลิลิตร จำนวน 2 ครั้ง ตะกอนจะละลายหมด จากนั้นนำไปสกัดด้วย CH₂Cl₂ 3 ครั้ง ครั้งละ 15 มิลลิลิตร นำส่วนที่สกัดด้วย CH₂Cl₂ ไปเติม Na₂SO₄ anhydrous เพื่อคูดน้ำออกและกรอง Na₂SO₄ anhydrous ออกโดยใช้กรวยกรอง นำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ตะกอนสีขาวของสาร (1)

ละลายสาร (1) ด้วยเมทานอลร้อน 25 มิลลิลิตร เติมสารละลายใน flask B2 และ C ลงในสารละลายตามลำดับมีตะกอนสีดำเกิดขึ้น ทำการกรองตะกอนออกโดยใช้กรวยกรองได้สารละลายใสไม่มีสี วางสารละลายไว้ที่อุณหภูมิห้องเป็นเวลา 4 วันมีผลึกสีขาวของ **An-OCH₃** เกิดขึ้น กรองผลึกแบบลดความดันและนำผลึกไปทำให้แห้งโดยใช้ vacuum ได้ผลึกสีขาวของ Silver (I) 4-methoxybenzenesulfonate (**An-OCH₃**) (2.57 กรัม 59% mp. 243-245 °C)

ผลิตภัณฑ์เป็นของแข็งสีขาว (2.57 กรัม, 59%) จุดหลอมเหลว 243-245 °C (decomp.), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 7.78 (2H, d, J = 8.7), 6.86 (2H, d, J = 8.7 Hz), 3.82 (3H, s)

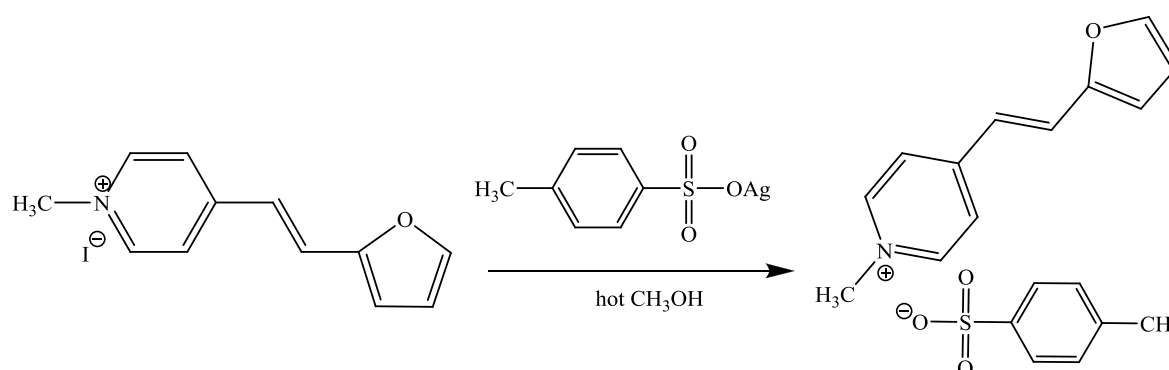
การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (AEP-An) ตาม Scheme 3.6



เมื่อ $X = \text{CH}_3$ (AEP-I-An-Me) หรือ PAC-1
 Br (AEP-I-An-Br) หรือ PAC-2
 Cl (AEP-I-An-Cl) หรือ PAC-3
 และ OCH_3 (AEP-I-An-OMe) หรือ PAC-4

สำหรับการเตรียมสารประกอบ PAC-1- PAC-4 เนื่องจากไม่สามารถเตรียม AEP-I ซึ่งเป็นสารตั้งต้นในการเตรียม PAC-1 ได้ จึงไม่สามารถทำการสังเคราะห์ PAC-1- PAC-4 ได้

การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (PAC 5)



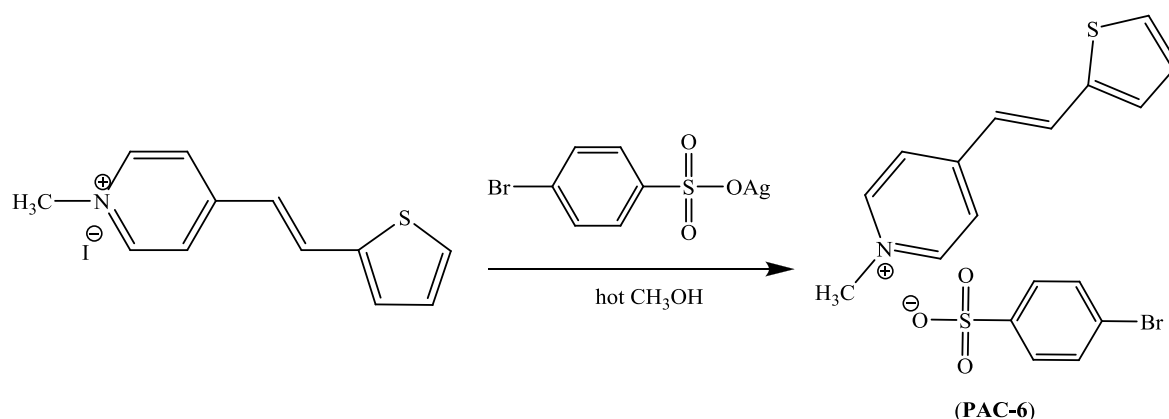
flask A: ละลาย An-CH₃ 0.084 กรัม (0.30 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมดได้สารละลายใส ไม่มีสี

flask B : ละลาย AEP-II 0.100 กรัม (0.30 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายสีน้ำตาล

นำสารละลายใน flask A และ B มาผสมกันมีตะกอนสีเหลืองของ AgI เกิดขึ้น กรองตะกอนออก โดยใช้กรวยกรองและนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีน้ำตาลของ PAC-5 (0.08 กรัม 75% mp. 232-234 °C)

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล (0.08 กรัม, 75%) จุดหลอมเหลว 232-234 °C, UV (CH₃OH) λ_{\max} (nm) (log ϵ): 220.9 (4.04), 251.4 (3.58), 379.2 (3.95), IR (KBr) $\nu(\text{cm}^{-1})$: 1523, (C=C stretching), 1186 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.72 (2H, *d*, *J* = 6.9 Hz), 7.94 (1H, *d*, *J* = 15.6 Hz), 7.93 (2H, *d*, *J* = 6.9 Hz), 7.59 (2H, *d*, *J* = 8.4 Hz), 7.49 (1H, *d*, *J* = 5.1 Hz), 7.37 (1H, *d*, *J* = 5.1 Hz), δ 7.04 (1H, *t*, *J* = 5.1 Hz), 7.01 (2H, *d*, *J* = 8.4 Hz), 6.91 (1H, *d*, *J* = 15.6 Hz), 4.22 (3H, *s*), 3.95 (3H, *s*)

การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (PAC 6)



flask A: ละลาย An-Br 0.089 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 60 มิลลิลิตร คนจนสารละลายหมดได้สารละลายใส ไม่มีสี

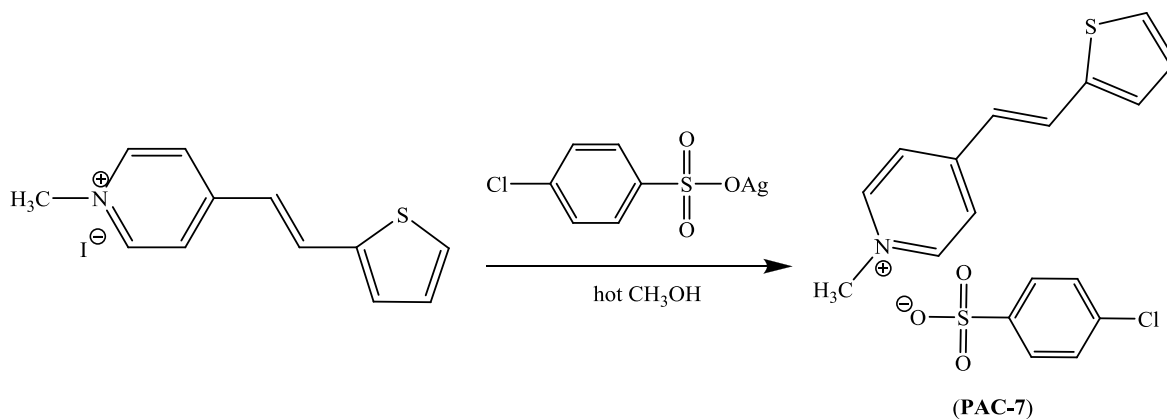
flask B : ละลาย AEP-II 0.100 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายสีน้ำตาลเข้ม

นำสารละลายใน flask A และ B มาผสมกันมีตะกอนสีเหลืองของ AgI เกิดขึ้น กรองตะกอนออก โดยใช้กรวยกรองและนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีน้ำตาลของ PAC-6 (0.10 กรัม 70% mp. 231-233 °C)

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล (0.10 กรัม, 70%) จุดหลอมเหลว 231-233 °C, UV (CH₃OH) λ_{\max} (nm) (log ϵ): 222.3 (4.26), 258.0 (3.62), 381.8 (2.34), IR (KBr) $\nu(\text{cm}^{-1})$: 1577 (C=C stretching), 1208 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.82 (2H, *J* = 6.9 Hz), 8.15

(2H, $J = 6.9$ Hz), 8.14 (1H, d , $J = 15.6$ Hz), 7.62 (1H, d , $J = 5.1$ Hz), 7.62 (2H, d , $J = 8.4$ Hz), 7.43 (2H, d , $J = 8.4$ Hz), 7.43 (1H, d , $J = 5.1$ Hz), 7.16 (1H, t , $J = 5.1$ Hz), 7.10 (1H, d , $J = 15.6$ Hz), 4.29 (3H, s)

การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (PAC 7)



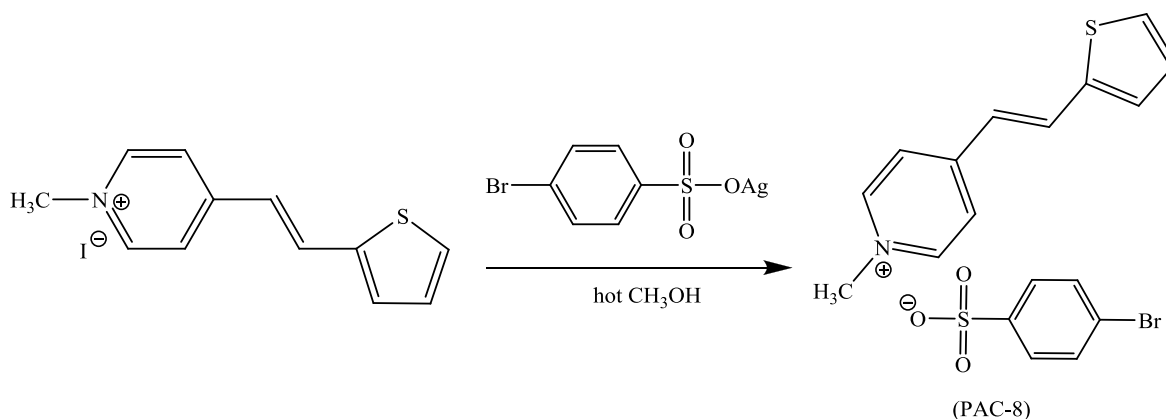
flask A: ละลาย **An-Cl** 0.089 กรัม (0.30 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลาย
หมด ได้สารละลายใส ไม่มีสี

flask B : ละลาย **AEP-II** 1.000 กรัม (0.30 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลาย
หมด ได้สารละลายสีน้ำตาลเข้ม

นำสารละลายใน flask A และ B มาผสมกันมีตะกอนสีเหลืองของ AgI เกิดขึ้น กรองตะกอนออก
โดยใช้กรวยกรองและนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีน้ำตาลของ **PAC-7** (0.11
กรัม 90% mp.230-232 °C)

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล (0.11 กรัม, 90%) จุดหลอมเหลว 230-232 °C, UV (CH₃OH)
 λ_{\max} (nm) (log \mathcal{E}): 220.9 (4.35), 251.4 (3.02) 379.2 (3.42), IR (KBr) $\nu(\text{cm}^{-1})$: 1523 (C=C stretching),
1210 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.79 (2H, $J = 6.9$ Hz), 8.02
(1H, d , $J = 15.6$ Hz), 8.01 (2H, d , $J = 6.9$ Hz), 7.79 (2H, d , $J = 8.4$ Hz), 7.58 (1H, d , $J = 5.1$ Hz), 7.47
(1H, d , $J = 5.1$ Hz), 7.30 (2H, d , $J = 8.4$ Hz), 7.14 (1H, t , $J = 5.1$ Hz), 6.99 (1H, d , $J = 15.6$ Hz), 4.34
(3H, s)

การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (PAC 8)



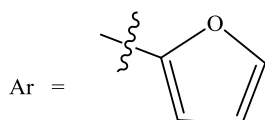
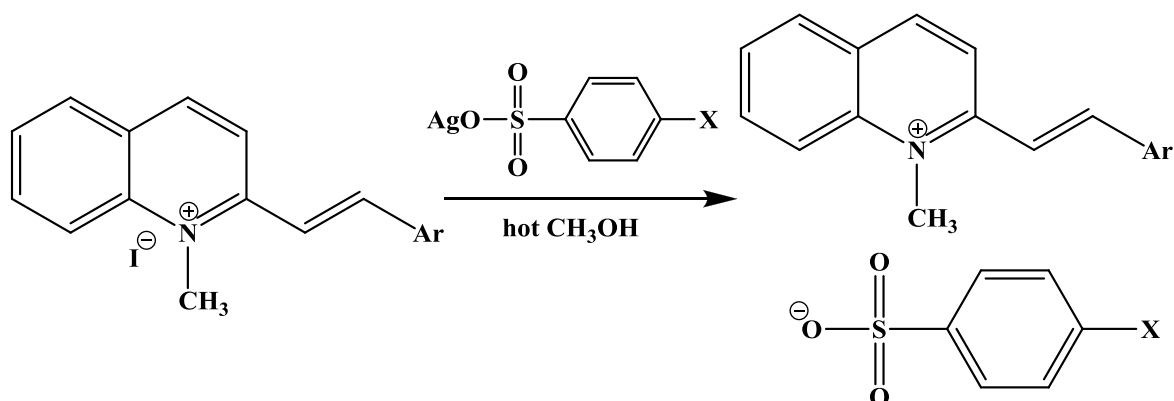
flask A: ละลาย **An-OCH₃** 0.088 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 30 มิลลิลิตร คนจนสารละลาย
หมด ได้สารละลายใส ไม่มีสี

flask B : ละลาย **AEP-II** 0.100 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลาย
หมด ได้สารละลายสีน้ำตาลเข้ม

นำสารละลายใน flask A และ B มาผสมกันมีตะกอนสีเหลืองของ AgI เกิดขึ้น กรองตะกอนออก
โดยใช้กรวยกรองและนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีเหลืองของ **PAC-8** (0.11
กรัม 87% mp.234-236 °C)

ผลิตภัณฑ์เป็นของแข็งสีเหลือง (0.11 กรัม, 87%) จุดหลอมเหลว 234-236 °C, UV (CH₃OH)
 λ_{max} (nm) (log ϵ): 230.2 (2.83), 381.1 (3.58), IR (KBr) $\nu(\text{cm}^{-1})$: 1590 (C=C stretching), 1188 (S=O
stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.82 (2H, *d*, *J* = 6.9 Hz), 8.01 (1H, *d*, *J*
= 15.6 Hz), 7.98 (2H, *d*, *J* = 6.9 Hz), 7.77 (2H, *d*, *J* = 8.4 Hz), 7.57 (1H, *d*, *J* = 5.1 Hz), 7.46 (1H, *d*, *J* =
5.1 Hz), 7.16 (1H, *t*, *J* = 5.1 Hz), 6.99 (1H, *d*, *J* = 15.6 Hz), 6.81 (2H, *d*, *J* = 8.4 Hz), 4.43 (3H, *s*), 3.79
(3H, *s*)

การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (AEQ-An) ตาม scheme 3.7



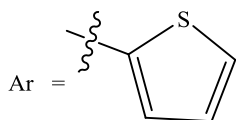
และ X = CH₃ (AEQ-I-An-Me) หรือ PAC-9

Br (AEQ-I-An-Br) หรือ PAC-10

Cl (AEQ-I-An-Cl) หรือ PAC-11

และ OCH₃ (AEQ-I-An-OMe) หรือ PAC-12

สำหรับการเตรียมสารประกอบ PAC-9 - PAC-12 เนื่องจากไม่สามารถเตรียม AEQ-I ซึ่งเป็นสารตั้งต้นในการเตรียม PAC-9 - PAC-12 ได้ จึงไม่สามารถทำการสังเคราะห์ PAC-9 - PAC-12 ได้



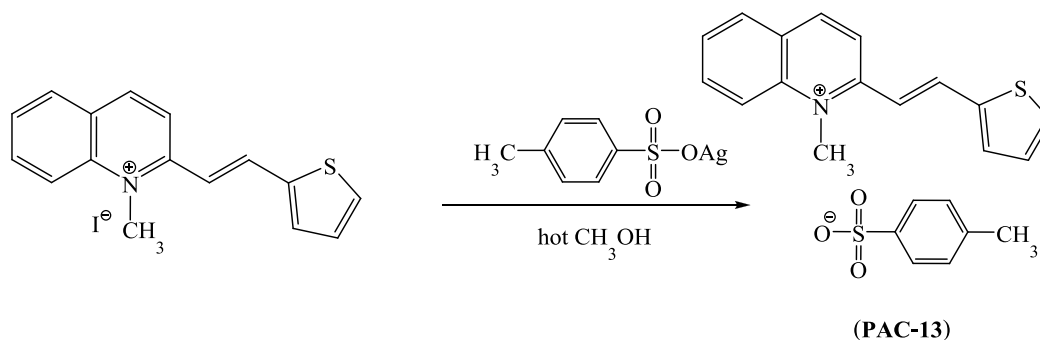
และ X = CH₃ (AEQ-II-An-Me) หรือ PAC-13

Br (AEQ-II-An-Br) หรือ PAC-14

Cl (AEQ-II-An-Cl) หรือ PAC-15

และ OCH₃ (AEQ-II-An-OMe) หรือ PAC-16

การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (PAC-13)



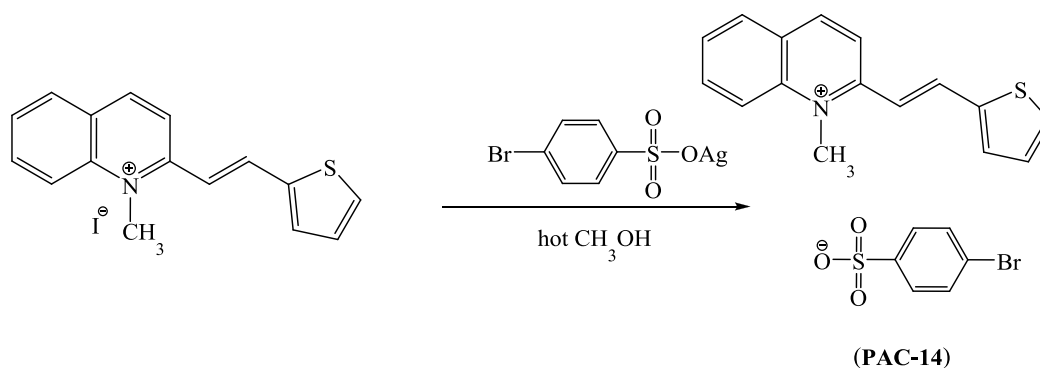
flask A: ละลาย **An-CH₃** 0.084 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 30 มิลลิลิตร คนจนสารละลาย
หมด ได้สารละลายใส ไม่มีสี

flask B : ละลาย **AEQ-II** 0.114 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลาย
หมด ได้สารละลายสีน้ำตาลเข้ม

นำสารละลายใน flask A และ B มาผสมกันมีตะกอนสีดำของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรองและนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีน้ำตาลของ **PAC-13** (0.12 กรัม 71% mp.200-202 °C)

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล (0.12 กรัม, 71%) จุดหลอมเหลว 200-202 °C, UV (CH₃OH)
 λ_{\max} (nm) (log ϵ): 205.1 (9.83), 226.2 (10.97), 270.5 (2.61), 310.3 (1.92), 401.0 (4.27), IR (KBr)
V(cm⁻¹): 1600, (C=C stretching), 1220 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300
MHz): 8.40 (1H, *d*, *J* = 8.1 Hz), 7.97 (1H, *d*, *J* = 8.7 Hz), 7.93 (1H, *d*, *J* = 7.8 Hz), 7.85 (1H, *d*, *J* = 15.6
Hz), 7.78 (1H, *d*, *J* = 8.1 Hz), 7.66 (1H, *t*, *J* = 7.8 Hz), 7.42 (1H, *t*, *J* = 7.8 Hz), 7.28 (1H, *d*, *J* = 8.7
Hz), 7.25 (1H, *d*, *J* = 8.7 Hz), 7.19 (2H, *t*, *J* = 7.8 Hz), 7.03 (1H, *d*, *J* = 15.6 Hz), 6.74 (1H, *t*, *J* = 8.7
Hz), 6.60 (2H, *d*, *J* = 7.8 Hz), 4.10 (3H, *s*), 1.85 (3H, *s*)

การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (PAC-14)



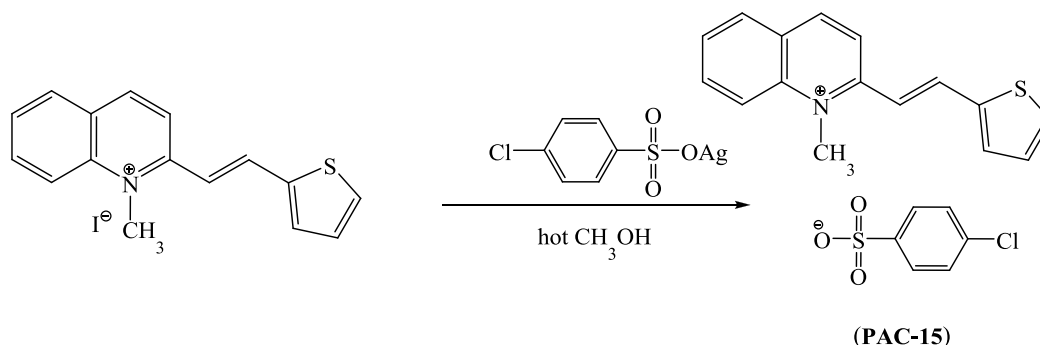
flask A: ละลาย **An-Br** 0.103 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 30 มิลลิลิตร คนจนสารละลายหมด
ได้สารละลายใส ไม่มีสี

flask B : ละลาย **AEQ-II** 0.114 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลาย
หมด ได้สารละลายสีน้ำตาลเข้ม

นำสารละลายใน flask A และ B มาผสมกันมีตะกอนสีดำของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรองและนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีน้ำตาลเข้มของ **PAC-14** (0.18 กรัม 95% mp.256-258 °C)

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาลเข้ม (0.18 กรัม, 95%) จุดหลอมเหลว 256-258 °C, UV (CH₃OH)
 λ_{\max} (nm) (log ϵ): 204.4 (11.8), 222.9 (12.70), 287.1 (2.76), 313.6 (2.21), 405.0 (4.75), IR (KBr)
V(cm⁻¹): 1605, (C=C stretching), 1210 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300
MHz): 9.30 (1H, *d*, *J* = 8.7 Hz), 8.55 (1H, *d*, *J* = 7.8 Hz), 8.53 (1H, *d*, *J* = 7.8 Hz), 8.40 (1H, *d*, *J* = 15.6
Hz), 8.30 (1H, *d*, *J* = 8.7 Hz), 8.16 (1H, *t*, *J* = 7.8 Hz), 7.97 (1H, *t*, *J* = 7.8 Hz), 7.82 (1H, *d*, *J* = 8.4
Hz), 7.75 (1H, *d*, *J* = 8.4 Hz), 7.60 (2H, *d*, *J* = 9.0 Hz), 7.58 (1H, *d*, *J* = 15.6 Hz), 7.45 (2H, *d*, *J* = 9.0
Hz), 7.25 (2H, *t*, *J* = 8.4 Hz), 4.52 (3H, *s*)

การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (PAC-15)



flask A: ละลาย **An-Cl** 0.090 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 30 มิลลิลิตร คนจน

สารละลายหมด ได้สารละลายใส ไม่มีสี

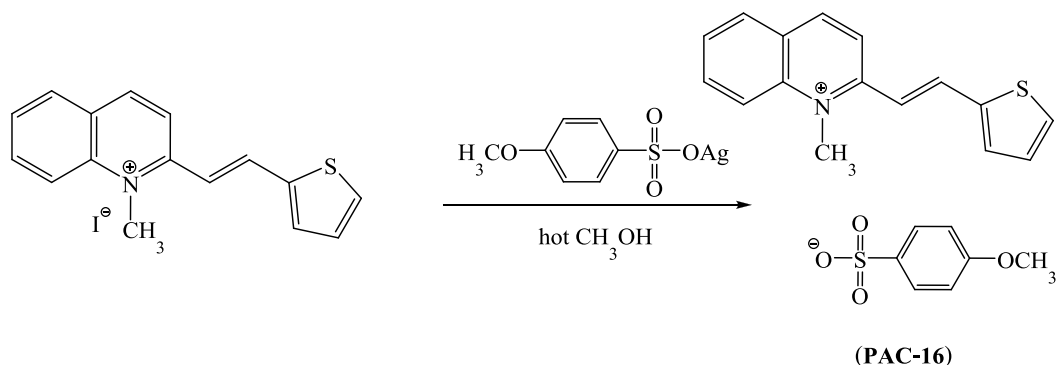
flask B : ละลาย **AEQ-II** 0.114 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลาย

หมด ได้สารละลายสีน้ำตาลเข้ม

นำสารละลายใน flask A และ B มาผสมกันมีตะกอนสีดำของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรองและนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีน้ำตาลเข้มของ **PAC-15** (0.15 กรัม 83% mp. 230-232 °C)

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาลเข้ม (0.15 กรัม, 83%) จุดหลอมเหลว 230-232 °C, UV (CH₃OH) λ_{max} (nm) (log ϵ): 220.9 (9.47), 242.1 (11.02), 285.1 (2.73), 311.6 (2.58), 406.3 (3.65), IR (KBr) $\nu(\text{cm}^{-1})$: 1600, (C=C stretching), 1230 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 9.00 (1H, *d*, *J* = 8.4 Hz), 8.54 (1H, *d*, *J* = 7.8 Hz), 8.50 (1H, *d*, *J* = 7.8 Hz), 8.40 (1H, *d*, *J* = 15.6 Hz), 8.32 (1H, *d*, *J* = 8.4 Hz), 8.16 (1H, *t*, *J* = 7.8 Hz), 7.98 (1H, *d*, *J* = 8.7 Hz), 7.97 (1H, *t*, *J* = 7.8 Hz), 7.80 (1H, *d*, *J* = 8.7 Hz), 7.60 (2H, *d*, *J* = 15.6 Hz), 7.59 (2H, *d*, *J* = 8.1 Hz), 7.37 (2H, *t*, *J* = 8.1 Hz), 7.35 (1H, *t*, *J* = 8.7 Hz), 4.50 (3H, *s*)

การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (PAC-16)



flask A: ละลาย **An-OCH₃** 0.089 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 30 มิลลิลิตร คนจน

สารละลายหมด ได้สารละลายใส ไม่มีสี

flask B : ละลาย **AEP-II** 0.114 กรัม (0.3 มิลลิโมล) ด้วยเมทานอลร้อน 10 มิลลิลิตร คนจนสารละลาย

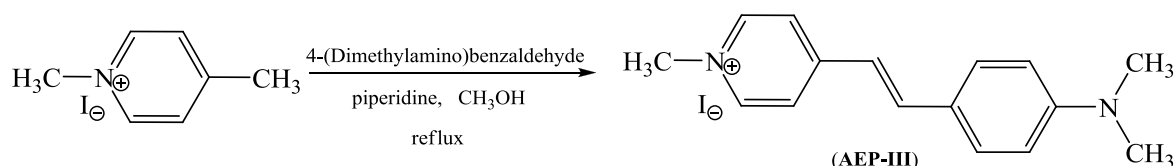
หมด ได้สารละลายสีน้ำตาลเข้ม

นำสารละลายใน flask A และ B มาผสมกันมีตะกอนสีดำของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรองและนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีน้ำตาลของ **PAC-16** (0.15 กรัม 88% mp.218-220 °C)

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล (0.15 กรัม, 88%) จุดหลอมเหลว 218-220 °C, UV (CH₃OH) λ_{max} (nm) (log ϵ): 203.1 (9.39), 228.2 (10.70), 276.5 (2.52), 312.3 (1.74), 405.0 (3.61), IR (KBr) $\nu(\text{cm}^{-1})$: 1600, (C=C stretching), 1200 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.92 (1H, *d*, *J* = 8.4 Hz), 8.50 (1H, *d*, *J* = 7.8 Hz), 8.40 (1H, *d*, *J* = 7.8 Hz), 8.38 (1H, *d*, *J* = 15.9 Hz), 8.25 (1H, *d*, *J* = 8.4 Hz), 8.15 (1H, *t*, *J* = 7.8 Hz), 7.90 (1H, *t*, *J* = 7.8 Hz), 7.76 (1H, *d*, *J* = 8.7 Hz), 7.75 (2H, *d*, *J* = 8.1 Hz), 7.70 (1H, *d*, *J* = 8.7 Hz), 7.55 (1H, *d*, *J* = 15.9 Hz), 7.23 (1H, *t*, *J* = 8.7 Hz), 6.80 (2H, *d*, *J* = 8.1 Hz), 4.60 (3H, *s*), 3.80 (3H, *s*)

จากการสังเคราะห์สารตามแผนการสังเคราะห์ดัง scheme 3.3 และ scheme 3.4 ไม่สามารถเตรียมสาร **AEP-I** และ **AEQ-I** ได้ แสดงว่า 2-furaldehyde ไม่เหมาะสมในการทำปฏิกิริยาเพื่อให้เกิดสาร **AEP-I** และ **AEQ-I** ผู้วิจัยจึงได้ทำวิจัยเพิ่มเติมโดยการสังเคราะห์สาร **AEP-III** และ **AEQ-III** โดยในส่วนของอัลดีไฮด์เลือกใช้ 4-(dimethylamino)benzaldehyde ได้ผลดังนี้

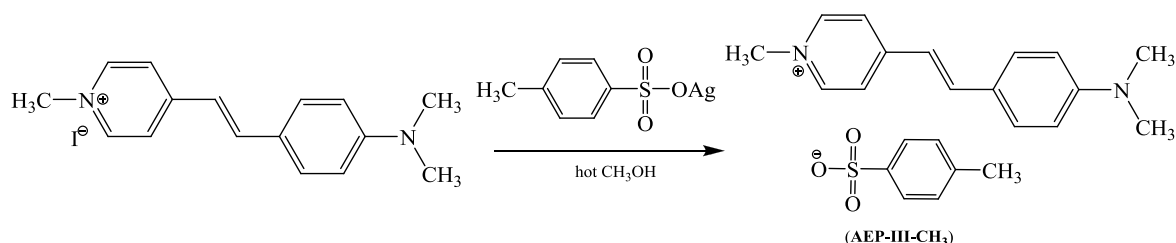
การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (AEP-III-X)



ละลาย 1,4-dimethylpyridinium iodide 2.00 กรัม (8.51 มิลลิโมล) ด้วยเมทานอลร้อน 5 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ 4-dimethylaminobenzaldehyde 1.27 กรัม (8.51 มิลลิโมล) และ piperidine 0.84 มิลลิลิตร (8.51 มิลลิโมล) ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกัน ได้สารละลายสีแดงเข้ม ทำการรีฟลักซ์สารผสมภายใต้บรรยากาศไนโตรเจนที่อุณหภูมิ 55-60 °C ทำการรีฟลักซ์เป็นเวลา 3 ชั่วโมง มีตะกอนสีแดงเข้มเกิดขึ้น นำขวดปฏิกิริยาไปทำให้เย็นในตู้เย็นเป็นเวลา 2 วัน กรองตะกอนแบบลดความดัน ล้างตะกอนด้วยคลอโรฟอร์ม นำตะกอนไปทำให้แห้งโดยใช้ vacuum ได้ของแข็งสีน้ำตาลอ่อนของ (*E*)-4-(4-(dimethylamino)styryl)-1-methylpyridinium iodide (AEP-III) (3.11 กรัม 99% m.p. 155-157 °C)

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาลอ่อน (3.11 กรัม, 99%) จุดหลอมเหลว 155-157 °C, UV (CH₃OH) λ_{\max} (nm) (log \mathcal{E}): 203.7 (5.49), 271.2 (6.42), 474.5 (5.70), IR (KBr) ν (cm⁻¹): 1579 (C=C stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.64 (2H, *d*, *J* = 6.2 Hz), 7.97 (2H, *d*, *J* = 6.2 Hz), 7.82 (1H, *d*, *J* = 15.9 Hz), 7.54 (2H, *d*, *J* = 8.7 Hz), 7.05 (1H, *d*, *J* = 15.9 Hz), 6.69 (2H, *d*, *J* = 8.7 Hz), 4.19 (3H, *s*), 3.02 (6H, *s*)

การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (AEP-III-CH₃)



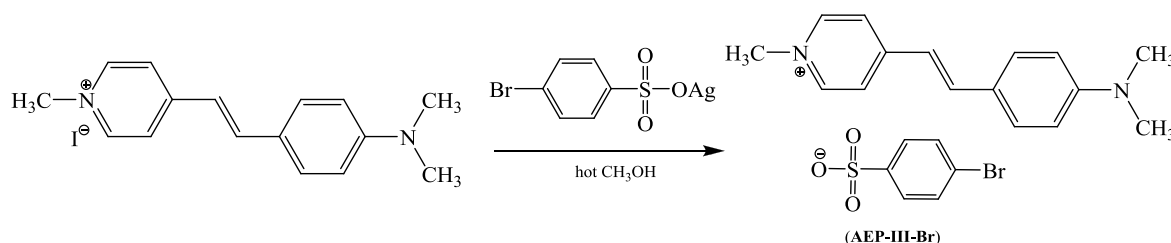
flask A : ละลาย An-CH₃ 0.15 กรัม (0.55 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายใสไม่มีสี

flask B : ละลาย **AEP-III** 0.20 กรัม (0.55 มิลลิโมล) ด้วยเมทานอลร้อน 25 มิลลิลิตร คนจน สารละลาย
หมด ได้สารละลายสีแดง

นำสารละลายใน flask A และ flask B มาผสมกันมีตะกอนสีน้ำตาลของ AgI เกิดขึ้น กรอง
ตะกอนออกโดยใช้กรวยกรอง และนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีส้มของ
AEP-III-CH₃ (0.20 กรัม 86% m.p.126-127 °C)

ผลิตภัณฑ์เป็นของแข็งสีส้ม (0.20 กรัม, 86%) จุดหลอมเหลว 126-127 °C, UV (CH₃OH) λ_{\max}
(nm) (log \mathcal{E}): 204.4 (5.01), 267.9 (5.44), 473.8 (5.04), IR (KBr) $\nu(\text{cm}^{-1})$: 1587 (C=C stretching), 1370
(S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.65 (2H, *d*, *J* = 6.8 Hz), 7.94
(2H, *d*, *J* = 6.8 Hz), 7.77 (1H, *d*, *J* = 15.8 Hz), 7.65 (2H, *d*, *J* = 7.9 Hz), 7.56 (2H, *d*, *J* = 7.8 Hz), 7.11
(2H, *d*, *J* = 7.9 Hz), 7.02 (1H, *d*, *J* = 15.8 Hz), 6.73 (2H, *d*, *J* = 7.8 Hz), 4.24 (3H, *s*), 3.07 (6H, *s*), 2.33
(3H, *s*)

การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (**AEP-III-Br**)



flask A : ละลาย **An-Br** 0.19 กรัม (0.55 มิลลิโมล) ด้วยเมทานอลร้อน 50 มิลลิลิตร คนจนสารละลายหมด
ได้สารละลายใสไม่มีสี

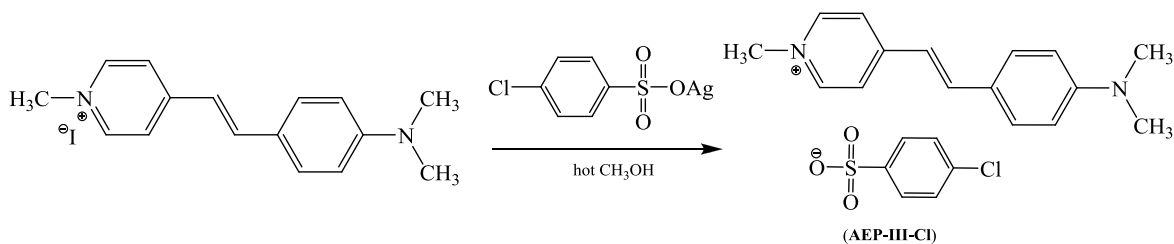
flask B : ละลาย **AEP-III** 0.20 กรัม (0.55 มิลลิโมล) ด้วยเมทานอลร้อน 25 มิลลิลิตร คนจนสารละลาย
หมด ได้สารละลายสีแดง

นำสารละลายใน flask A และ flask B มาผสมกันมีตะกอนสีน้ำตาลของ AgI เกิดขึ้น กรอง
ตะกอนออกโดยใช้กรวยกรอง และนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีแดงเข้มของ
AEP-III-Br (0.22 กรัม 84% m.p.263-264 °C)

ผลิตภัณฑ์เป็นของแข็งสีแดงเข้ม (0.22 กรัม, 84%) จุดหลอมเหลว 263-264 °C, UV (CH₃OH)
 λ_{\max} (nm) (log \mathcal{E}): 202.4 (5.22), 225.6 (5.51), 270.6 (5.90), 475.2 (5.26), IR (KBr) $\nu(\text{cm}^{-1})$: 1578 (C=C
stretching), 1375 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.67 (2H, *d*,
J = 6.6 Hz), 8.02 (2H, *d*, *J* = 6.6 Hz), 7.86 (1H, *d*, *J* = 16.4 Hz), 7.60 (2H, *d*, *J* = 2.1 Hz), 7.58 (2H, *d*,

$J = 2.1$ Hz), 7.48 (2H, *d*, $J = 8.7$ Hz), 7.12 (1H, *d*, $J = 16.4$ Hz), 6.75 (2H, *d*, $J = 8.7$ Hz), 4.20 (3H, *s*), 3.05 (6H, *s*)

การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (AEP-III-Cl)



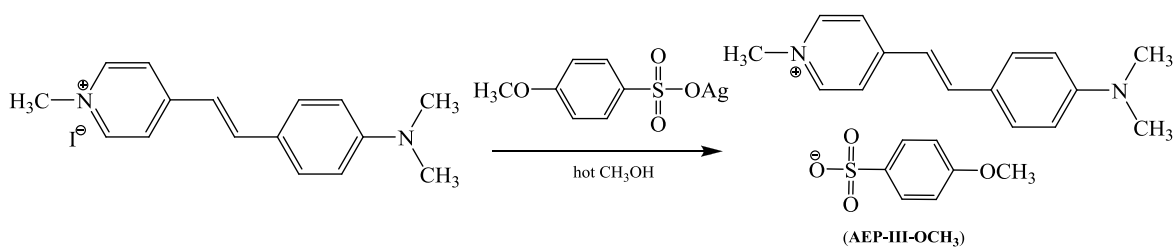
flask A : ละลาย **An-Cl** 0.16 กรัม (0.55 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายใสไม่มีสี

flask B : ละลาย **AEP-III** 0.20 กรัม (0.55 มิลลิโมล) ด้วยเมทานอลร้อน 25 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายสีแดง

นำสารละลายใน flask A และ flask B มาผสมกันมีตะกอนสีน้ำตาลของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรอง และนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีแดงของ **AEP-III-Cl** (0.22 กรัม 92% m.p.171-172 °C)

ผลิตภัณฑ์เป็นของแข็งสีแดง (0.22 กรัม, 92%) จุดหลอมเหลว 171-172 °C, UV (CH₃OH) λ_{\max} (nm) ($\log \epsilon$): 203.1 (5.57), 273.9 (7.10), 472.5 (5.78), IR (KBr) $\nu(\text{cm}^{-1})$: 1589 (C=C stretching), 1384 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.66 (2H, *d*, $J = 6.8$ Hz), 7.97 (2H, *d*, $J = 6.8$ Hz), 7.81 (1H, *d*, $J = 15.9$ Hz), 7.73 (2H, *d*, $J = 8.4$ Hz), 7.58 (2H, *d*, $J = 9.0$ Hz), 7.32 (2H, *d*, $J = 8.4$ Hz), 7.05 (1H, *d*, $J = 15.9$ Hz), 6.73 (2H, *d*, $J = 9.0$ Hz), 4.25 (3H, *s*), 3.07 (6H, *s*)

การสังเคราะห์ Aryl-ethenylpyridinium benzenesulfonates (AEP-III-OCH₃)



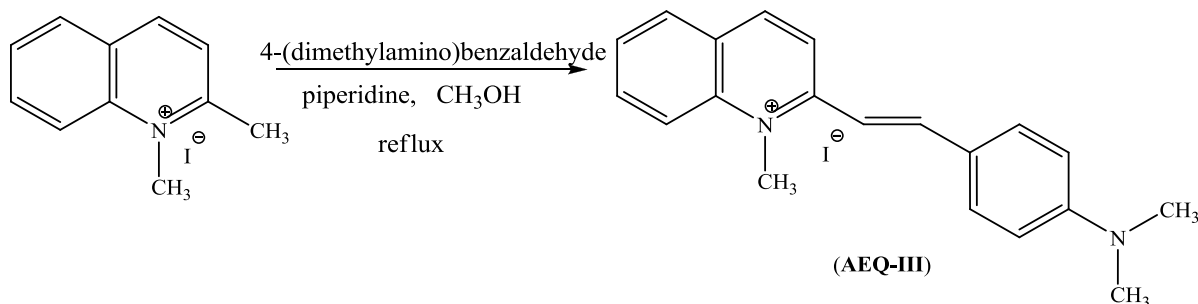
flask A : ละลาย **An-OCH₃** 0.16 กรัม (0.55 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายใสไม่มีสี

flask B : ละลาย **AEP-III** 0.20 กรัม (0.55 มิลลิโมล) ด้วยเมทานอลร้อน 25 มิลลิลิตร คนจน สารละลายหมด ได้สารละลายสีแดง

นำสารละลายใน flask A และ flask B มาผสมกันมีตะกอนสีน้ำตาลของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรอง และนำสารละลายที่ได้ไประเหยตัวทำละลายออกได้ของแข็งสีแดงของ **AEP-III-OCH₃** (0.20 กรัม 86% m.p.198-200 °C)

ผลิตภัณฑ์เป็นของแข็งสีแดง (0.20 กรัม, 86%) จุดหลอมเหลว 198-200 °C, UV (CH₃OH) λ_{\max} (nm) (log ϵ): 203.1 (5.28), 225.6 (5.43), 269.9 (5.81), 473.8 (5.26), IR (KBr) $\nu(\text{cm}^{-1})$: 1577 (C=C stretching), 1375 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.67 (2H, *J* = 6.9 Hz), 8.02 (2H, *J* = 6.9 Hz), 7.87 (1H, *d*, *J* = 16.2 Hz), 7.59 (2H, *d*, *J* = 8.9 Hz), 7.58 (2H, *d*, *J* = 8.7 Hz), 7.12 (1H, *d*, *J* = 16.2 Hz), 6.83 (2H, *d*, *J* = 8.7 Hz), 6.75 (2H, *t*, *J* = 8.9 Hz), 4.19 (3H, *s*), 3.76 (3H, *s*), 3.04 (6H, *s*)

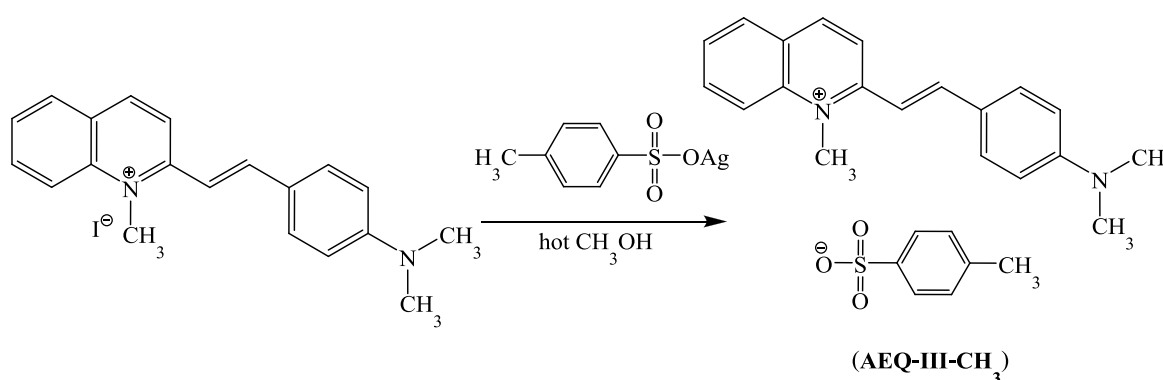
การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (AEQ-III-X)



ละลาย 1,2-dimethylquinolinium iodide 2.00 กรัม (7.01 มิลลิโมล) ด้วยเมทานอล 10 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ 4-(Dimethylamino)benzaldehyde 1.04 กรัม และ piperidine 0.69 มิลลิลิตร ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกัน ได้สารละลายสีแดง ทำการรีฟลักซ์เป็นเวลา 6 ชั่วโมง นำขวดปฏิกิริยาไปทำให้เย็นในตู้เย็นเป็นเวลา 3 วัน กรองตะกอนแบบลดความดัน ล้างตะกอนด้วยเมทานอลนำตะกอนไปทำให้แห้งโดยใช้ vacuum ได้ของแข็งสีแดงของ (E)-2-(4-dimethylamino)styryl]-1-methylquinolinium iodide (**AEQ-III**) (2.60 กรัม 89% mp 218-219°C)

ผลิตภัณฑ์เป็นของแข็งสีดำ (1.81 กรัม, 89%) จุดหลอมเหลว 218-219 °C, UV (CH₃OH) λ_{\max} (nm) (log \mathcal{E}): 205.3 (4.12), 221.9 (2.51), 280.9 (3.16), 326.8 (4.02), 521.13 (4.89), IR (KBr) $\nu(\text{cm}^{-1})$: 1600 (C=C stretching), 1280 (C-N stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.70 (1H, *d*, *J* = 9.0 Hz), 8.40 (1H, *d*, *J* = 9.0 Hz), 8.31 (1H, *d*, *J* = 7.5 Hz), 8.14 (1H, *d*, *J* = 7.8 Hz), 8.05 (1H, *d*, *J* = 15.3 Hz), 8.01 (1H, *t*, *J* = 7.8 Hz), 7.80 (1H, *t*, *J* = 7.8 Hz), 7.78 (2H, *d*, *J* = 8.7 Hz), 7.50 (1H, *d*, *J* = 15.3 Hz), 6.80 (2H, *d*, *J* = 8.7 Hz), 4.50 (3H, *s*), 3.15 (6H, *s*)

การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (AEQ-III-CH₃)



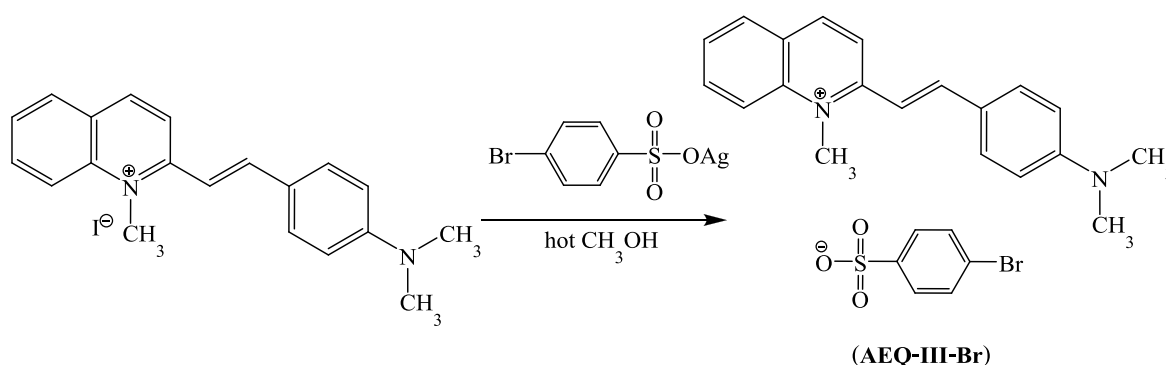
Flask A : ละลาย **An-CH₃** 0.06 กรัม (0.24 มิลลิโมล) ด้วยเมทานอลร้อน 25 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายใสไม่มีสี

Flask B : ละลาย **AEQ-III** 0.10 กรัม (0.24 มิลลิโมล) ด้วยเมทานอลร้อน 40 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายสีชมพู

นำสารละลายใน flask A และ flask B มาผสมกันมีตะกอนสีดำของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรอง และนำสารละลายที่ได้ไประเหยตัวทำละลายออกจนเกือบหมดจะได้ของแข็งสีเขียวของ **AEQ-III-CH₃** (0.06 กรัม 57% mp 284-285 °C)

ผลิตภัณฑ์เป็นของแข็งสีเขียว (0.06 กรัม, 57%) จุดหลอมเหลว 284-285 °C, UV (CH₃OH) λ_{\max} (nm) (log \mathcal{E}): 328.6 (4.26), 521.1 (3.62), IR (KBr) $\nu(\text{cm}^{-1})$: 1567 (C=C stretching), 1167 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.71 (1H, *d*, *J* = 9.0 Hz), 8.42 (1H, *d*, *J* = 9.0 Hz), 8.35 (1H, *d*, *J* = 7.8 Hz), 8.35 (1H, *d*, *J* = 7.8 Hz), 8.12 (1H, *t*, *J* = 7.8 Hz), 8.00 (1H, *d*, *J* = 15.6 Hz), 7.80 (1H, *t*, *J* = 7.8 Hz), 7.73 (2H, *d*, *J* = 8.7 Hz), 7.60 (1H, *d*, *J* = 15.6 Hz), 7.55 (2H, *d*, *J* = 8.1 Hz), 7.10 (2H, *d*, *J* = 8.1 Hz), 6.80 (2H, *d*, *J* = 8.7 Hz), 4.50 (3H, *s*), 3.15 (6H, *s*)

การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (AEQ-III-Br)



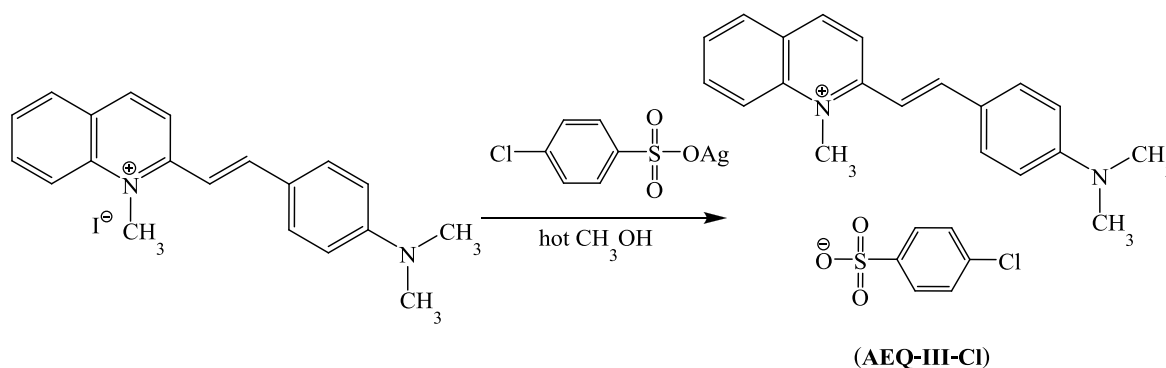
Flask A : ละลาย **An-Br** 0.08 กรัม (0.24 มิลลิโมล) ด้วยเมทานอลร้อน 25 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายใส ไม่มีสี

Flask B : ละลาย **AEQ-III** 0.10 กรัม (0.24 มิลลิโมล) ด้วยเมทานอลร้อน 40 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายสีชมพู

นำสารละลายใน flask A และ flask B มาผสมกันมีตะกอนสีน้ำตาลแดงของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรอง และนำสารละลายที่ได้ไประเหยตัวทำละลายออกจนเกือบหมดจะได้ของแข็งสีดำของ **AEQ-III-Br** (0.07 กรัม 59% mp 282-283°C)

ผลิตภัณฑ์เป็นของแข็งสีดำ (0.07 กรัม, 59%) จุดหลอมเหลว 282-283 °C, UV (CH₃OH) λ_{\max} (nm) (log \mathcal{E}): 289.5 (4.52), 328.1 (3.14), 522.3 (2.72), IR (KBr) $\nu(\text{cm}^{-1})$: 1570 (C=C stretching), 1190 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.70 (1H, *d*, *J* = 9.0 Hz), 8.41 (1H, *d*, *J* = 9.0 Hz), 8.37 (1H, *d*, *J* = 7.8 Hz), 8.14 (1H, *d*, *J* = 7.8 Hz), 8.05 (1H, *d*, *J* = 15.3 Hz), 8.01 (1H, *t*, *J* = 7.8 Hz), 7.88 (1H, *t*, *J* = 7.8 Hz), 7.82 (2H, *d*, *J* = 7.5 Hz), 7.72 (1H, *d*, *J* = 15.3 Hz), 7.63 (2H, *d*, *J* = 8.7 Hz), 6.95 (2H, *d*, *J* = 8.7 Hz), 6.80 (2H, *d*, *J* = 7.5 Hz), 4.52 (3H, *s*), 2.50 (6H, *s*)

การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (AEQ-III-Cl)



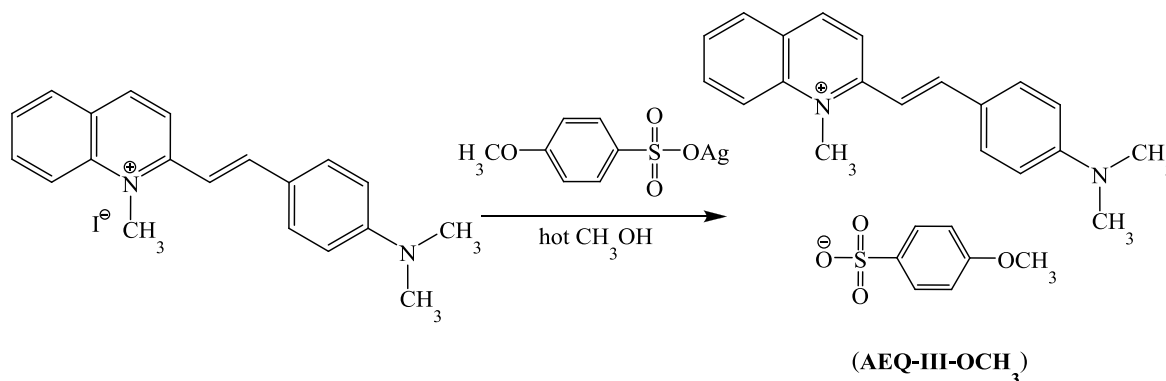
Flask A : ละลาย **An-Cl** 0.08 กรัม (0.24 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายใสไม่มีสี

Flask B : ละลาย **AEQ-III** 0.10 กรัม (0.24 มิลลิโมล) ด้วยเมทานอลร้อน 50 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายสีชมพู

นำสารละลายใน flask A และ flask B มาผสมกันมีตะกอน ของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรอง และนำสารละลายที่ได้ไประเหยตัวทำละลายออกจนเกือบหมดจะได้ของแข็งสีแดงของ **AEQ-III-Cl** (0.06 กรัม 54% mp 284-285°C)

ผลิตภัณฑ์เป็นของแข็งสีแดง (0.06 กรัม, 54%) จุดหลอมเหลว 284-285 °C, UV (CH₃OH) λ_{\max} (nm) (log \mathcal{E}): 289.5 (4.38), 326.9 (3.76), 522.8 (2.36), IR (KBr) $\nu(\text{cm}^{-1})$: 1571 (C=C stretching), 1164 (S=O stretching), ¹H NMR(CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.90 (1H, *d*, *J* = 9.0 Hz), 8.46 (1H, *d*, *J* = 9.0 Hz), 8.40 (1H, *d*, *J* = 7.8 Hz), 8.35 (1H, *d*, *J* = 7.8 Hz), 8.12 (1H, *t*, *J* = 7.8 Hz), 8.09 (1H, *d*, *J* = 15.3 Hz), 7.91 (1H, *t*, *J* = 7.8 Hz), 7.88 (2H, *d*, *J* = 8.7 Hz), 7.63 (2H, *d*, *J* = 8.1 Hz), 7.50 (1H, *d*, *J* = 15.3 Hz), 7.30 (2H, *d*, *J* = 8.1 Hz), 7.05 (2H, *d*, *J* = 8.7 Hz), 4.50 (3H, *s*), 3.12 (6H, *s*)

การสังเคราะห์ Aryl-ethenylquinolinium benzenesulfonates (AEQ-III-OCH₃)



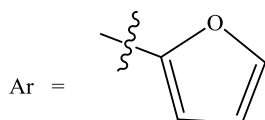
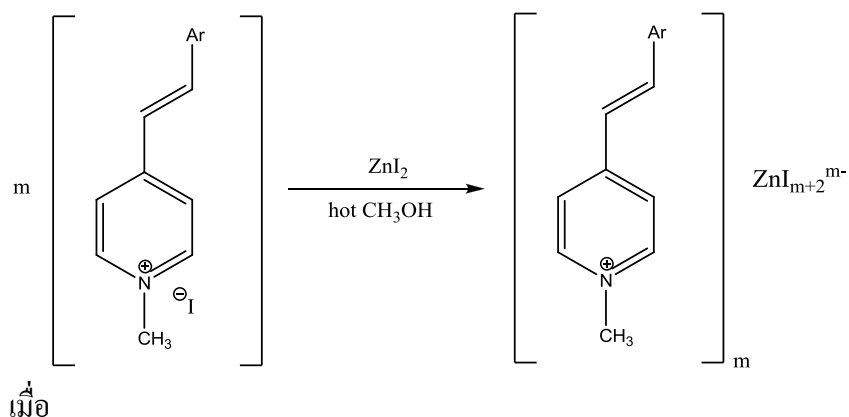
Flask A : ละลาย **An-OCH₃** 0.07 กรัม (0.24 มิลลิโมล) ด้วยเมทานอลร้อน 20 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายใสไม่มีสี

Flask B : ละลาย **AEQ-III** 0.10 กรัม (0.24 มิลลิโมล) ด้วยเมทานอลร้อน 40 มิลลิลิตร คนจนสารละลายหมด ได้สารละลายสี

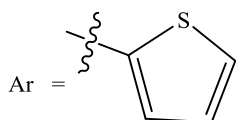
นำสารละลายใน flask A และ flask B มาผสมกันมีตะกอนสีดำของ AgI เกิดขึ้น กรองตะกอนออกโดยใช้กรวยกรอง และนำสารละลายที่ได้ไประเหยตัวทำละลายออกจนเกือบหมดจะได้ของแข็งสีเขียวของ **AEQ-III-OCH₃** (0.09 กรัม 81% mp 279-281°C)

ผลิตภัณฑ์เป็นของแข็งสีเขียว (0.09 กรัม, 81%) จุดหลอมเหลว 279-281 °C, UV (CH₃OH) λ_{\max} (nm) (log ϵ): 254.6 (3.24), 521.7 (4.52), IR (KBr) ν (cm⁻¹): 1568 (C=C stretching), 1163 (S=O stretching), ¹H NMR (CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.70 (1H, *d*, *J* = 9.0 Hz), 8.41 (1H, *d*, *J* = 9.0 Hz), 8.31 (1H, *d*, *J* = 7.9 Hz), 8.16 (1H, *d*, *J* = 7.9 Hz), 8.09 (1H, *d*, *J* = 15.3 Hz), 7.99 (1H, *t*, *J* = 7.9 Hz), 7.81 (1H, *t*, *J* = 7.9 Hz), 7.76 (2H, *d*, *J* = 8.7 Hz), 7.69 (2H, *d*, *J* = 8.1 Hz), 7.50 (1H, *d*, *J* = 15.3 Hz), 6.81 (2H, *d*, *J* = 8.1 Hz), 6.80 (2H, *d*, *J* = 8.7 Hz), 4.50 (3H, *s*), 3.13 (6H, *s*)

การสังเคราะห์ Aryl-ethenylpyridinium zinc iodide (AEP-ZnI) ตาม scheme 3.8



AEP-I-ZnI หรือ PAC-17

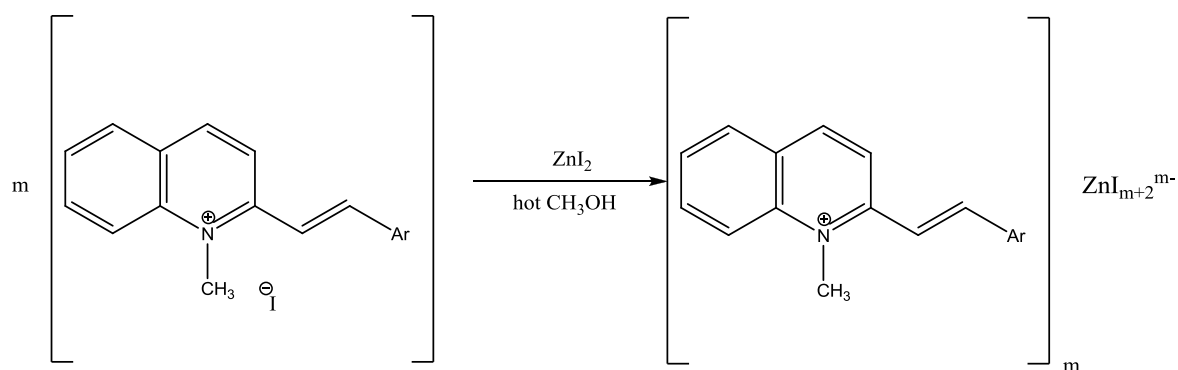


AEP-II-ZnI หรือ PAC-18

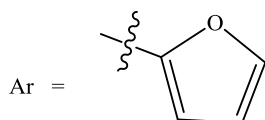
สำหรับการเตรียมสารประกอบ PAC-17 และ PAC-18 เนื่องจากไม่สามารถเตรียม AEP-I ซึ่งเป็นสารตั้งต้นในการเตรียม PAC-17 จึงไม่สามารถทำการสังเคราะห์ PAC-17

สำหรับ PAC-18 ไม่สามารถสังเคราะห์ได้แม้ว่าจะเปลี่ยนเงื่อนไขของปฏิกิริยาหลายสถานะแล้วก็ตาม

การสังเคราะห์ Aryl-ethenylpyridinium zinc iodide (AEQ-ZnI) ตาม scheme 3.9

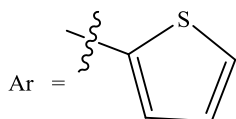


เมื่อ



AEQ-I-ZnI หรือ PAC-19

และ

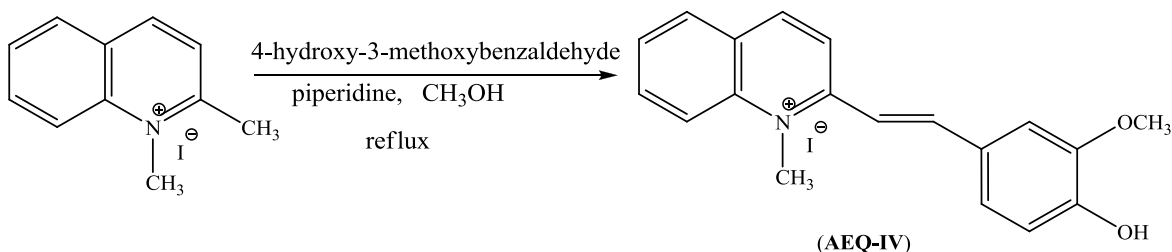


AEQ-II-ZnI หรือ PAC-20

สำหรับการเตรียมสารประกอบ PAC-19 และ PAC-20 เนื่องจากไม่สามารถเตรียม AEQ-I ซึ่งเป็นสารตั้งต้นในการเตรียม PAC-19 จึงไม่สามารถทำการสังเคราะห์ PAC-19 ได้

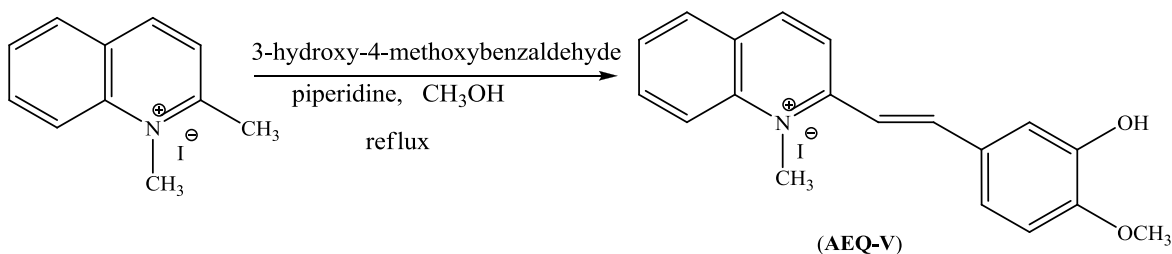
สำหรับ PAC-20 ไม่สามารถสังเคราะห์ได้แม้ว่าจะเปลี่ยนเงื่อนไขของปฏิกิริยาหลายสถานะแล้วก็ตาม

จากการสังเคราะห์สารตามแผนการสังเคราะห์ดัง scheme 13.8 และ scheme 13.9 ไม่สามารถเตรียมสาร PAC-17, PAC-18, PAC-19 และ PAC-20 ได้ แสดงว่า สารทั้งสี่สารไม่เหมาะสมที่จะเกิดสารประกอบเชิงซ้อนกับโลหะ Zn(II) ผู้วิจัยจึงได้ทำวิจัยเพิ่มเติมโดยการสังเคราะห์สาร AEQ-IV, AEQ-V, AEQ-VI และ AEQ-VII เพื่อทำการสังเคราะห์สารประกอบเชิงซ้อนกับ Zn(II) ได้ผลดังนี้



ละลาย 1,2-dimethylquinolinium iodide 2.98 กรัม (10.05 มิลลิโมล) ด้วยเมทานอล 10 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ vanillin 1.60 กรัม และ piperidine 1.00 มิลลิลิตร ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกัน ทำการรีฟลักซ์เป็นเวลา 3 ชั่วโมง นำขวดปฏิกิริยาไปทำให้เย็นในตู้เย็นเป็นเวลา 2 วัน กรองตะกอนแบบลดความดัน ล้างตะกอนด้วยไดเอทิลอีเทอร์ นำตะกอนไปทำให้แห้งโดยใช้ vacuum ได้ของแข็งสีแดงเข้มของ 4-[(E)-2-(4-hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (AEQ-IV) (2.87 กรัม 68% mp 248-250°C).

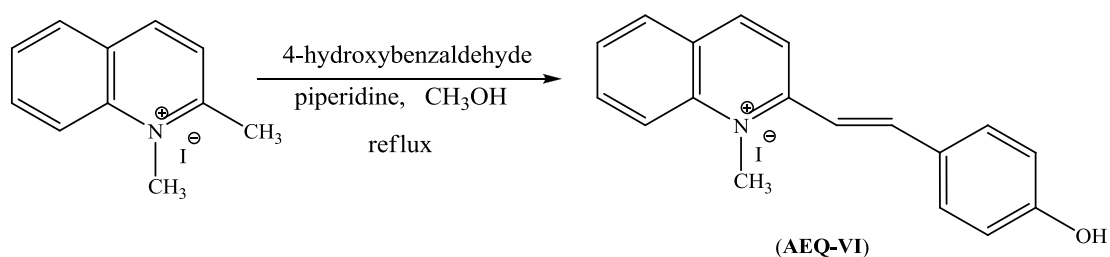
ผลิตภัณฑ์เป็นของแข็งสีแดงเข้ม ^1H NMR ($\text{CDCl}_3 + \text{DMSO-}d_6$) (δ ppm) (300 MHz): 10.02 (1H, s), 8.94 (1H, d, $J = 9.0$), 8.53 (1H, d, $J = 9.0$), 8.50 (1H, d, $J = 7.5$), 8.30 (1H, dd, $J = 1.2, 7.5$ Hz), 8.17 (1H, d, $J = 15.6$ Hz), 8.15 (1H, dt, $J = 1.2, 7.5$ Hz), 7.90 (1H, t, $J = 7.5$ Hz), 7.73 (1H, d, $J = 15.6$ Hz), 7.58 (1H, d, $J = 1.8$ Hz), 7.41 (1H, dd, $J = 1.8, 8.1$ Hz), 6.93 (1H, d, $J = 8.1$ Hz), 4.62 (3H, s), 3.95 (3H, s)



ละลาย 1,2-dimethylquinolinium iodide 2.98 กรัม (10.05 มิลลิโมล) ด้วยเมทานอล 10 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ isovanillin 1.60 กรัม และ piperidine 1.00 มิลลิลิตร ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกัน ทำการรีฟลักซ์เป็นเวลา 2 ชั่วโมง นำขวดปฏิกิริยาไปทำให้เย็นในตู้เย็นเป็นเวลา 2 วัน กรองตะกอนแบบลดความดัน ล้างตะกอนด้วยไดเอทิล

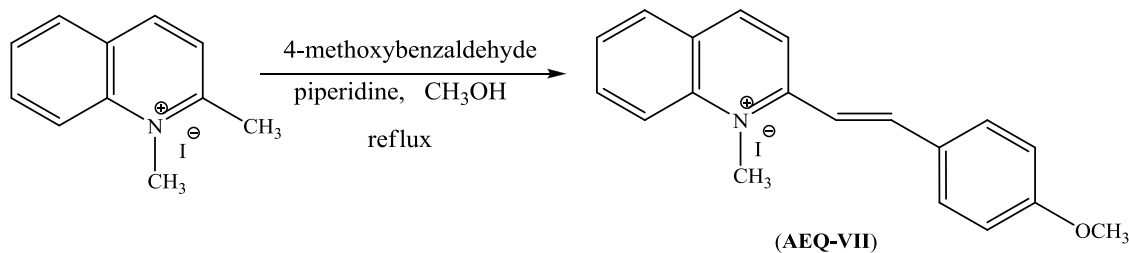
อีเทอร์ นำตะกอนไปทำให้แห้งโดยใช้ vacuum ได้ของแข็งน้ำตาล-แดงของ 4-[(*E*)-2-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (**AEQ-V**) (2.70 g 64% mp 218-220°C).

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล-แดง $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO}-d_6$) (δ ppm) (300 MHz): 9.52 (1H, *s*), 8.95 (1H, *d*, $J = 9.0$ Hz), 8.852 (1H, *d*, $J = 9.0$ Hz), 8.49 (1H, *d*, $J = 7.5$ Hz), 8.32 (1H, *d*, $J = 7.5$ Hz), 8.18 (1H, *dt*, $J = 1.5, 7.5$ Hz), 8.09 (1H, *d*, $J = 15.9$ Hz), 7.93 (1H, *t*, $J = 7.5$ Hz), 7.69 (1H, *d*, $J = 15.9$ Hz), 7.49 (1H, *d*, $J = 2.1$ Hz), 7.41 (1H, *br d*, $J = 8.4$ Hz), 7.36 (1H, *d*, $J = 8.4$ Hz), 4.65 (3H, *s*), 3.95 (3H, *s*)



ละลาย 1,2-dimethylquinolinium iodide 2.00 กรัม (7.01 มิลลิโมล) ด้วยเมทานอล 10 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ 4-hydroxybenzaldehyde 0.86 กรัม และ piperidine 0.69 มิลลิลิตร ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกัน ทำการรีฟลักซ์เป็นเวลา 3 ชั่วโมง นำขวดปฏิกิริยาไปทำให้เย็นในตู้เย็นเป็นเวลา 2 วัน กรองตะกอนแบบลดความดัน ล้างตะกอนด้วยไดเอทิลอีเทอร์ นำตะกอนไปทำให้แห้งโดยใช้ vacuum ได้ของแข็งน้ำตาลของ 4-[(*E*)-2-(4-hydroxyphenyl)ethenyl]-1-methylquinolinium iodide (**AEQ-VI**) (1.99 กรัม 73% mp 192-194°C).

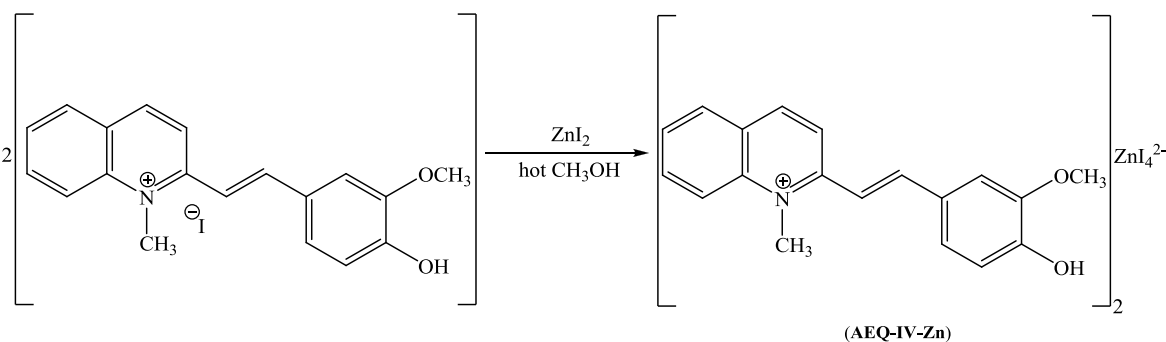
ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO}-d_6$) (δ ppm) (300 MHz): 9.64 (1H, *s*), 8.47 (1H, *d*, $J = 9.0$ Hz), 8.22 (1H, *d*, $J = 9.0$ Hz), 8.15 (1H, *d*, $J = 8.4$ Hz), 8.05 (1H, *br d*, $J = 8.1$ Hz), 8.01 (1H, *ddd*, $J = 1.5, 7.2, 8.4$ Hz), 7.98 (1H, *d*, $J = 15.3$ Hz), 7.72 (1H, *dd*, $J = 7.2, 8.1$ Hz), 7.68 (2H, *d*, $J = 9.0$ Hz), 7.02 (1H, *d*, $J = 15.3$ Hz), 6.72 (2H, *d*, $J = 9.0$ Hz), 4.35 (3H, *s*)



ละลาย 1,2-dimethylquinolinium iodide 1.00 กรัม (3.51 มิลลิโมล) ด้วยเมทานอล 10 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ 4-methoxybenzaldehyde 0.43 กรัม และ piperidine 0.35 มิลลิลิตร ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกัน ทำการรีฟลักซ์เป็นเวลา 7 ชั่วโมง นำขวดปฏิกิริยาไปทำให้เย็นในตู้เย็นเป็นเวลา 2 วัน กรองตะกอนแบบลดความดัน ล้างตะกอนด้วยไดเอทิลอีเทอร์ นำตะกอนไปทำให้แห้งโดยใช้ vacuum ได้ของแข็งน้ำตาลของ 4-[(E)-2-(4-hydroxyphenyl)ethenyl]-1-methylquinolinium iodide (AEQ-VII) (1.03 กรัม 73% mp 192-194°C).

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO-}d_6$) (δ ppm) (300 MHz): 8.91 (1H, *d*, $J = 9.0$ Hz), 8.47 (1H, *d*, $J = 9.0$ Hz), 8.42 (1H, *d*, $J = 8.1$ Hz), 8.27 (1H, *br d*, $J = 8.1$ Hz), 8.17 (1H, *dt*, $J = 1.5, 8.1$ Hz), 8.10 (1H, *d*, $J = 15.6$ Hz), 7.92 (1H, *t*, $J = 8.1$ Hz), 7.90 (2H, *d*, $J = 8.7$ Hz), 7.72 (1H, *d*, $J = 15.6$ Hz), 7.04 (2H, *d*, $J = 8.7$ Hz), 4.62 (3H, *s*), 3.91 (3H, *s*)

การสังเคราะห์ Aryl-ethenylpyridinium zinc iodide (AEQ-IV-Zn)

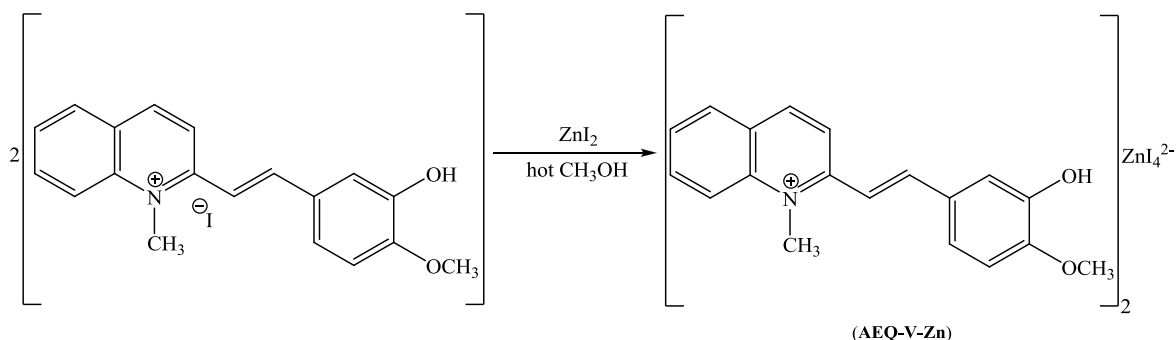


ละลาย AEQ-IV 0.40 กรัม (0.80 มิลลิโมล) ด้วยเมทานอล 10 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ zinc(II) iodide 0.15 กรัม (0.40 มิลลิโมล) ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกันเวลา 1 ชั่วโมง นำสารละลายที่ได้ไประเหยตัวทำละลายให้แห้งโดยใช้ evaporator ได้ของแข็งน้ำตาลของ (AEQ-IV-Zn) (0.14 กรัม 40% mp 225-226°C).

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล (0.14 กรัม, 40%) จุดหลอมเหลว 225-226 °C, UV (CH_3OH) λ_{max} (nm) ($\log \mathcal{E}$): 217.3 (4.87), 311.6 (3.83), 440.9 (5.04), 561.8 (4.60), IR (KBr) $\text{V}(\text{cm}^{-1})$: 3437 (O-H stretching), 1579 (C=C stretching), $^1\text{H NMR}$ ($\text{CDCl}_3 + \text{DMSO-}d_6$) (δ ppm) (300 MHz): 9.87 (1H, *s*), 8.89 (1H, *d*, $J = 9.0$ Hz), 8.48 (1H, *d*, $J = 9.0$ Hz), 8.45 (1H, *d*, $J = 7.5$ Hz), 8.27 (1H, *dd*, $J = 1.2, 7.5$ Hz), 8.14 (1H, *dt*, $J = 1.2, 7.5$ Hz), 7.92 (1H, *d*, $J = 15.9$ Hz), 7.90 (1H, *t*, $J = 7.5$ Hz), 7.70 (1H, *d*,

$J = 15.9$ Hz), 7.52 (1H, *d*, $J = 1.8$ Hz), 7.39 (1H, *dd*, $J = 1.8, 8.1$ Hz), 6.95 (1H, *d*, $J = 8.1$ Hz), 4.62 (3H, *s*), 4.00 (3H, *s*)

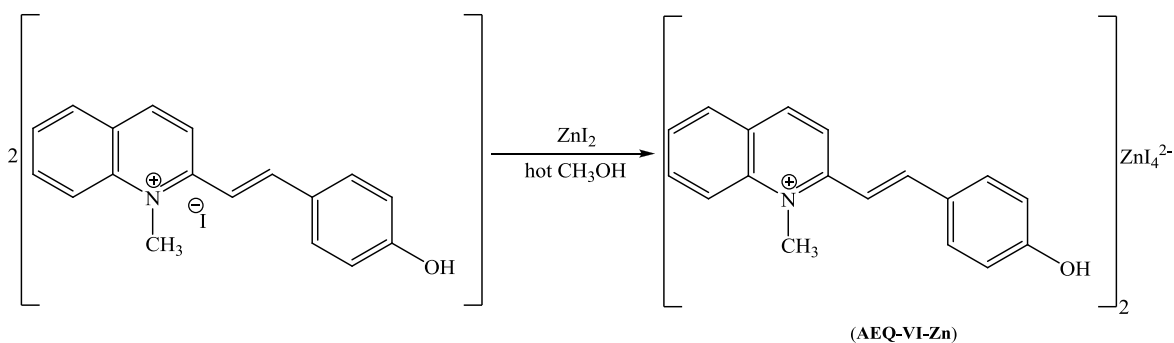
การสังเคราะห์ Aryl-ethenylpyridinium zinc iodide (AEQ-V-Zn)



ละลาย AEQ-V 0.40 กรัม (0.80 มิลลิโมล) ด้วยเมทานอล 10 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ zinc(II) iodide 0.15 กรัม (0.40 มิลลิโมล) ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกันเวลา 1 ชั่วโมง นำสารละลายที่ได้ไประเหยตัวทำละลายให้แห้งโดยใช้ evaporator ได้ของแข็งน้ำตาลของ (AEQ-V-Zn) (0.14 กรัม 40% mp 220-221°C).

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล (0.14 กรัม, 40%) จุดหลอมเหลว 220-221 °C, UV (CH₃OH) λ_{\max} (nm) (log ϵ): 218.2 (5.24), 305.4 (4.51), 430.9 (4.99), IR (KBr) $\nu(\text{cm}^{-1})$: 3436 (O-H stretching), 1585 (C=C stretching), 1221 (C-O stretching), ¹H NMR(CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 9.31 (1H, *s*), 8.97 (1H, *d*, $J = 9.0$ Hz), 8.54 (1H, *d*, $J = 9.0$ Hz), 8.50 (1H, *d*, $J = 7.5$ Hz), 8.31 (1H, *d*, $J = 7.5$ Hz), 8.15 (1H, *dt*, $J = 1.5, 7.5$ Hz), 8.11 (1H, *d*, $J = 15.9$ Hz), 7.91 (1H, *t*, $J = 7.5$ Hz), 7.70 (1H, *d*, $J = 15.9$ Hz), 7.47 (1H, *d*, $J = 2.1$ Hz), 7.41 (1H, *br d*, $J = 8.4$ Hz), 7.04 (1H, *d*, $J = 8.4$ Hz), 4.57 (3H, *s*), 3.92 (3H, *s*)

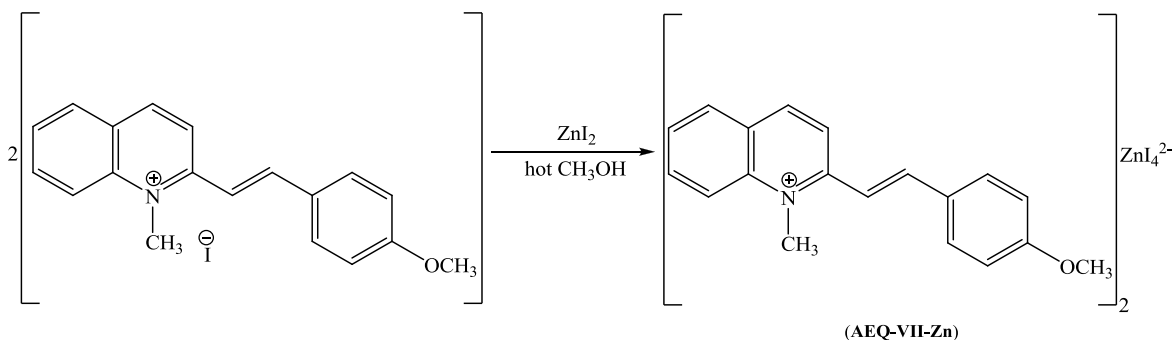
การสังเคราะห์ Aryl-ethenylpyridinium zinc iodide (AEQ-VI-Zn)



ละลาย **AEQ-VI** 0.60 กรัม (1.54 มิลลิโมล) ด้วยเมทานอล 10 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ zinc(II) iodide 0.25 กรัม (0.77 มิลลิโมล) ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกันเวลา 1 ชั่วโมง นำสารละลายที่ได้ไประเหยตัวทำละลายให้แห้งโดยใช้ evaporator ใต้ของแข็งแห้งของ **(AEQ-VI-Zn)** (0.37 กรัม 43% mp 234-236 °C).

ผลิตภัณฑ์เป็นของแข็งสีแดงเข้ม (0.37 กรัม, 43%) จุดหลอมเหลว 234-236 °C, UV (CH₃OH) λ_{\max} (nm) (log ϵ): 220.9 (3.38), 260.6 (3.02), 312.2 (2.79), 426.8 (3.32), IR (KBr) ν (cm⁻¹): 3421 (O-H stretching), 1586 (C=C stretching), ¹H NMR(CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 9.68 (1H, *s*), 8.86 (1H, *d*, *J* = 9.0 Hz), 8.46 (1H, *d*, *J* = 9.0 Hz), 8.41 (1H, *d*, *J* = 8.1 Hz), 8.25 (1H, *br d*, *J* = 8.1 Hz), 8.12 (1H, *dt*, *J* = 1.5, 8.1 Hz), 8.10 (1H, *d*, *J* = 15.3 Hz), 7.87 (1H, *t*, *J* = 8.1 Hz), 7.78 (2H, *d*, *J* = 9.0 Hz), 7.64 (1H, *d*, *J* = 15.3 Hz), 6.92 (2H, *d*, *J* = 9.0 Hz), 4.48 (3H, *s*)

การสังเคราะห์ Aryl-ethenylpyridinium zinc iodide (AEQ-VII-Zn)

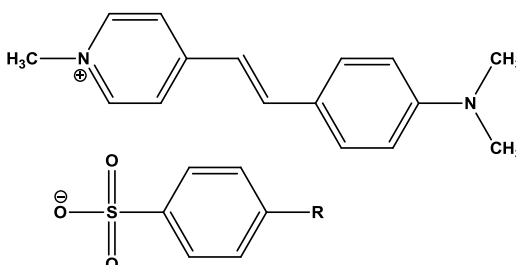


ละลาย **AEQ-VII** 0.60 กรัม (1.48 มิลลิโมล) ด้วยเมทานอล 10 มิลลิลิตร คนจนสารละลายหมด เติมสารละลายของ zinc(II) iodide 0.24 กรัม (0.74 มิลลิโมล) ลงในสารละลายข้างต้นตามลำดับ คนจนสารละลายเป็นเนื้อเดียวกันเวลา 1 ชั่วโมง นำสารละลายที่ได้ไประเหยตัวทำละลายให้แห้งโดยใช้ evaporator ได้ของแข็งสีน้ำตาลของ (**AEQ-VII-Zn**) (0.40 กรัม 73% mp 229-231°C).

ผลิตภัณฑ์เป็นของแข็งสีน้ำตาล (0.40 กรัม, 73%) จุดหลอมเหลว 229-231 °C, UV (CH₃OH) λ_{max} (nm) (log ϵ): 219.1 (3.92), 249.2 (3.73), 407.2 (3.68), IR (KBr) $\nu(\text{cm}^{-1})$: 1581 (C=C stretching), 1220 (C-O stretching), ¹H NMR(CDCl₃ + DMSO-*d*₆) (δ ppm) (300 MHz): 8.97 (1H, *d*, *J* = 8.7 Hz), 8.53 (1H, *d*, *J* = 8.7 Hz), 8.51 (1H, *d*, *J* = 7.2 Hz), 8.32 (1H, *d*, *J* = 7.2 Hz), 8.25-8.14 (1H, *m*), 8.20 (1H, *d*, *J* = 15.9 Hz), 8.02-7.90 (1H, *m*), 7.95 (2H, *d*, *J* = 8.7 Hz), 7.79 (1H, *d*, *J* = 15.9 Hz), 7.08 (2H, *d*, *J* = 8.7 Hz), 4.57 (3H, *s*), 3.59 (3H, *s*)

เนื่องจากสารที่สังเคราะห์ได้ตกผลึกใน centrosymmetric space group ซึ่งไม่แสดงสมบัติ second order non linear optical ตามที่คาดหมายไว้ เพื่อให้เกิดประโยชน์ต่องานวิจัย จากการตรวจสอบเอกสารเพิ่มเติมพบว่า สารอนุพันธ์ pyridinium และ quinolinium ที่มีหมู่แทนที่เป็น amino และ thiophene หลายชนิดแสดงฤทธิ์ทางชีวภาพที่น่าสนใจ ดังนั้นผู้วิจัยจึงได้นำสารอนุพันธ์ pyridinium และ quinolinium ที่มีหมู่แทนที่เป็น amino และหมู่ thiophene ที่สังเคราะห์ได้ไปทดสอบฤทธิ์ด้านเชื้อแบคทีเรีย และพบว่าสำหรับสารประกอบที่มีหมู่แทนที่ thiophene คือสาร **AEP-II** และ **PAC5 – PAC8** ไม่ออกฤทธิ์ด้านเชื้อแบคทีเรีย ในขณะที่สาร **AEQ-II** และ **PAC13 – PAC16** แสดงฤทธิ์ด้านเชื้อแบคทีเรียต่ำมาก

สำหรับสารประกอบที่มีหมู่แทนที่ เป็น dimethylamino (**AEP-III-X** และ **AEQ-III-X**) แสดงฤทธิ์ด้านเชื้อแบคทีเรียที่น่าสนใจ ดังตารางที่ 1 และตารางที่ 2



AEP-III = (*E*)-4-(4-(dimethylamino)styryl)-1-methylpyridinium iodide

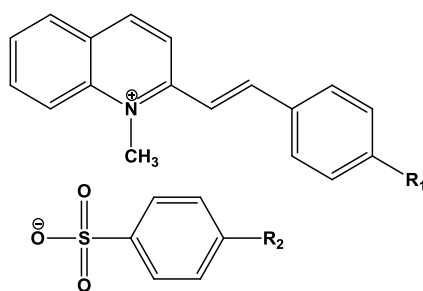
ตารางที่ 1 ฤทธิ์ต้านเชื้อแบคทีเรียของสาร AEP-III-X

Compound	MIC ($\mu\text{g/ml}$)							
	Gram-positive bacteria					Gram-negative bacteria		
	MRSA*	<i>S. aureus</i>	<i>B. subtilis</i>	VRE**	<i>E. faecalis</i>	<i>P. aeruginosa</i>	<i>S. typhi</i>	<i>S. sonnei</i>
AEP-III-CH ₃	18.75	-	-	-	-	300	-	-
AEP-III-Br	37.5	-	-	-	-	-	-	-
AEP-III-Cl	18.75	-	300	300	300	150	-	-
AEP-III-OCH ₃	18.75	-	300	300	300	150	-	-
BZK	9.37	<2.34	150	9.37	9.37	300	9.37	-
Vancomycin	<2.34	4.68	2.34	2.34	<2.34	2.34	4.68	4.68

- No activity was observed up to 300 $\mu\text{g/mL}$.

* Methicillin-Resistant *S. aureus* ATCC 43300

** Vancomycin-Resistant *E. faecalis* ATCC 51299



AEQ-III = (*E*)-2-(4-(dimethylamino)styryl)-1-methylquinolinium iodide

ตารางที่ 2ฤทธิ์ต้านเชื้อแบคทีเรียของสาร AEQ-III-X

Compound	MIC ($\mu\text{g/ml}$)							
	Gram-positive bacteria					Gram-negative bacteria		
	MRSA	<i>S.</i>	<i>B.</i>	VRE**	<i>E.</i>	<i>P.</i>	<i>S.</i>	<i>S.</i>
	*	<i>aureus</i>	<i>subtilis</i>		<i>faecalis</i>	<i>aeruginosa</i>	<i>typhi</i>	<i>sonnei</i>
AEQ-III-CH ₃	2.34	2.34	2.34	2.34	2.34	300	300	2.34
AEQ-III-Br	2.34	2.34	2.34	2.34	2.34	300	300	2.34
AEQ-III-Cl	2.34	2.34	2.34	2.34	2.34	300	300	2.34
AEQ-III-OCH ₃	2.34	-	75	150	150	-	-	150
BZK	9.37	<2.34	150	9.37	9.37	300	9.37	-
Vancomycin	<2.34	9.37	2.34	2.34	9.375	2.34	2.34	2.34

- No activity was observed up to 300 $\mu\text{g/mL}$.

* Methicillin-Resistant *S. aureus* ATCC 43300

** Vancomycin-Resistant *E. faecalis* ATCC 51299

Bacteria strains

Gram-positive bacteria

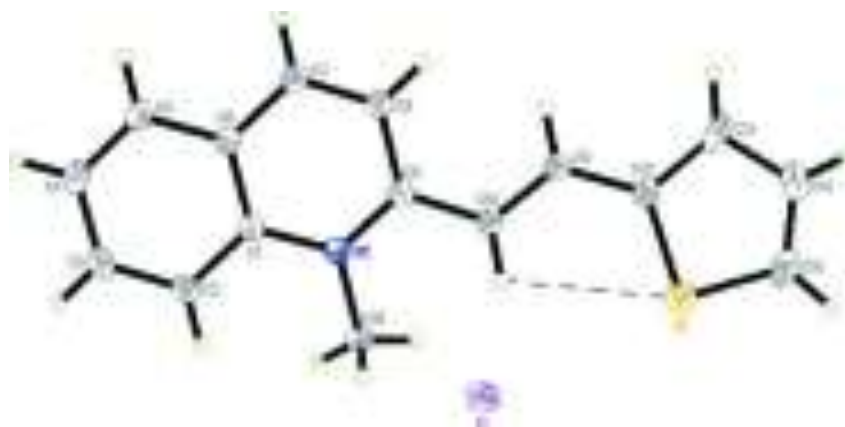
- *Bacillus subtilis*
- *Enterococcus faecalis*
- *Staphylococcus aureus*
- Methicillin-Resistant *Staphylococcus aureus*
- Vancomycin-Resistant *Enterococcus faecalis*

Gram-negative bacteria

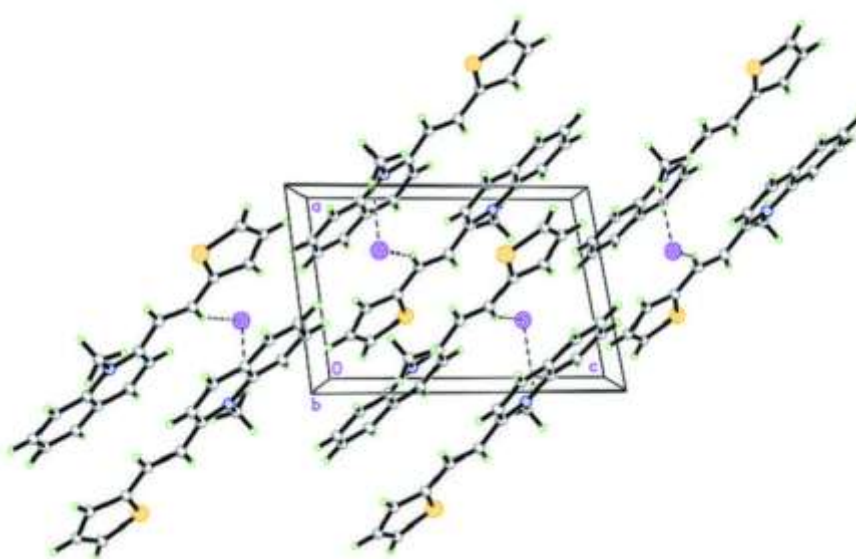
- *Pseudomonas aeruginosa*
- *Salmonella typhi*
- *Shigella sonnei*

5. โครงสร้างผลึก

จากสารที่สังเคราะห์ได้เมื่อนำมาตกผลึกเพื่อหาโครงสร้างสารด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์บนผลึกเดี่ยว สามารถตกผลึกและหาโครงสร้างสารด้วยเทคนิคดังกล่าวจำนวน 9 สาร คือ **AEQ-II**, **PAC-5**, **PAC-7**, **PAC-14**, **AEQ-III**, **AEP-III-CH₃**, **AEP-III-Br**, **AEP-III-Cl** และ **AEQ-III-OCH₃** โครงสร้างผลึกของสารประกอบทั้ง 7 สาร แสดงดังต่อไปนี้



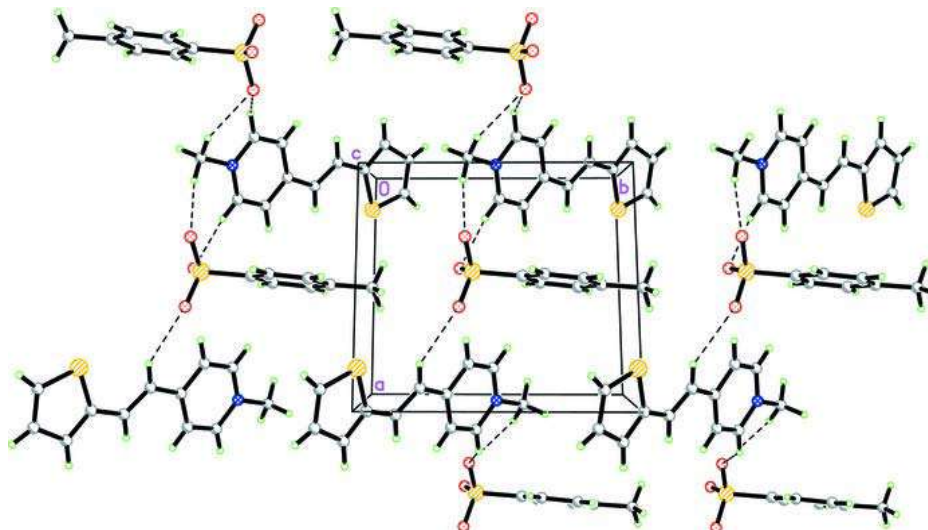
โครงสร้างของสารประกอบ **AEQ-II** (centrosymmetric $P\bar{1}$ space group)



โครงสร้างผลึกของสารประกอบ **AEQ-II**



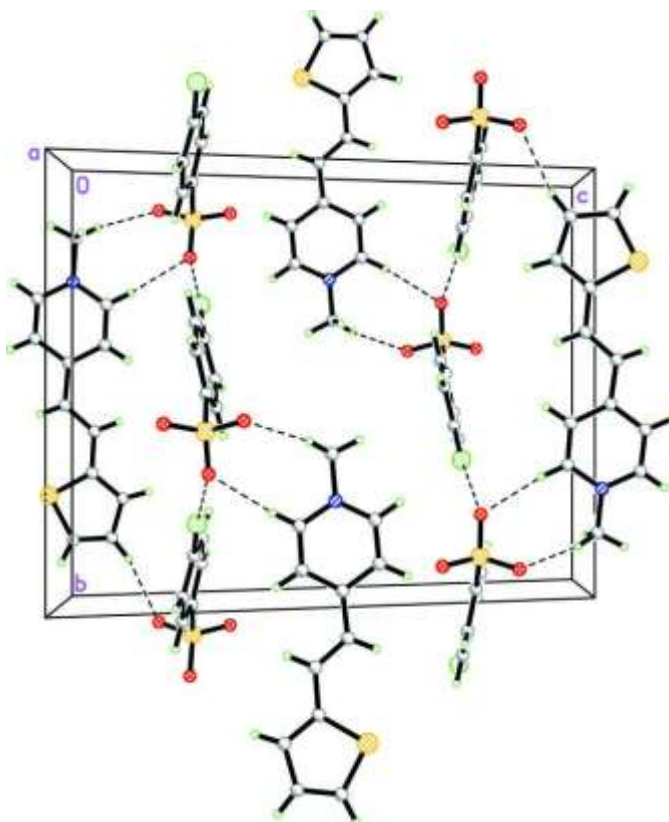
โครงสร้างของสารประกอบ PAC-5 (centrosymmetric $P\bar{1}$ space group)



โครงสร้างผลึกของสารประกอบ PAC-5



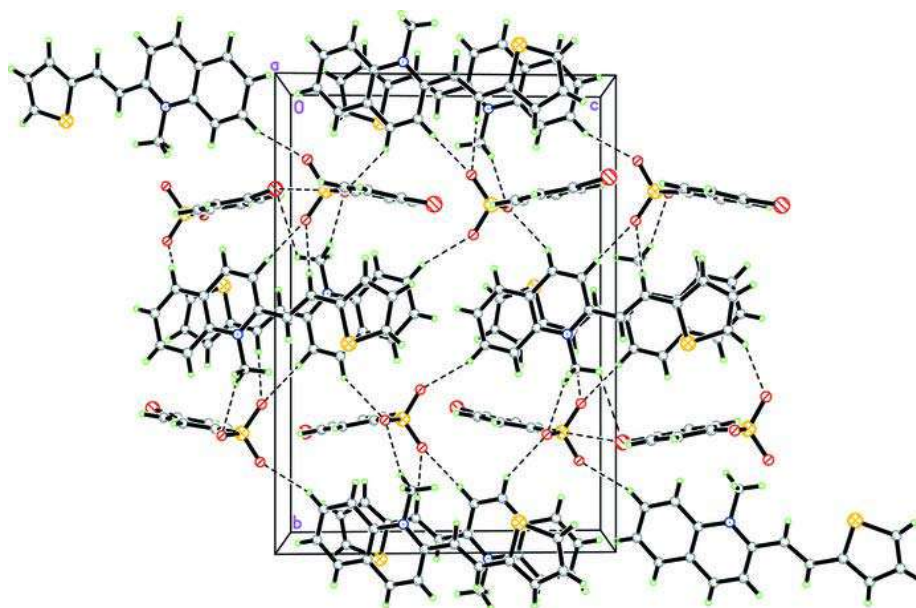
โครงสร้างของสารประกอบ PAC-7 (centrosymmetric $P2_1/c$ space group)



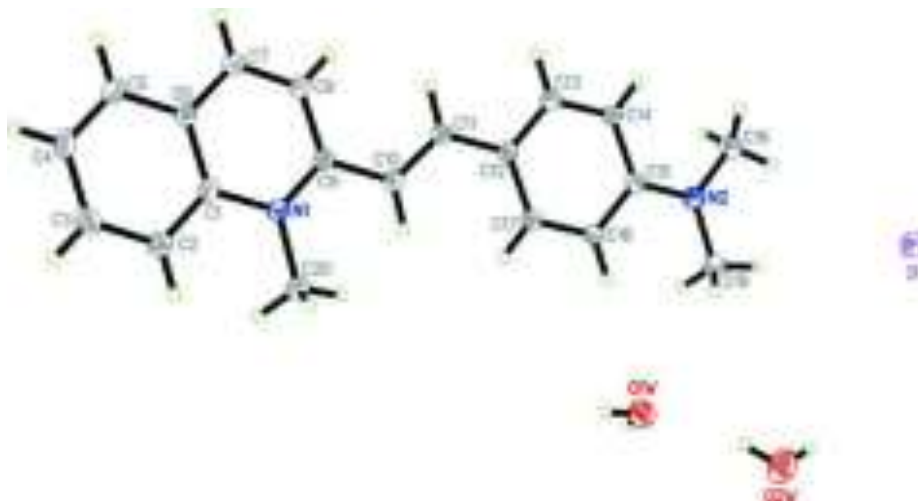
โครงสร้างผลึกของสารประกอบ PAC-7



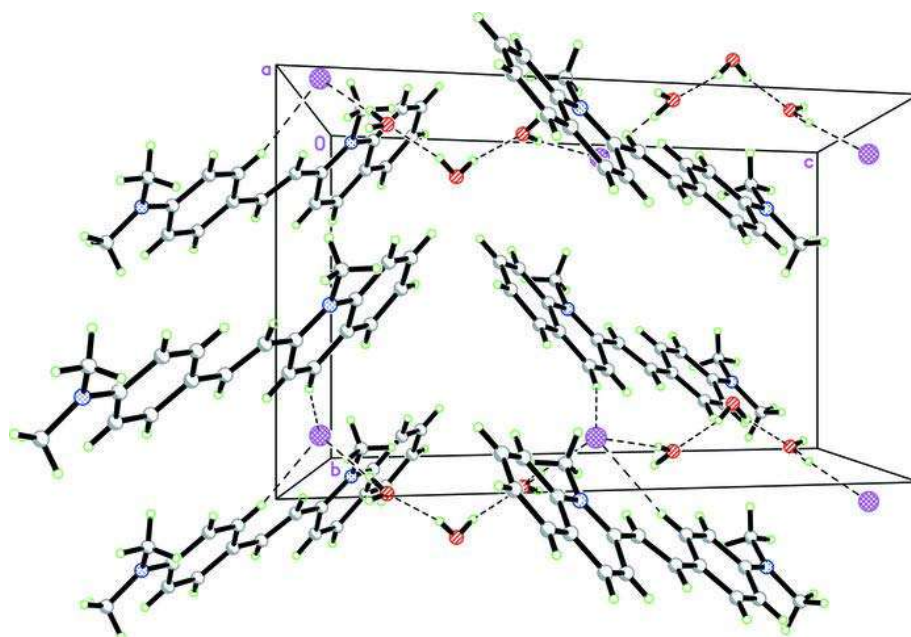
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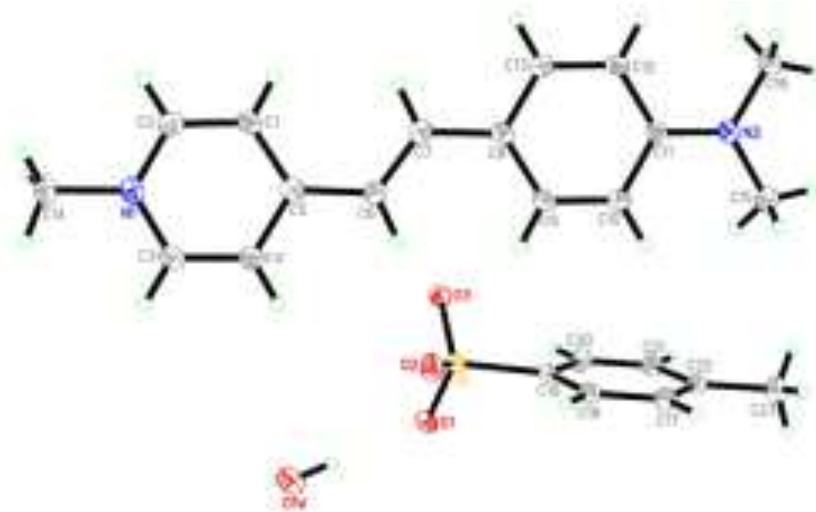
โครงสร้างผลึกของสารประกอบ PAC-14



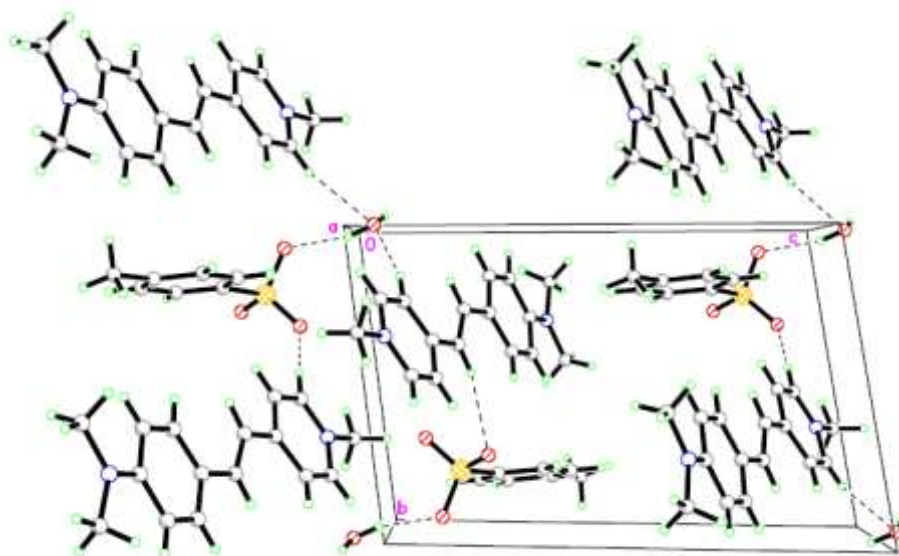
โครงสร้างของสารประกอบ AEQ-III (centrosymmetric $C2/c$ space group)



โครงสร้างผลึกของสารประกอบ AEQ-III



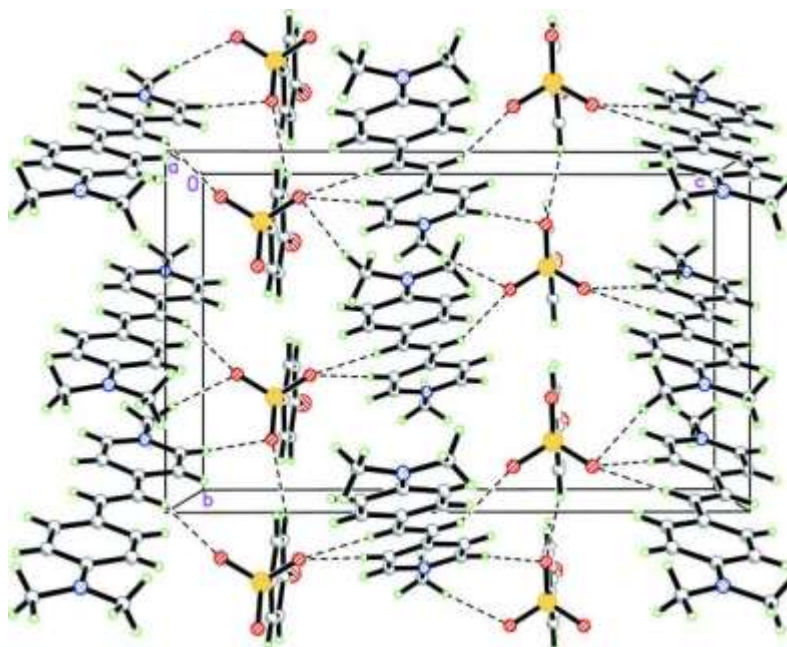
โครงสร้างของสารประกอบ **AEP-III-CH₃** (centrosymmetric $P\bar{1}$ space group)



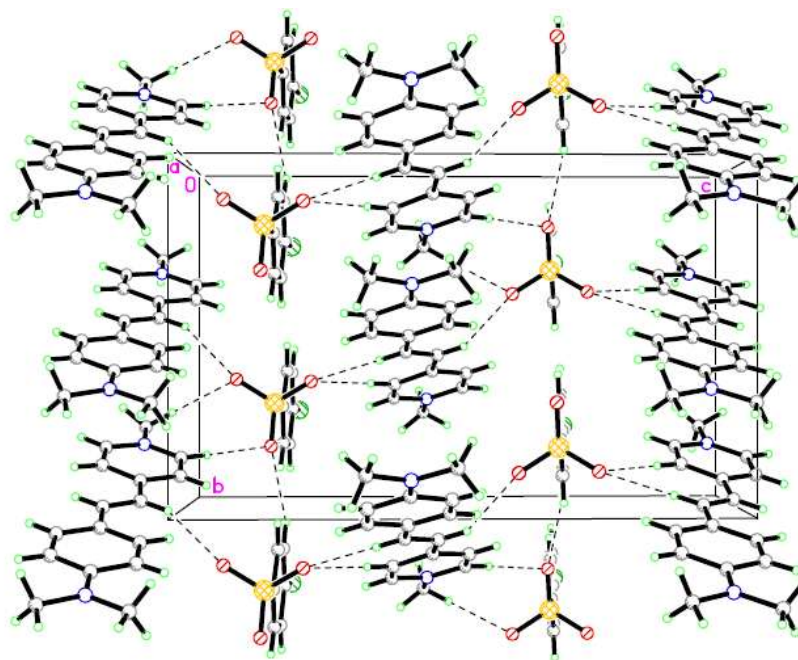
โครงสร้างผลึกของสารประกอบ **AEP-III-CH₃**



โครงสร้างของสารประกอบ **AEP-III-Br** (centrosymmetric *Cc* space group)



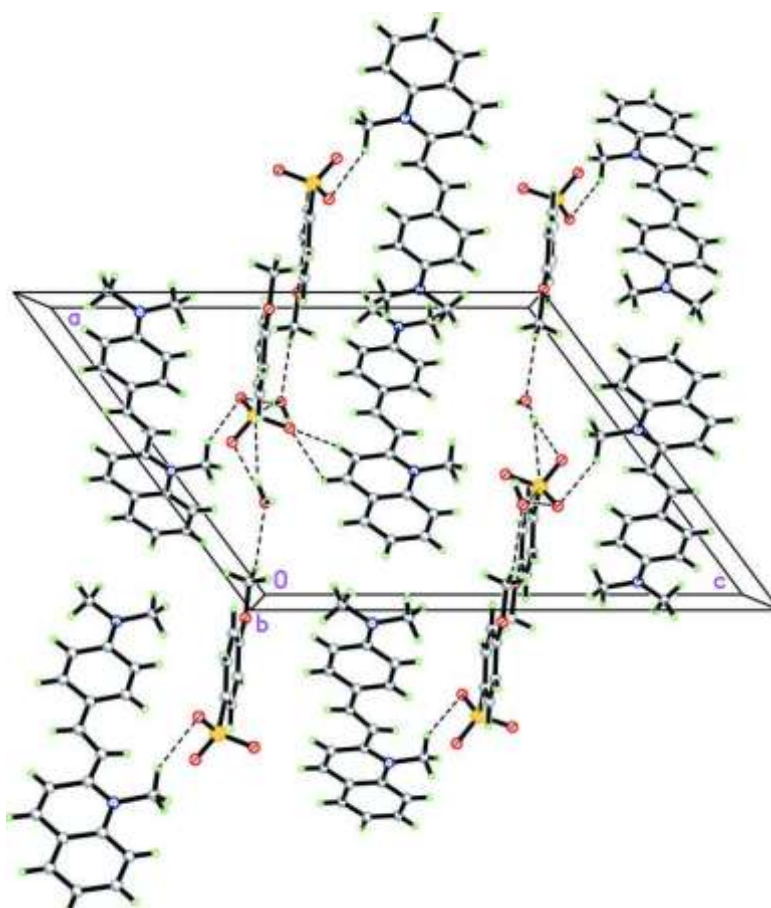
โครงสร้างผลึกของสารประกอบ **AEP-III-Br**



โครงสร้างผลึกของสารประกอบ **AEP-III-Cl**



โครงสร้างของสารประกอบ AEQ-III-OCH₃ (centrosymmetric $P2_1/c$ space group)



โครงสร้างผลึกของสารประกอบ AEQ-III-OCH₃

6. สรุป

จากการดำเนินการวิจัยของโครงการวิจัยได้ผลดังนี้

- สามารถที่สังเคราะห์สารอนุพันธ์ pyridinium และ quinolinium ได้จำนวน 20 สาร คือ AEP-II, AEQ-II, PAC-5, PAC-6, PAC-7, PAC-8, PAC-13, PAC-14, PAC-15, PAC-16, AEP-III, AEP-III-CH₃, AEP-III-Br, AEP-III-Cl, AEP-III-OCH₃, AEQ-III, AEQ-III-CH₃, AEQ-III-Br, AEQ-III-Cl และ AEQ-III-OCH₃,

- สามารถที่สังเคราะห์ประกอบเชิงซ้อนของ Zn ได้จำนวน 4 สาร คือ AEQ-IV-Zn, AEQ-V-Zn, AEQ-VI-Zn และ AEQ-VII-Zn

- สามารถตกผลึกและหาโครงสร้างทางรังสีเอกซ์ของสารได้ ได้ 9 สาร คือ AEQ-II, PAC-5, PAC-7, PAC-14, AEQ-III, AEP-III-CH₃, AEP-III-Br, AEP-III-Cl และ AEQ-III-OCH₃ และพบว่า สาร AEQ-II, PAC-5 และ AEP-III-CH₃ ตกผลึกใน centrosymmetric $P\bar{1}$ space group PAC-7, PAC-14 และ AEQ-III-OCH₃ ตกผลึกใน centrosymmetric $P2_1/c$ space group AEQ-III ตกผลึกใน centrosymmetric $C2/c$ space group AEP-III-Br และ AEP-III-Cl ตกผลึกใน centrosymmetric Cc space group ซึ่งสารทั้งเก้าชนิดไม่แสดงสมบัติทางทัศนศาสตร์แบบไม่เชิงเส้นอันดับสอง (second-order nonlinear optic)

- ได้สารที่แสดงฤทธิ์ต้านเชื้อแบคทีเรีย 8 สาร คือ AEP-III-CH₃, AEP-III-Br, AEP-III-Cl, AEP-III-OCH₃, AEQ-III-CH₃, AEQ-III-Br, AEQ-III-Cl และ AEQ-III-OCH₃ ซึ่งออกฤทธิ์ต้านเชื้อแบคทีเรียที่น่าสนใจคือมีความจำเพาะเจาะจงต่อเชื้อแบคทีเรียชนิด MRSA

มีผลงานตีพิมพ์ในวารสารวิชาการระดับนานาชาติ (SCI journals) 8 เรื่อง ดังนี้

1. Suchada Chantrapromma*, Chotika Laksana, Pumsak Ruanwas and Hoong-Kun Fun (2008).

“1-Methyl-4-[(E)-2-(2-thienyl)ethenyl]pyridinium 4-chlorobenzenesulfonate”

Acta Cryst., E64, o574-o575. (Reprint 1)

2. Thawanrat Kobkeatthawin, Pumsak Ruanwas, Suchada Chantrapromma* and

Hoong-Kun Fun (2008).

“(E)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methoxybenzenesulfonate monohydrate”

Acta Cryst., E64, o642-o643. (Reprint 2)

3. **Suchada Chantrapromma***, Thawanrat Kobkeatthawin, Kullapa Chanawanno, Chatchanok Karalai and Hoong-Kun Fun (2008).
“(E)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium iodide sesquihydrate”
Acta Cryst., **E64**, o876-o877. (**Reprint 3**)

4. Pumsak Ruanwas, Thawanrat Kobkeatthawin, **Suchada Chantrapromma***, Hoong-Kun Fun and Chatchanok Karalai (2008)
“1-Methyl-2-[(E)-2-(2-thienyl)ethenyl]quinolinium iodide”
Acta Cryst., **E64**, o1453-o1454. (**Reprint 4**)

5. **Suchada Chantrapromma***, Pumsak Ruanwas, Hoong-Kun Fun and Chatchanok Karalai (2008)
“1-Methyl-4-[(E)-2-(2-thienyl)ethenyl]pyridinium 4-methylbenzenesulfonate”
Acta Cryst., **E64**, o2072-o2073. (**Reprint 5**)

6. **Suchada Chantrapromma***, Patcharaporn Jansrisewangwong, Rusmeenee Musor and Hoong-Kun Fun (2009)
“(E)-4-[4-(Dimethylamino)styryl]-1-methylpyridinium 4-bromobenzenesulfonate”
Acta Cryst., **E65**, o217-o218. (**Reprint 6**)

7. Hoong-Kun Fun, Thawanrat Kobkeatthawin and **Suchada Chantrapromma*** (2010)
“1-Methyl-2-[(E)-2-(2-thienyl)ethenyl]quinolinium 4-bromobenzenesulfonate”
Acta Cryst., **E66**, o1053-o1054. (**Reprint 7**)

8. Kullapa Chanawanno, **Suchada Chantrapromma***, Theerasak Anantapong, Akkharawit Kanjana-Opas, Hoong-Kun Fun (2010)
“Synthesis, structure and in vitro antibacterial activities of new hybrid disinfectants quaternary ammonium compounds: Pyridinium and quinolinium stilbene benzenesulfonates”
Eur. J. Med. Chem., **45**, 4199-4208. (**Reprint8**)

เอกสารอ้างอิง

- Chantrapromma, S., Jindawong, B., Fun, H.-K., Patil, P.-S. and Karalai, C. (2006)
 “2-[(E)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium 4-chloro”
Acta Cryst., E62: o1802-o1804.
- Crasta, V., Ravindrachary, V., Bhajantri, R. F. and Gonsalves, R. (2004)
 “Growth and characterization of an organic NLO crystal: 1-(4-methylphenyl)-3-(4-methoxyphenyl)-2-propen-1-one” *J. Cryst.Growth* 267: 129-133.
- Hong, H.-K., Park, J. W., Lee, K.-S. and Yoon, C.-S. (2005)
 “Growth of highly nonlinear optical organic crystal, 3-methyl-4-methoxy-4'-nitrostilbene (MMONS)” *J. Cryst.Growth* 277: 509-517.
- Jindawong, B., Chantrapromma, S., Fun, H.-K., Yu, X.-L. and Karalai, C. (2005)
 “4(4'-Hydroxy-3'-methoxystyryl)-1-Methylpyridinium 4-bromobenzenesulfonate”,
Acta Cryst., E61, o1340-o1342.
- Lakshmanaperumal, C. K., Arulchakkaravarthi, A., Balamurugan, N., Santharaghavan, P. and Ramasamy, P. (2004) “Synthesis, Crystal growth and Characterization of novel NLO material: 4-hydroxy benzaldehyde-N-methyl-4-stilbazolium tosylate”,
Journal of Crystal Growth 265: 260-265.
- Lakshmanaperumal, C. K., Arulchakkaravarthi, A., Rajesh, N. P., Raghavan, P.S., Huang, Y. C., Ichimura, M. and Ramasamy, P. (2002) “Synthesis, Crystal growth and FTIR, NMR, SHG studies of 4-methoxy benzaldehyde-N-methyl-4-stilbazolium tosylate (MBST)”,
Journal of Crystal Growth 240: 212-217.
- Nogi, K., Usman, A., Tsuji, K., Duan, X.-M., Okada, S., Oikawa, H., Matsuda, H. and Nakanishi, H. (2000) “Preparation of Polyene Analogues of Stilbazolium”,
Nonlinear Optics 24: 35-40.

Umezawa, H., Tsuji, K., Usman, A., Duan, X.-M., Okada, S., Oikawa, H., Matsuda, H. and Nakanishi, H. (2000) "Synthesis of Stilbazolium Derivatives having 2-(6-Dimethylamino)Naphthyl Group for Nonlinear Optics", *Nonlinear Optics* 24: 73-78.

Usman, A., Duan, X.-M., Komatsu, K., Okada, S., Matsuda, H., Oikawa, H. and Nakanishi, H. (1997) "Second-Order Hyperpolarizability of Pyridinium Cations", *Chemistry Letters*. 247-248.

Usman, A., Duan, X.-M., Komatsu, K., Okada, S., Oikawa, H., Matsuda, H. and Nakanishi, H. (1999) "Synthesis of Substituted pyridinium-benzenesulfonates crystals for second-harmonic generation", *Nonlinear Optics*, 22: 251-254.

Usman, A., Duan, X.-M., Okada, S., Matsuda, H., Oikawa, H. and Nakanishi, H. (1998) "First Hyperpolarizability of benzoate anions and esters", *J. Chem. Soc. Perkin. Trans 2*: 2451-2457.

Usman, A., Komatsu, K., Okada, S., Oikawa, H., Matsuda, H. and Nakanishi, H. (1999) "Synthesis, Crystal Structures and Second-Order Nonlinear Optic Properties of New Colorless 4-Carbamoylpyridinium Benzenesulfonate Salts", *Organic Nonlinear Optical Materials* 3796: 218-228.

Usman, A., Kosuge, H., Okada, S., Oikawa, H. and Nakanishi, H. (2001) "4-(Dimethylamino)-1-ethylpyridinium Iodide: A New Colorless Organic Ionic Crystal for Second-Order Nonlinear Optics", *Jpn. J. Appl. Phys* 40: 4213-4216.

Usman, A., Okada, S., Oikawa, H. and Nakanishi, H. (2000) "Preparation and Crystal Structures of New Colorless 4-Amino-1-methylpyridinium Benzenesulfonate Salts for Second-Order Nonlinear Optics", *Chem. Mater* 12: 1162-1170.

Rahman, A. A., Razak, I. A., Fun, H.-K., Saene, P., Boonwasana, J., Chantrapromma, S. and Kararai, C. (2003) "4-(4'-hydroxy-3'-methoxyphenyl)ethenyl-N-methyl pyridinium p-toluenesulfonate", *Acta Cryst.*, E59, o1798-o1800.

Williams, D. J. (1984). *Angew. Chem. Int. Ed. Engl.* 23, 690-703.

ภาคผนวก

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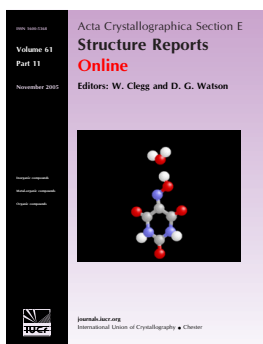
Editors: W. Clegg and D. G. Watson

1-Methyl-4-[(*E*)-2-(2-thienyl)ethenyl]pyridinium 4-chlorobenzenesulfonate

Suchada Chantrapromma, Chotika Laksana, Pumsak Ruanwas and
Hoong-Kun Fun

Acta Cryst. (2008). **E64**, o574–o575

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1-Methyl-4-[(*E*)-2-(2-thienyl)ethenyl]-pyridinium 4-chlorobenzenesulfonate¹

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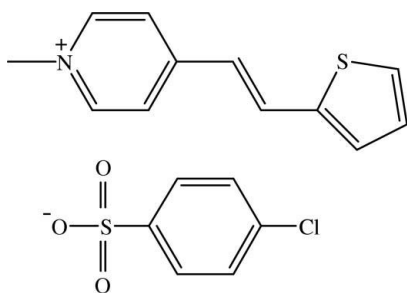
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Key indicators: single-crystal X-ray study; *T* = 100 K; mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$; *R* factor = 0.038; *wR* factor = 0.095; data-to-parameter ratio = 20.7.

In the title compound, $\text{C}_{12}\text{H}_{12}\text{NS}^+\cdot\text{C}_6\text{H}_4\text{ClO}_3\text{S}^-$, the cation is almost planar and exists in the *E* configuration. The cations and anions form alternate layers parallel to the *ab* plane. Within each layer, both cations and anions form chains directed along the *b* axis. The molecules are interconnected by weak $\text{C}-\text{H}\cdots\text{O}$ interactions into a three-dimensional network. The crystal structure is further stabilized by $\text{C}-\text{H}\cdots\pi$ interactions involving the thiophene ring. The sulfonate and thiophene groups are involved in weak intramolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{S}$ interactions, respectively. The latter intramolecular hydrogen bonds produce *S*(5) ring motifs.

Related literature

For bond lengths and angles, see Allen (2002); Allen *et al.* (1987). For related literature on hydrogen-bond motifs, see Bernstein *et al.* (1995). For related structures, see for example Chantrapromma *et al.* (2005, 2006*a,b*, 2007*a,b,c,d*); Drost *et al.* (1995); Jindawong *et al.* (2005); Subramaniyan *et al.* (2003).



¹ This paper is dedicated to the late Her Royal Highness Princess Galyani Vadhana Krom Luang Naradhiwas Rajanagarindra for her patronage of Science in Thailand.

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Experimental

Crystal data

$\text{C}_{12}\text{H}_{12}\text{NS}^+\cdot\text{C}_6\text{H}_4\text{ClO}_3\text{S}^-$
M_r = 393.91
Monoclinic, *P*2₁/*c*
a = 7.3532 (1) Å
b = 14.0250 (2) Å
c = 18.3755 (2) Å
 β = 111.232 (1)°
V = 1766.41 (4) Å³
Z = 4
Mo *K*α radiation
 μ = 0.47 mm⁻¹
T = 100.0 (1) K
0.49 × 0.22 × 0.18 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.883, *T_{max}* = 0.919
23692 measured reflections
4688 independent reflections
3913 reflections with *I* > 2σ(*I*)
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.094$
S = 1.06
4688 reflections
227 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the S1/C8–C11 thiophene ring.

<i>D</i> – <i>H</i> ⋯ <i>A</i>	<i>D</i> – <i>H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> – <i>H</i> ⋯ <i>A</i>
C3–H3A⋯O3 ⁱ	0.93	2.31	3.211 (2)	164
C6–H6A⋯S1	0.93	2.84	3.228 (2)	106
C7–H7A⋯O1 ⁱⁱ	0.93	2.39	3.266 (2)	157
C9–H9A⋯O3 ⁱⁱ	0.93	2.58	3.495 (2)	166
C10–H10A⋯O2 ⁱⁱⁱ	0.93	2.39	3.302 (2)	167
C11–H11A⋯O2 ^{iv}	0.93	2.55	3.063 (2)	115
C12–H12C⋯O2 ⁱ	0.96	2.39	3.334 (2)	168
C17–H17A⋯O2 ^{iv}	0.93	2.41	3.318 (2)	166
C18–H18A⋯O3	0.93	2.51	2.892 (2)	105
C12–H12B⋯ <i>Cg</i> 1 ⁱ	0.96	2.69	3.515 (2)	144

Symmetry codes: (i) $-x + 2, -y + 2, -z + 1$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x + 2, -y + 1, -z + 1$; (iv) $x - 1, y, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2086).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* **2**, pp. S1–S19.
Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

- Bruker (2005). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chantrapromma, S., Jindawong, B. & Fun, H.-K. (2006a). *Acta Cryst.* **E62**, o4004–o4006.
- Chantrapromma, S., Jindawong, B. & Fun, H.-K. (2007a). *Acta Cryst.* **E63**, o2020–o2022.
- Chantrapromma, S., Jindawong, B., Fun, H.-K., Anjum, S. & Karalai, C. (2005). *Acta Cryst.* **E61**, o2096–o2098.
- Chantrapromma, S., Jindawong, B., Fun, H.-K. & Patil, P. S. (2007b). *Acta Cryst.* **E63**, o2321–o2323.
- Chantrapromma, S., Jindawong, B., Fun, H.-K., Patil, P. S. & Karalai, C. (2006b). *Acta Cryst.* **E62**, o1802–o1804.
- Chantrapromma, S., Jindawong, B., Fun, H.-K., Patil, P. S. & Karalai, C. (2007c). *Anal. Sci.* **23**, x27–x28.
- Chantrapromma, S., Suwanwong, T. & Fun, H.-K. (2007d). *Acta Cryst.* **E63**, o821–o823.
- Drost, K. J., Jen, A. K.-J. & Roa, V. P. (1995). *Chemtech*, **25**, 16–25.
- Jindawong, B., Chantrapromma, S., Fun, H.-K., Yu, X.-L. & Karalai, C. (2005). *Acta Cryst.* **E61**, o1340–o1342.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Subramanian, G., Raghunathan, R. & Castro, A. M. M. (2003). *Tetrahedron*, **59**, 335–340.

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1-Methyl-4-[(*E*)-2-(2-thienyl)ethenyl]pyridinium 4-chlorobenzenesulfonate

S. Chantrapromma, C. Laksana, P. Ruanwas and H.-K. Fun

Comment

Molecules with extended π systems have been extensively used in attempts to obtain materials with non-linear optical (NLO) properties. Organic crystal with the required conjugated π electrons are attractive candidates because of the large NLO coefficients. In our research for second-order NLO materials, we have previously synthesized and crystallized several organic ionic salts of pyridinium and quinolinium derivatives to study their non-linear optical properties (Chantrapromma *et al.*, 2005; 2006a; 2006b; 2007a; 2007b; 2007c; 2007 d; Jindawong *et al.*, 2005). An earlier study carried out by Drost *et al.* (1995) has revealed that the products of the dipole moment and the molecular hyperpolarizability (β) of thiophene-containing conjugated moieties are larger than those of the phenyl analogues. Based on this reason, we have synthesized the title compound which was designed by replacement of the cationic phenyl ring by the thiophene ring that is present in 4-(4'-Hydroxy-3'-methoxystyryl)-1-methylpyridinium 4-chlorobenzenesulfonate (Chantrapromma *et al.*, 2005).

The asymmetric unit of the title compound consists of the $C_{12}H_{12}NS^+$ cation and the $C_6H_4ClO_3S^-$ anion. The cation is almost planar and exists in the *E* configuration with respect to the C6=C7 double bond [1.334 (3) Å]. The cation is almost perpendicular to the anion as is indicated by the angles between the mean planes of the chlorophenyl ring to the pyridinium as well as to the thiophene ring being 87.64 (9)° and 86.73 (9)°, respectively. The dihedral angle between the pyridinium and the thiophene rings is 5.74 (10)°. The ethenyl unit is nearly planar. The torsion angles C4-C5-C6-C7 = -4.3 (3)° and C6-C7-C8-S1 = -1.5 (3)°.

The atom O3 of the sulfonate and the S atom of the thiophene contribute to the C—H \cdots O and C—H \cdots S intramolecular weak interactions (Fig. 1 and Table 1) forming S(5) ring motifs (Bernstein *et al.*, 1995). The bond lengths and angles are normal (Allen *et al.*, 1987) and are comparable with closely related structures (Chantrapromma *et al.*, 2005; 2006b; 2007c; 2007 d).

All the O atoms of 4-chlorobenzenesulfonate anion are involved in the C—H \cdots O weak interactions (Table 1). The cations and anions form alternate layers parallel to the *ab* plane. Within each respective layer, the ions are interconnected by C—H \cdots O weak interactions and in each respective layer can be distinguished chains directed along the *b* axis. The alternating layers are separated by 4.282 (2) Å and are further linked into a three dimensional network by C—H \cdots O weak interactions (Table 1). The sulfonate as well as the thiophene are involved in C—H \cdots O and C—H \cdots S intramolecular weak interactions, respectively. These weak hydrogen bonds participate in S(5) ring motifs. The crystal structure is further stabilized by the C12—H12B $\cdots\pi$ interaction to the thiophene ring C8-C11/S1: C12—H12B=0.96; H12B \cdots Cg1ⁱ=2.692; C12—Cg1ⁱ=3.515 (2) Å; C12—H12B \cdots Cg1ⁱ=144°. [Cg1ⁱ is the centroid of the S1/C8-C11 thiophene ring (symmetry code: (i): 2 - x, 2 - y, 1 - z).]

A very interesting feature is the short non-bonding contact between C11 and O3 that is 2.963 (1) Å long only. A search in the Cambridge Structural Database (version 5.29 and addenda up to 25-th January 2008; Allen, 2002) among the structures which have been flagged with no error or disorder as well as with *R*-factor < 0.05 and which contained chloro-phenyl with

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any substituent in the *para* position showed that the present structure contains an unprecedentedly short contact of this kind. The up-to-now shortest contact of this type was 2.996 (2) Å long and it was observed in MUTDOU [Spiro(2-carbomethoxy-3-(4-chlorophenyl)-5-(*S,R*)-(cis-1-(4-methoxyphenyl) -3-phenyl-4-oxoazetidin-2-(*S,R*)-yl)pyrrolidine-4,3¹-chroman-4¹-one)] determined by Subramaniyan *et al.* (2003).

Experimental

4-(2-Thiophenestryl)-1-methylpyridinium iodide (compound A) was synthesized by mixing a solution (1:1:1 molar ratio) of 1,4-dimethylpyridinium iodide (2.00 g, 8.5 mmol), 2-thiophenecarboxaldehyde (6.00 ml, 8.5 mmol) and piperidine (0.84 ml, 8.5 mmol) in hot methanol (40 ml). The resulting solution was refluxed for 5 h under a nitrogen atmosphere. The resultant solid was filtered off, washed with diethyl ether and recrystallized from methanol. The title compound was synthesized by mixing compound A (0.10 g, 0.3 mmol) in hot methanol (20 ml) and silver(I) 4-chlorobenzenesulfonate (0.08 g, 0.3 mmol) in hot methanol (30 ml). Silver(I) 4-chlorobenzenesulfonate was synthesized according to our previously reported procedure (Chantrapromma *et al.*, 2006b). The mixture immediately yielded a grey solid of silver iodide. After stirring the mixture for *ca* 30 min, the precipitate of silver iodide was removed and the resulting solution was evaporated and a brown solid was obtained. Brown block-shaped single crystals of the title compound suitable for *x*-ray structure determination were recrystallized from methanol solvent by slow evaporation of the solvent at room temperature after several days (Mp. 503–505 K).

Refinement

All the hydrogen atoms could have been discerned in the difference Fourier map. Nevertheless, all the H atoms attached to the carbon atoms were constrained in a riding motion approximation with $C_{\text{aryl}}\text{—H}=0.93$ and $C_{\text{methyl}}\text{—H}=0.968$ Å. The U_{iso} values were constrained to be $1.5U_{\text{eq}}$ of the carrier atom for methyl H atoms and $1.2U_{\text{eq}}$ for the remaining H atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at 0.75 Å from C8 and the deepest hole is located at 0.50 Å from S1.

Figures

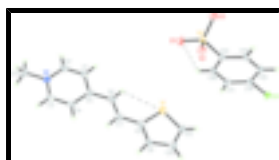


Fig. 1. The title molecules showing 50% probability displacement ellipsoids and the atom-numbering scheme. The intramolecular C—H...O and C—H...S weak interactions are drawn as dashed lines.

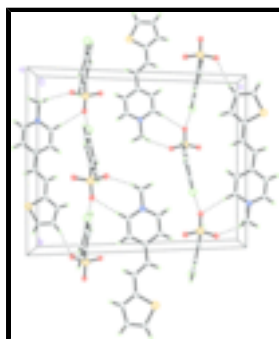


Fig. 2. The packing diagram of the title structure viewed along the *a* axis. The weak C—H...O and C—H...S interactions are drawn as dashed lines.

1-Methyl-4-[(E)-2-(2-thienyl)ethenyl]pyridinium 4-chlorobenzenesulfonate

Crystal data

$C_{12}H_{12}NS^+ \cdot C_6H_4ClO_3S^-$	$F_{000} = 816$
$M_r = 393.91$	$D_x = 1.481 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Melting point: 503-505 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation
$a = 7.3532 (1) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 14.0250 (2) \text{ \AA}$	Cell parameters from 4688 reflections
$c = 18.3755 (2) \text{ \AA}$	$\theta = 1.9\text{--}29.0^\circ$
$\beta = 111.232 (1)^\circ$	$\mu = 0.47 \text{ mm}^{-1}$
$V = 1766.41 (4) \text{ \AA}^3$	$T = 100.0 (1) \text{ K}$
$Z = 4$	Block, brown
	$0.49 \times 0.22 \times 0.18 \text{ mm}$

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	4688 independent reflections
Radiation source: fine-focus sealed tube	3913 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.037$
Detector resolution: 8.33 pixels mm^{-1}	$\theta_{\text{max}} = 29.0^\circ$
$T = 100.0(1) \text{ K}$	$\theta_{\text{min}} = 1.9^\circ$
ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$k = -19 \rightarrow 19$
$T_{\text{min}} = 0.883$, $T_{\text{max}} = 0.919$	$l = -21 \rightarrow 25$
23692 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.094$	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 1.1208P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
4688 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
227 parameters	$\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$
63 constraints	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
Primary atom site location: difference Fourier map	Extinction correction: none

Special details

Experimental. The low-temperature data was collected with the Oxford Cryosystem Cobra low-temperature attachment.

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Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.57131 (7)	0.72654 (3)	0.43805 (3)	0.02450 (11)
S2	1.05267 (5)	0.60506 (3)	0.27447 (2)	0.01477 (10)
Cl1	0.37650 (6)	0.31936 (3)	0.25045 (2)	0.02092 (10)
O1	1.09007 (17)	0.58763 (9)	0.20315 (7)	0.0219 (3)
O2	1.21870 (16)	0.58102 (9)	0.34443 (7)	0.0196 (3)
O3	0.97435 (17)	0.69943 (8)	0.27824 (7)	0.0210 (3)
N1	0.8323 (2)	1.24164 (11)	0.49389 (9)	0.0214 (3)
C1	0.6981 (3)	1.10669 (14)	0.41625 (11)	0.0273 (4)
H1A	0.6342	1.0808	0.3669	0.033*
C2	0.7408 (3)	1.20156 (14)	0.42351 (11)	0.0265 (4)
H2A	0.7060	1.2394	0.3790	0.032*
C3	0.8863 (3)	1.18711 (14)	0.55895 (11)	0.0259 (4)
H3A	0.9501	1.2150	0.6075	0.031*
C4	0.8481 (3)	1.09132 (14)	0.55424 (11)	0.0267 (4)
H4A	0.8881	1.0547	0.5995	0.032*
C5	0.7490 (2)	1.04783 (13)	0.48184 (11)	0.0216 (3)
C6	0.6999 (3)	0.94698 (14)	0.47236 (11)	0.0239 (4)
H6A	0.6262	0.9252	0.4226	0.029*
C7	0.7537 (3)	0.88364 (13)	0.53044 (11)	0.0227 (4)
H7A	0.8268	0.9066	0.5799	0.027*
C8	0.7098 (2)	0.78300 (13)	0.52426 (10)	0.0213 (3)
C9	0.7700 (2)	0.72058 (12)	0.58541 (10)	0.0190 (3)
H9A	0.8451	0.7379	0.6363	0.023*
C10	0.7037 (3)	0.62467 (13)	0.56186 (11)	0.0234 (4)
H10A	0.7313	0.5730	0.5958	0.028*
C11	0.5956 (3)	0.61854 (13)	0.48386 (11)	0.0234 (4)
H11A	0.5415	0.5622	0.4586	0.028*
C12	0.8779 (3)	1.34470 (13)	0.50102 (12)	0.0287 (4)
H12A	0.8119	1.3754	0.4518	0.043*
H12B	1.0161	1.3535	0.5159	0.043*
H12C	0.8353	1.3722	0.5400	0.043*
C13	0.8648 (2)	0.52345 (12)	0.27171 (9)	0.0151 (3)
C14	0.8824 (2)	0.42781 (12)	0.25482 (9)	0.0165 (3)
H14A	0.9944	0.4067	0.2475	0.020*
C15	0.7332 (2)	0.36386 (12)	0.24892 (10)	0.0174 (3)

H15A	0.7434	0.3000	0.2372	0.021*
C16	0.5682 (2)	0.39778 (12)	0.26093 (9)	0.0165 (3)
C17	0.5512 (2)	0.49151 (12)	0.28055 (10)	0.0186 (3)
H17A	0.4417	0.5120	0.2902	0.022*
C18	0.7013 (2)	0.55480 (12)	0.28563 (10)	0.0181 (3)
H18A	0.6920	0.6183	0.2984	0.022*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0255 (2)	0.0248 (2)	0.0196 (2)	-0.00284 (17)	0.00382 (17)	0.00120 (17)
S2	0.01233 (18)	0.01553 (19)	0.01604 (19)	0.00021 (14)	0.00465 (14)	0.00095 (14)
C11	0.01861 (19)	0.0189 (2)	0.0272 (2)	-0.00466 (14)	0.01069 (16)	-0.00201 (16)
O1	0.0200 (6)	0.0292 (7)	0.0181 (6)	-0.0020 (5)	0.0090 (5)	0.0007 (5)
O2	0.0144 (5)	0.0239 (6)	0.0174 (6)	0.0000 (4)	0.0022 (5)	0.0013 (5)
O3	0.0181 (6)	0.0143 (6)	0.0314 (7)	-0.0003 (4)	0.0099 (5)	0.0002 (5)
N1	0.0225 (7)	0.0214 (7)	0.0240 (8)	-0.0001 (6)	0.0127 (6)	0.0011 (6)
C1	0.0289 (9)	0.0304 (10)	0.0204 (9)	-0.0058 (8)	0.0063 (7)	-0.0019 (7)
C2	0.0298 (10)	0.0285 (10)	0.0192 (8)	-0.0031 (8)	0.0066 (7)	0.0034 (7)
C3	0.0309 (9)	0.0293 (10)	0.0174 (8)	-0.0016 (8)	0.0085 (7)	-0.0019 (7)
C4	0.0329 (10)	0.0273 (10)	0.0208 (9)	0.0009 (8)	0.0108 (8)	0.0035 (7)
C5	0.0192 (8)	0.0227 (9)	0.0256 (9)	-0.0001 (6)	0.0114 (7)	-0.0001 (7)
C6	0.0219 (8)	0.0285 (9)	0.0209 (8)	-0.0034 (7)	0.0073 (7)	-0.0016 (7)
C7	0.0192 (8)	0.0274 (9)	0.0224 (9)	0.0001 (7)	0.0086 (7)	-0.0019 (7)
C8	0.0181 (8)	0.0239 (9)	0.0227 (8)	-0.0015 (6)	0.0085 (7)	-0.0015 (7)
C9	0.0176 (8)	0.0251 (9)	0.0133 (7)	-0.0012 (6)	0.0045 (6)	0.0008 (6)
C10	0.0219 (8)	0.0249 (9)	0.0220 (9)	-0.0019 (7)	0.0061 (7)	0.0044 (7)
C11	0.0225 (8)	0.0211 (9)	0.0242 (9)	-0.0038 (7)	0.0058 (7)	0.0004 (7)
C12	0.0318 (10)	0.0219 (9)	0.0376 (11)	-0.0020 (8)	0.0186 (9)	-0.0005 (8)
C13	0.0139 (7)	0.0171 (8)	0.0142 (7)	-0.0002 (6)	0.0048 (6)	-0.0002 (6)
C14	0.0145 (7)	0.0190 (8)	0.0170 (8)	0.0024 (6)	0.0068 (6)	-0.0008 (6)
C15	0.0186 (7)	0.0148 (7)	0.0192 (8)	0.0016 (6)	0.0075 (6)	-0.0010 (6)
C16	0.0148 (7)	0.0176 (8)	0.0166 (7)	-0.0027 (6)	0.0051 (6)	0.0008 (6)
C17	0.0148 (7)	0.0180 (8)	0.0249 (9)	0.0018 (6)	0.0094 (7)	0.0001 (6)
C18	0.0182 (8)	0.0148 (8)	0.0217 (8)	0.0011 (6)	0.0078 (6)	-0.0014 (6)

Geometric parameters (\AA , $^\circ$)

S1—C11	1.7105 (19)	C7—C8	1.443 (3)
S1—C8	1.7335 (18)	C7—H7A	0.9300
S2—O1	1.4541 (12)	C8—C9	1.366 (2)
S2—O3	1.4550 (12)	C9—C10	1.443 (2)
S2—O2	1.4560 (12)	C9—H9A	0.9300
S2—C13	1.7806 (16)	C10—C11	1.367 (3)
C11—C16	1.7428 (16)	C10—H10A	0.9300
N1—C2	1.346 (2)	C11—H11A	0.9300
N1—C3	1.352 (2)	C12—H12A	0.9600
N1—C12	1.479 (2)	C12—H12B	0.9600
C1—C2	1.363 (3)	C12—H12C	0.9600

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C1—C5	1.395 (3)	C13—C18	1.388 (2)
C1—H1A	0.9300	C13—C14	1.393 (2)
C2—H2A	0.9300	C14—C15	1.390 (2)
C3—C4	1.369 (3)	C14—H14A	0.9300
C3—H3A	0.9300	C15—C16	1.393 (2)
C4—C5	1.404 (3)	C15—H15A	0.9300
C4—H4A	0.9300	C16—C17	1.381 (2)
C5—C6	1.455 (3)	C17—C18	1.393 (2)
C6—C7	1.334 (3)	C17—H17A	0.9300
C6—H6A	0.9300	C18—H18A	0.9300
C11—S1—C8	91.87 (9)	C8—C9—C10	112.16 (15)
O1—S2—O3	113.77 (7)	C8—C9—H9A	123.9
O1—S2—O2	112.64 (7)	C10—C9—H9A	123.9
O3—S2—O2	112.86 (7)	C11—C10—C9	112.22 (16)
O1—S2—C13	105.32 (7)	C11—C10—H10A	123.9
O3—S2—C13	105.65 (7)	C9—C10—H10A	123.9
O2—S2—C13	105.68 (7)	C10—C11—S1	112.19 (14)
C2—N1—C3	119.87 (16)	C10—C11—H11A	123.9
C2—N1—C12	120.78 (16)	S1—C11—H11A	123.9
C3—N1—C12	119.34 (16)	N1—C12—H12A	109.5
C2—C1—C5	120.86 (18)	N1—C12—H12B	109.5
C2—C1—H1A	119.6	H12A—C12—H12B	109.5
C5—C1—H1A	119.6	N1—C12—H12C	109.5
N1—C2—C1	121.28 (17)	H12A—C12—H12C	109.5
N1—C2—H2A	119.4	H12B—C12—H12C	109.5
C1—C2—H2A	119.4	C18—C13—C14	120.17 (15)
N1—C3—C4	120.76 (17)	C18—C13—S2	120.39 (13)
N1—C3—H3A	119.6	C14—C13—S2	119.44 (12)
C4—C3—H3A	119.6	C15—C14—C13	120.28 (15)
C3—C4—C5	120.70 (17)	C15—C14—H14A	119.9
C3—C4—H4A	119.6	C13—C14—H14A	119.9
C5—C4—H4A	119.6	C14—C15—C16	118.36 (15)
C1—C5—C4	116.51 (17)	C14—C15—H15A	120.8
C1—C5—C6	119.63 (17)	C16—C15—H15A	120.8
C4—C5—C6	123.86 (17)	C17—C16—C15	122.20 (15)
C7—C6—C5	124.26 (17)	C17—C16—C11	118.91 (12)
C7—C6—H6A	117.9	C15—C16—C11	118.89 (13)
C5—C6—H6A	117.9	C16—C17—C18	118.65 (15)
C6—C7—C8	126.54 (17)	C16—C17—H17A	120.7
C6—C7—H7A	116.7	C18—C17—H17A	120.7
C8—C7—H7A	116.7	C13—C18—C17	120.27 (15)
C9—C8—C7	124.44 (16)	C13—C18—H18A	119.9
C9—C8—S1	111.55 (13)	C17—C18—H18A	119.9
C7—C8—S1	124.01 (14)		
C3—N1—C2—C1	1.0 (3)	C8—C9—C10—C11	-0.1 (2)
C12—N1—C2—C1	179.98 (18)	C9—C10—C11—S1	-0.2 (2)
C5—C1—C2—N1	-0.3 (3)	C8—S1—C11—C10	0.36 (15)
C2—N1—C3—C4	-0.4 (3)	O1—S2—C13—C18	-130.91 (14)

C12—N1—C3—C4	-179.30 (17)	O3—S2—C13—C18	-10.19 (16)
N1—C3—C4—C5	-1.1 (3)	O2—S2—C13—C18	109.65 (14)
C2—C1—C5—C4	-1.0 (3)	O1—S2—C13—C14	48.59 (15)
C2—C1—C5—C6	179.41 (18)	O3—S2—C13—C14	169.30 (13)
C3—C4—C5—C1	1.7 (3)	O2—S2—C13—C14	-70.85 (14)
C3—C4—C5—C6	-178.76 (17)	C18—C13—C14—C15	2.4 (2)
C1—C5—C6—C7	175.16 (18)	S2—C13—C14—C15	-177.09 (12)
C4—C5—C6—C7	-4.4 (3)	C13—C14—C15—C16	-0.5 (2)
C5—C6—C7—C8	-179.72 (17)	C14—C15—C16—C17	-1.9 (3)
C6—C7—C8—C9	179.23 (18)	C14—C15—C16—C11	177.84 (12)
C6—C7—C8—S1	-1.5 (3)	C15—C16—C17—C18	2.4 (3)
C11—S1—C8—C9	-0.44 (14)	C11—C16—C17—C18	-177.33 (13)
C11—S1—C8—C7	-179.82 (15)	C14—C13—C18—C17	-1.9 (2)
C7—C8—C9—C10	179.78 (16)	S2—C13—C18—C17	177.59 (13)
S1—C8—C9—C10	0.40 (19)	C16—C17—C18—C13	-0.5 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C3—H3A...O3 ⁱ	0.93	2.31	3.211 (2)	164
C6—H6A...S1	0.93	2.84	3.228 (2)	106
C7—H7A...O1 ⁱⁱ	0.93	2.39	3.266 (2)	157
C9—H9A...O3 ⁱⁱ	0.93	2.59	3.495 (2)	166
C10—H10A...O2 ⁱⁱⁱ	0.93	2.39	3.302 (2)	167
C11—H11A...O2 ^{iv}	0.93	2.55	3.063 (2)	115
C12—H12C...O2 ⁱ	0.96	2.39	3.334 (2)	168
C17—H17A...O2 ^{iv}	0.93	2.41	3.318 (2)	166
C18—H18A...O3	0.93	2.51	2.892 (2)	105
C12—H12B...Cg1 ⁱ	0.96	2.69	3.515 (2)	144

Symmetry codes: (i) $-x+2, -y+2, -z+1$; (ii) $x, -y+3/2, z+1/2$; (iii) $-x+2, -y+1, -z+1$; (iv) $x-1, y, z$.

Fig. 1

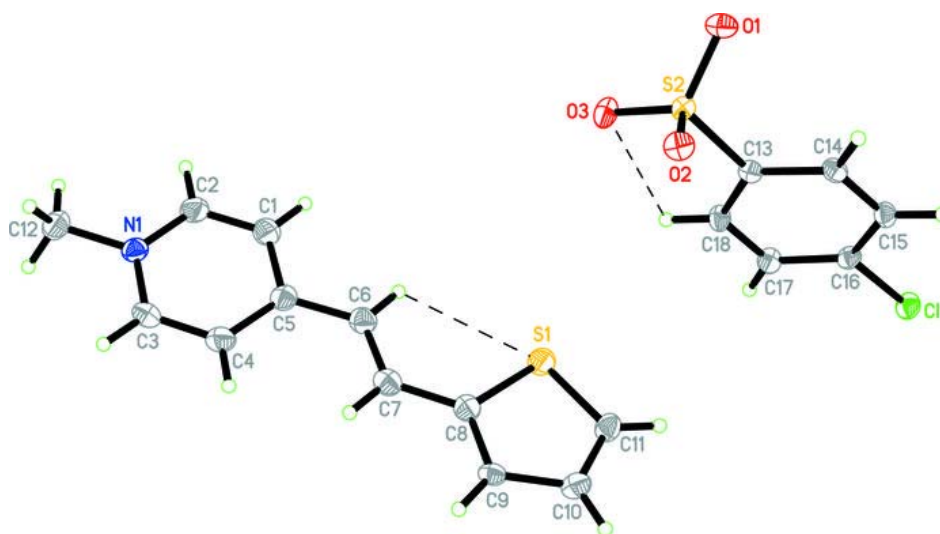
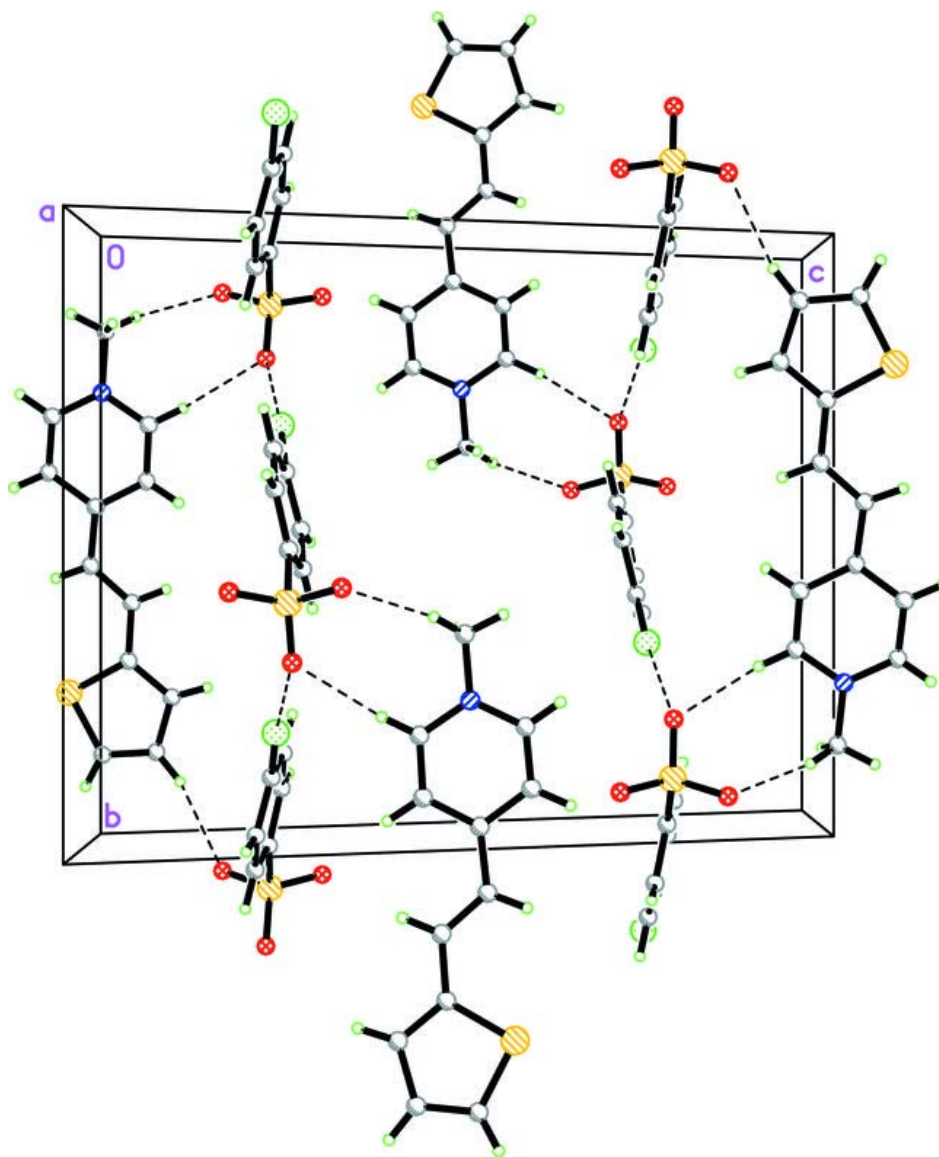


Fig. 2



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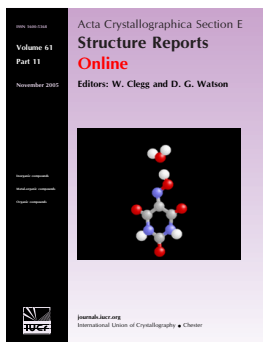
Editors: W. Clegg and D. G. Watson

(*E*)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methoxybenzenesulfonate monohydrate

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(E)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methoxybenzenesulfonate monohydrate¹

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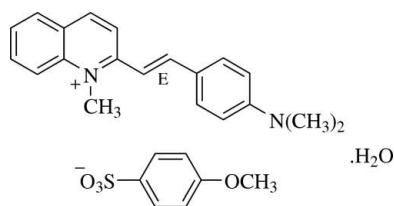
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Key indicators: single-crystal X-ray study; *T* = 100 K; mean σ (C–C) = 0.003 Å; *R* factor = 0.053; *wR* factor = 0.140; data-to-parameter ratio = 19.9.

In the title compound, C₂₀H₂₁N₂⁺·C₇H₇O₄S[−]·H₂O, the cation is nearly planar and exists in the *E* configuration. The cations and anions form individual chains along the *b* axis and are interconnected by weak C–H···O interactions. The 4-methoxybenzenesulfonate anions are linked to water molecules through O–H···O hydrogen bonds, forming a three-dimensional network. The crystal structure is further stabilized by a C–H··· π interaction involving the methoxyphenyl ring. The sulfonate anion is also involved in a weak intramolecular C–H···O interaction which generates an *S*(5) ring motif.

Related literature

For bond lengths and angles, see: Allen (2002); Allen *et al.* (1987). For details of hydrogen-bond motifs, see: Bernstein *et al.* (1995). For background to NLO materials research, see: Chia *et al.*, (1995); Otero *et al.*, (2002). For related structures, see for example: Chantrapromma *et al.* (2006, 2007, 2007a,b); Jindawong *et al.* (2005); Dittrich *et al.* (2003); Nogi *et al.* (2000); Sato *et al.* (1999).



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Experimental

Crystal data

C₂₀H₂₁N₂⁺·C₇H₇O₄S[−]·H₂O
M_r = 494.60
 Monoclinic, *P*2₁/*c*
a = 14.6064 (5) Å
b = 10.4253 (4) Å
c = 19.5025 (6) Å
 β = 126.737 (2)°
V = 2379.94 (16) Å³
Z = 4
 Mo *K* α radiation
 μ = 0.18 mm^{−1}
T = 100.0 (1) K
 0.58 × 0.27 × 0.19 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.904, *T_{max}* = 0.967
 33983 measured reflections
 6953 independent reflections
 5445 reflections with *I* > 2 σ (*I*)
R_{int} = 0.045

Refinement

R[*F*² > 2 σ (*F*²)] = 0.052
wR(*F*²) = 0.139
S = 1.06
 6953 reflections
 350 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}}$ = 0.74 e Å^{−3}
 $\Delta\rho_{\text{min}}$ = −0.42 e Å^{−3}

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1W—H1W···O2 ⁱ	0.84	2.04	2.875 (3)	169
O1W—H2W···O4 ⁱⁱ	0.85	2.10	2.926 (2)	161
C7—H7A···O3 ⁱⁱⁱ	0.93	2.49	3.015 (3)	116
C8—H8A···O3 ⁱⁱⁱ	0.93	2.57	3.049 (3)	113
C20—H20A···O4 ^{iv}	0.96	2.46	3.325 (2)	151
C23—H23A···O1W ^v	0.93	2.44	3.365 (2)	176
C26—H26A···O4	0.93	2.56	2.921 (2)	104
C27—H27A···O1W ^{vi}	0.96	2.58	3.160 (3)	119
C27—H27A···O1 ^{vii}	0.96	2.55	3.282 (2)	133
C16—H16A···Cg1 ^{iv}	0.93	2.81	3.6513 (19)	151

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x, -y - \frac{1}{2}, z + \frac{1}{2}$; (vi) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (vii) $-x + 2, -y - 1, -z + 2$. Cg1 is the centroid of the C21–C26 methoxyphenyl ring.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2466).

References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

- Bruker (2005). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chantrapromma, S., Jindawong, B., Fun, H.-K. & Patil, P. S. (2007a). *Anal. Sci.* **23**, x81–x82.
- Chantrapromma, S., Jindawong, B., Fun, H.-K. & Patil, P. S. (2007b). *Acta Cryst.* **E63**, o2124–o2126.
- Chantrapromma, S., Jindawong, B., Fun, H.-K., Patil, P. S. & Karalai, C. (2006). *Acta Cryst.* **E62**, o1802–o1804.
- Chantrapromma, S., Jindawong, B., Fun, H.-K., Patil, P. S. & Karalai, C. (2007). *Anal. Sci.* **23**, x27–x28.
- Chia, W.-L., Chen, C.-N. & Sheu, H.-J. (1995). *Mater. Res. Bull.* **30**, 1421–1430.
- Dittrich, Ph., Bartlome, R., Montemezzani, G. & Günter, P. (2003). *Appl. Surf. Sci.* **220**, 88–95.
- Jindawong, B., Chantrapromma, S., Fun, H.-K. & Karalai, C. (2005). *Acta Cryst.* **E61**, o3237–o3239.
- Nogi, K., Anwar, U., Tsuji, K., Duan, X.-M., Okada, S., Oikawa, H., Matsuda, H. & Nakanishi, H. (2000). *Nonlinear Optics*, **24**, 35–40.
- Otero, M., Herranz, M. A., Seoane, C., Martín, N., Garín, J., Orduna, J., Alcalá, R. & Villacampa, B. (2002). *Tetrahedron*, **58**, 7463–7475.
- Sato, N., Rikukawa, M., Sanui, K. & Ogata, N. (1999). *Synth. Met.* **101**, 132–133.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

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(*E*)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methoxybenzenesulfonate monohydrate

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Comment

A lot of research have been done to search for second-order nonlinear optic (NLO) materials. Organic crystals with the required conjugated π electrons are attractive candidates because of their large NLO coefficients (Chia *et al.*, 1995; Dittrich *et al.*, 2003; Otero *et al.*, 2002; Nogi *et al.*, 2000; Sato *et al.*, 1999). In our research on this kind of materials, we have previously synthesized and crystallized several organic ionic salts of quinolinium derivatives to study their non-linear optical properties (Chantrapromma *et al.*, 2006; 2007a,b; 2007; Jindawong *et al.*, 2005). Previous studies (Dittrich *et al.*, 2003; Nogi *et al.*, 2000; Sato *et al.*, 1999) have shown that the 1-methyl-4-(2-(4-(dimethylamino)phenyl)ethynyl)pyridinium *p*-toluenesulfonate (DAST) and its analogues exhibit second-order non-linear optical properties. Based on these previous studies, we have synthesized the title compound which was designed to increase the π -conjugation in the system with the replacement of the cationic 4-hydroxy-3-methoxyphenyl ring that is present in 2-[(*E*)-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate (Chantrapromma *et al.*, 2007a) by the 4-dimethylaminophenyl ring. The synthesis and crystal structure of the title compound, (I), Fig 1, are reported in this study. Unfortunately this crystal does not have second-order NLO properties because it crystallized out in a centrosymmetric space group.

The asymmetric unit of the title compound consists of the $C_{20}H_{21}N_2^+$ cation, $C_7H_7O_4S^-$ anion and one H_2O molecule. The cation exists in the *E* configuration with respect to the $C10=C11$ double bond [1.350 (2) Å] and is nearly planar as indicated by the dihedral angle between the quinolinium and the dimethylaminophenyl rings being 3.41 (7)° and the torsion angles $C8-C9-C10-C11 = -8.7$ (2)° and $C10-C11-C12-C17 = 3.2$ (3)°. The relative arrangement of cation and anion is shown by the angles between the mean plane of the methoxyphenyl ring and those of the quinolinium and dimethylaminophenyl systems which are 81.29 (7)° and 78.29 (8)°, respectively.

The atom O4 of the sulfonate contributes to a weak intramolecular $C-H\cdots O$ interaction (Fig. 1 and Table 1) forming an S(5) ring motif (Bernstein *et al.*, 1995). The bond lengths and angles are normal (Allen *et al.*, 1987) and are comparable with closely related structures (Chantrapromma *et al.*, 2006; 2007a; 2007b; 2007c).

In the crystal packing, the O2 and O4 atoms of 4-methoxybenzenesulfonate anion are involved in the $O-H\cdots O$ hydrogen bonds whereas O3 and O4 atoms are involved in weak $C-H\cdots O$ interactions (Table 1). The cations and anions form individual chains along the *b* axis and are interconnected by weak $C-H\cdots O$ interactions. The 4-methoxybenzenesulfonate anions are linked to water molecules through $O-H\cdots O$ hydrogen bonds forming a three dimensional network (Fig. 2). The crystal structure is further stabilized by a $C16-H16A\cdots\pi$ interaction to the methoxyphenyl ring [C21-C26]: $C16-H16A=0.93$; $H16A\cdots Cg_1^i=2.8096$; $C16-Cg_1^i=3.6513$ (19) Å; $C16-H16A\cdots Cg_1^i=151^\circ$. [Cg_1^i is the centroid of the C21-C26 methoxyphenyl ring (symmetry code: (i): $1-x, 1-y, 1-z$).]

Experimental

2-(4-dimethylaminostyryl)-1-methylquinolinium iodide (compound A) was synthesized by mixing a solution (1:1:1 molar ratio) of 1,2-dimethylquinolinium iodide (2.00 g, 7.01 mmol), dimethylaminobenzaldehyde (1.05 g, 7.01 mmol) and piperidine (0.70 g, 7.01 mmol) in hot methanol (50 ml). The resulting solution was refluxed for 6 h under a nitrogen atmosphere. The resultant solid was filtered off, washed with methanol and recrystallized from methanol to give green crystals of compound A. Silver(I) 4-methoxybenzenesulfonate (compound B) was synthesized according to our previously reported procedure (Chantrapromma *et al.*, 2007a). The title compound was synthesized by mixing compound A (0.2 g, 0.48 mmol) in hot methanol (50 ml) and compound B (0.14 g, 0.48 mmol) in hot methanol (20 ml). The mixture immediately yielded a grey precipitate of silver iodide. After stirring the mixture for *ca* 30 min, the precipitate was removed and the resulting solution was evaporated yielding a brown solid. Brown block-shaped single crystals of the title compound suitable for *x*-ray structure determination were recrystallized from methanol/ethanol solvent (3:1 *v/v*) by slow evaporation of the solvent at room temperature after a few weeks. (Mp. 545–547 K).

Refinement

All H atoms were placed in calculated positions with $d(\text{O—H}) = 0.85 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{O})$, $d(\text{C—H}) = 0.93 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aromatic and CH, 0.96 \AA , $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$ for CH_3 atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at 0.88 \AA from C9 and the deepest hole is located at 0.69 \AA from S1.

Figures

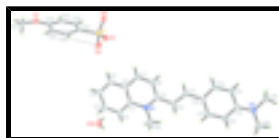


Fig. 1. The asymmetric unit of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. The weak intramolecular C—H...O interaction is drawn as a dashed line.

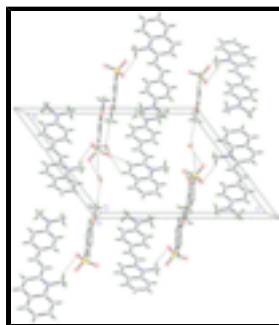


Fig. 2. The crystal packing of (I) viewed along the *b* axis. The O—H...O and weak C—H...O interactions are drawn as dashed lines.

(*E*)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methoxybenzenesulfonate monohydrate

Crystal data

$\text{C}_{20}\text{H}_{21}\text{N}_2^+ \cdot \text{C}_7\text{H}_7\text{O}_4\text{S}^- \cdot \text{H}_2\text{O}$

$M_r = 494.60$

Monoclinic, $P2_1/c$

$F_{000} = 1048$

$D_x = 1.380 \text{ Mg m}^{-3}$

Melting point: 545–547 K

Hall symbol: -P 2ybc

$a = 14.6064$ (5) Å

$b = 10.4253$ (4) Å

$c = 19.5025$ (6) Å

$\beta = 126.737$ (2)°

$V = 2379.94$ (16) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 6593 reflections

$\theta = 2.1$ – 30.0°

$\mu = 0.18$ mm⁻¹

$T = 100.0$ (1) K

Block, brown

$0.58 \times 0.27 \times 0.19$ mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 8.33 pixels mm⁻¹

$T = 100.0$ (1) K

ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\min} = 0.904$, $T_{\max} = 0.967$

33983 measured reflections

6953 independent reflections

5445 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\text{max}} = 30.0^\circ$

$\theta_{\text{min}} = 2.1^\circ$

$h = -20 \rightarrow 19$

$k = -14 \rightarrow 14$

$l = -24 \rightarrow 27$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.139$

$S = 1.06$

6953 reflections

350 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 1.1852P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.75$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.42$ e Å⁻³

Extinction correction: none

Special details

Experimental. The low-temperature data was collected with the Oxford Cryosystem Cobra low-temperature attachment.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculat-

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ing R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R - factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.61826 (3)	0.05907 (4)	0.76956 (2)	0.02112 (11)
O1	0.95438 (10)	-0.35916 (12)	0.95862 (7)	0.0250 (3)
O2	0.53003 (10)	0.00579 (13)	0.68519 (7)	0.0275 (3)
O3	0.57692 (12)	0.08820 (15)	0.81913 (8)	0.0360 (3)
O4	0.67900 (11)	0.16597 (13)	0.76497 (8)	0.0301 (3)
O1W	0.66931 (11)	0.09083 (15)	0.33524 (10)	0.0429 (4)
H1W	0.6058	0.0660	0.3224	0.058 (8)*
H2W	0.6633	0.1682	0.3187	0.050 (7)*
N1	0.56771 (11)	0.67419 (14)	0.49475 (8)	0.0215 (3)
N2	0.05342 (12)	1.30700 (15)	0.29537 (8)	0.0235 (3)
C1	0.64527 (13)	0.57400 (17)	0.54367 (9)	0.0217 (3)
C2	0.70847 (15)	0.51470 (19)	0.52077 (11)	0.0277 (4)
H2A	0.7021	0.5417	0.4726	0.038 (6)*
C3	0.77995 (16)	0.4162 (2)	0.56969 (11)	0.0322 (4)
H3A	0.8227	0.3772	0.5545	0.055 (7)*
C4	0.79097 (16)	0.37240 (19)	0.64227 (11)	0.0304 (4)
H4A	0.8393	0.3040	0.6737	0.043 (6)*
C5	0.73095 (14)	0.42956 (18)	0.66701 (10)	0.0268 (4)
H5A	0.7384	0.4009	0.7153	0.024 (5)*
C6	0.65650 (13)	0.53407 (17)	0.61789 (10)	0.0229 (3)
C7	0.59337 (14)	0.59648 (18)	0.64128 (10)	0.0237 (3)
H7A	0.5989	0.5687	0.6889	0.026 (5)*
C8	0.52447 (14)	0.69699 (18)	0.59453 (10)	0.0241 (3)
H8A	0.4857	0.7396	0.6120	0.024 (5)*
C9	0.51057 (13)	0.73831 (17)	0.51874 (9)	0.0216 (3)
C10	0.43701 (13)	0.84531 (17)	0.46835 (10)	0.0220 (3)
H10A	0.4384	0.8763	0.4243	0.032 (6)*
C11	0.36646 (13)	0.90197 (17)	0.48240 (9)	0.0211 (3)
H11A	0.3685	0.8710	0.5280	0.033 (6)*
C12	0.28800 (13)	1.00599 (16)	0.43337 (9)	0.0197 (3)
C13	0.22320 (13)	1.05721 (17)	0.45820 (9)	0.0218 (3)
H13A	0.2324	1.0239	0.5062	0.039 (6)*
C14	0.14611 (13)	1.15578 (17)	0.41354 (9)	0.0215 (3)
H14A	0.1048	1.1876	0.4321	0.029 (5)*
C15	0.12911 (12)	1.20908 (16)	0.33990 (9)	0.0188 (3)
C16	0.19398 (13)	1.15699 (17)	0.31446 (9)	0.0202 (3)
H16A	0.1845	1.1893	0.2661	0.025 (5)*
C17	0.27101 (13)	1.05893 (17)	0.36003 (9)	0.0206 (3)
H17A	0.3128	1.0270	0.3419	0.023 (5)*
C18	-0.01161 (15)	1.3601 (2)	0.32301 (11)	0.0292 (4)
H18A	0.0396	1.3844	0.3821	0.029 (5)*
H18B	-0.0642	1.2968	0.3162	0.034 (6)*

H18C	-0.0532	1.4341	0.2890	0.054 (8)*
C19	0.03078 (15)	1.35334 (19)	0.21618 (10)	0.0260 (4)
H19A	0.1000	1.3866	0.2277	0.036 (6)*
H19B	-0.0257	1.4200	0.1926	0.043 (7)*
H19C	0.0031	1.2839	0.1760	0.028 (5)*
C20	0.54745 (16)	0.7057 (2)	0.41323 (11)	0.0288 (4)
H20A	0.4713	0.7384	0.3738	0.051 (7)*
H20B	0.5564	0.6299	0.3898	0.044 (7)*
H20C	0.6014	0.7695	0.4228	0.048 (7)*
C21	0.72090 (13)	-0.06494 (16)	0.82541 (9)	0.0190 (3)
C22	0.68657 (13)	-0.19286 (17)	0.81620 (9)	0.0210 (3)
H22A	0.6094	-0.2136	0.7793	0.024 (5)*
C23	0.76655 (14)	-0.28880 (17)	0.86144 (9)	0.0218 (3)
H23A	0.7432	-0.3737	0.8553	0.032 (6)*
C24	0.88269 (13)	-0.25763 (16)	0.91662 (9)	0.0198 (3)
C25	0.91782 (13)	-0.13092 (16)	0.92572 (9)	0.0209 (3)
H25A	0.9950	-0.1102	0.9623	0.030 (5)*
C26	0.83634 (13)	-0.03516 (17)	0.87967 (9)	0.0207 (3)
H26A	0.8596	0.0497	0.8853	0.021 (5)*
C27	1.07377 (14)	-0.33401 (19)	1.02041 (11)	0.0272 (4)
H27A	1.1131	-0.4129	1.0475	0.024 (5)*
H27B	1.0848	-0.2755	1.0628	0.031 (5)*
H27C	1.1035	-0.2968	0.9924	0.038 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02159 (18)	0.0248 (2)	0.01629 (17)	0.00406 (15)	0.01098 (14)	0.00242 (14)
O1	0.0220 (5)	0.0216 (6)	0.0234 (5)	0.0026 (5)	0.0093 (4)	0.0033 (5)
O2	0.0230 (6)	0.0336 (7)	0.0176 (5)	0.0029 (5)	0.0077 (5)	0.0016 (5)
O3	0.0390 (7)	0.0486 (9)	0.0284 (6)	0.0158 (7)	0.0244 (6)	0.0072 (6)
O4	0.0289 (6)	0.0248 (7)	0.0309 (6)	0.0018 (5)	0.0148 (5)	0.0054 (5)
O1W	0.0259 (7)	0.0310 (8)	0.0591 (9)	0.0033 (6)	0.0186 (7)	0.0143 (7)
N1	0.0211 (6)	0.0261 (8)	0.0164 (6)	0.0002 (5)	0.0107 (5)	0.0007 (5)
N2	0.0241 (6)	0.0285 (8)	0.0181 (6)	0.0070 (6)	0.0128 (5)	0.0032 (5)
C1	0.0180 (7)	0.0230 (8)	0.0167 (6)	-0.0035 (6)	0.0065 (5)	-0.0007 (6)
C2	0.0264 (8)	0.0331 (10)	0.0228 (7)	0.0006 (7)	0.0143 (7)	-0.0013 (7)
C3	0.0326 (9)	0.0343 (11)	0.0284 (8)	0.0044 (8)	0.0175 (7)	-0.0010 (7)
C4	0.0309 (9)	0.0274 (10)	0.0274 (8)	0.0069 (7)	0.0145 (7)	0.0042 (7)
C5	0.0231 (7)	0.0299 (10)	0.0210 (7)	0.0015 (7)	0.0097 (6)	0.0015 (7)
C6	0.0194 (7)	0.0258 (9)	0.0205 (7)	-0.0050 (6)	0.0102 (6)	-0.0058 (6)
C7	0.0238 (7)	0.0290 (9)	0.0165 (6)	-0.0025 (7)	0.0109 (6)	-0.0001 (6)
C8	0.0213 (7)	0.0291 (9)	0.0210 (7)	0.0012 (7)	0.0121 (6)	0.0021 (6)
C9	0.0176 (6)	0.0240 (9)	0.0205 (7)	-0.0033 (6)	0.0099 (6)	-0.0048 (6)
C10	0.0205 (7)	0.0253 (9)	0.0177 (6)	0.0007 (6)	0.0101 (6)	-0.0001 (6)
C11	0.0207 (7)	0.0237 (8)	0.0171 (6)	-0.0009 (6)	0.0103 (6)	-0.0007 (6)
C12	0.0179 (6)	0.0217 (8)	0.0173 (6)	-0.0011 (6)	0.0094 (5)	-0.0020 (6)
C13	0.0215 (7)	0.0276 (9)	0.0169 (6)	-0.0001 (6)	0.0117 (6)	0.0012 (6)

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C14	0.0211 (7)	0.0278 (9)	0.0174 (6)	0.0014 (6)	0.0126 (6)	-0.0017 (6)
C15	0.0169 (6)	0.0208 (8)	0.0158 (6)	-0.0003 (6)	0.0082 (5)	-0.0020 (5)
C16	0.0202 (7)	0.0256 (8)	0.0160 (6)	-0.0007 (6)	0.0114 (6)	-0.0005 (6)
C17	0.0180 (6)	0.0275 (9)	0.0178 (6)	0.0009 (6)	0.0114 (5)	-0.0027 (6)
C18	0.0274 (8)	0.0354 (10)	0.0247 (8)	0.0099 (8)	0.0156 (7)	0.0014 (7)
C19	0.0251 (8)	0.0296 (9)	0.0191 (7)	0.0019 (7)	0.0110 (6)	0.0039 (6)
C20	0.0325 (9)	0.0341 (10)	0.0243 (8)	0.0077 (8)	0.0195 (7)	0.0077 (7)
C21	0.0202 (7)	0.0234 (8)	0.0139 (6)	0.0012 (6)	0.0105 (5)	0.0017 (6)
C22	0.0188 (7)	0.0259 (9)	0.0162 (6)	-0.0012 (6)	0.0093 (6)	0.0004 (6)
C23	0.0247 (7)	0.0210 (8)	0.0178 (6)	-0.0019 (6)	0.0118 (6)	0.0006 (6)
C24	0.0221 (7)	0.0222 (8)	0.0156 (6)	0.0028 (6)	0.0115 (6)	0.0020 (6)
C25	0.0187 (7)	0.0239 (8)	0.0157 (6)	-0.0011 (6)	0.0080 (6)	0.0000 (6)
C26	0.0221 (7)	0.0210 (8)	0.0175 (6)	-0.0016 (6)	0.0110 (6)	-0.0006 (6)
C27	0.0216 (7)	0.0300 (10)	0.0230 (7)	0.0039 (7)	0.0095 (6)	0.0039 (7)

Geometric parameters (Å, °)

S1—O3	1.4455 (13)	C11—H11A	0.9299
S1—O4	1.4602 (14)	C12—C13	1.401 (2)
S1—O2	1.4628 (12)	C12—C17	1.410 (2)
S1—C21	1.7754 (16)	C13—C14	1.382 (2)
O1—C24	1.3644 (19)	C13—H13A	0.9301
O1—C27	1.431 (2)	C14—C15	1.417 (2)
O1W—H1W	0.8450	C14—H14A	0.9297
O1W—H2W	0.8529	C15—C16	1.415 (2)
N1—C9	1.353 (2)	C16—C17	1.380 (2)
N1—C1	1.411 (2)	C16—H16A	0.9299
N1—C20	1.470 (2)	C17—H17A	0.9299
N2—C15	1.368 (2)	C18—H18A	0.9600
N2—C18	1.453 (2)	C18—H18B	0.9600
N2—C19	1.455 (2)	C18—H18C	0.9600
C1—C2	1.388 (2)	C19—H19A	0.9600
C1—C6	1.418 (2)	C19—H19B	0.9600
C2—C3	1.365 (3)	C19—H19C	0.9600
C2—H2A	0.9299	C20—H20A	0.9600
C3—C4	1.402 (3)	C20—H20B	0.9600
C3—H3A	0.9301	C20—H20C	0.9600
C4—C5	1.365 (3)	C21—C26	1.387 (2)
C4—H4A	0.9300	C21—C22	1.398 (2)
C5—C6	1.429 (2)	C22—C23	1.382 (2)
C5—H5A	0.9301	C22—H22A	0.9300
C6—C7	1.409 (2)	C23—C24	1.399 (2)
C7—C8	1.358 (2)	C23—H23A	0.9301
C7—H7A	0.9300	C24—C25	1.390 (2)
C8—C9	1.433 (2)	C25—C26	1.393 (2)
C8—H8A	0.9301	C25—H25A	0.9300
C9—C10	1.450 (2)	C26—H26A	0.9301
C10—C11	1.350 (2)	C27—H27A	0.9600
C10—H10A	0.9299	C27—H27B	0.9600

C11—C12	1.447 (2)	C27—H27C	0.9600
O3—S1—O4	113.13 (9)	C13—C14—H14A	119.6
O3—S1—O2	113.11 (8)	C15—C14—H14A	119.6
O4—S1—O2	112.31 (8)	N2—C15—C16	121.37 (14)
O3—S1—C21	106.25 (7)	N2—C15—C14	121.43 (14)
O4—S1—C21	105.80 (7)	C16—C15—C14	117.20 (14)
O2—S1—C21	105.44 (8)	C17—C16—C15	121.17 (14)
C24—O1—C27	118.33 (14)	C17—C16—H16A	119.4
H1W—O1W—H2W	109.3	C15—C16—H16A	119.4
C9—N1—C1	122.94 (14)	C16—C17—C12	121.62 (15)
C9—N1—C20	119.79 (14)	C16—C17—H17A	119.2
C1—N1—C20	117.24 (14)	C12—C17—H17A	119.2
C15—N2—C18	120.55 (14)	N2—C18—H18A	109.5
C15—N2—C19	120.40 (14)	N2—C18—H18B	109.5
C18—N2—C19	118.91 (14)	H18A—C18—H18B	109.5
C2—C1—N1	122.11 (15)	N2—C18—H18C	109.5
C2—C1—C6	120.29 (16)	H18A—C18—H18C	109.5
N1—C1—C6	117.60 (15)	H18B—C18—H18C	109.5
C3—C2—C1	119.21 (17)	N2—C19—H19A	109.5
C3—C2—H2A	120.4	N2—C19—H19B	109.5
C1—C2—H2A	120.4	H19A—C19—H19B	109.5
C2—C3—C4	121.91 (18)	N2—C19—H19C	109.5
C2—C3—H3A	119.0	H19A—C19—H19C	109.5
C4—C3—H3A	119.1	H19B—C19—H19C	109.5
C5—C4—C3	120.31 (18)	N1—C20—H20A	109.5
C5—C4—H4A	119.8	N1—C20—H20B	109.5
C3—C4—H4A	119.8	H20A—C20—H20B	109.5
C4—C5—C6	119.22 (16)	N1—C20—H20C	109.5
C4—C5—H5A	120.5	H20A—C20—H20C	109.5
C6—C5—H5A	120.3	H20B—C20—H20C	109.5
C7—C6—C1	119.76 (16)	C26—C21—C22	119.36 (15)
C7—C6—C5	121.21 (16)	C26—C21—S1	120.01 (13)
C1—C6—C5	119.03 (16)	C22—C21—S1	120.63 (11)
C8—C7—C6	120.31 (16)	C23—C22—C21	120.46 (14)
C8—C7—H7A	119.8	C23—C22—H22A	119.7
C6—C7—H7A	119.9	C21—C22—H22A	119.8
C7—C8—C9	121.03 (16)	C22—C23—C24	119.73 (16)
C7—C8—H8A	119.5	C22—C23—H23A	120.1
C9—C8—H8A	119.5	C24—C23—H23A	120.2
N1—C9—C8	118.18 (15)	O1—C24—C25	124.66 (14)
N1—C9—C10	120.42 (14)	O1—C24—C23	115.07 (15)
C8—C9—C10	121.40 (15)	C25—C24—C23	120.28 (15)
C11—C10—C9	123.04 (15)	C24—C25—C26	119.41 (14)
C11—C10—H10A	118.5	C24—C25—H25A	120.3
C9—C10—H10A	118.5	C26—C25—H25A	120.3
C10—C11—C12	126.36 (15)	C21—C26—C25	120.74 (16)
C10—C11—H11A	116.8	C21—C26—H26A	119.6
C12—C11—H11A	116.9	C25—C26—H26A	119.7
C13—C12—C17	117.13 (15)	O1—C27—H27A	109.5

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C13—C12—C11	119.28 (14)	O1—C27—H27B	109.5
C17—C12—C11	123.58 (15)	H27A—C27—H27B	109.5
C14—C13—C12	121.99 (15)	O1—C27—H27C	109.5
C14—C13—H13A	119.0	H27A—C27—H27C	109.5
C12—C13—H13A	119.0	H27B—C27—H27C	109.5
C13—C14—C15	120.88 (15)		
C9—N1—C1—C2	-175.88 (16)	C12—C13—C14—C15	0.3 (2)
C20—N1—C1—C2	5.9 (2)	C18—N2—C15—C16	-179.39 (16)
C9—N1—C1—C6	4.6 (2)	C19—N2—C15—C16	5.0 (2)
C20—N1—C1—C6	-173.66 (15)	C18—N2—C15—C14	0.4 (2)
N1—C1—C2—C3	-178.39 (16)	C19—N2—C15—C14	-175.14 (15)
C6—C1—C2—C3	1.1 (3)	C13—C14—C15—N2	-179.73 (15)
C1—C2—C3—C4	0.4 (3)	C13—C14—C15—C16	0.1 (2)
C2—C3—C4—C5	-1.1 (3)	N2—C15—C16—C17	179.42 (15)
C3—C4—C5—C6	0.3 (3)	C14—C15—C16—C17	-0.4 (2)
C2—C1—C6—C7	178.90 (16)	C15—C16—C17—C12	0.4 (2)
N1—C1—C6—C7	-1.6 (2)	C13—C12—C17—C16	0.0 (2)
C2—C1—C6—C5	-1.9 (2)	C11—C12—C17—C16	179.05 (15)
N1—C1—C6—C5	177.59 (14)	O3—S1—C21—C26	-97.34 (14)
C4—C5—C6—C7	-179.62 (17)	O4—S1—C21—C26	23.18 (15)
C4—C5—C6—C1	1.2 (2)	O2—S1—C21—C26	142.35 (13)
C1—C6—C7—C8	-1.9 (2)	O3—S1—C21—C22	81.83 (14)
C5—C6—C7—C8	178.93 (16)	O4—S1—C21—C22	-157.66 (13)
C6—C7—C8—C9	2.7 (3)	O2—S1—C21—C22	-38.48 (15)
C1—N1—C9—C8	-3.9 (2)	C26—C21—C22—C23	0.8 (2)
C20—N1—C9—C8	174.28 (15)	S1—C21—C22—C23	-178.35 (12)
C1—N1—C9—C10	176.41 (14)	C21—C22—C23—C24	-0.2 (2)
C20—N1—C9—C10	-5.4 (2)	C27—O1—C24—C25	3.9 (2)
C7—C8—C9—N1	0.2 (2)	C27—O1—C24—C23	-175.95 (14)
C7—C8—C9—C10	179.86 (16)	C22—C23—C24—O1	179.57 (14)
N1—C9—C10—C11	170.96 (15)	C22—C23—C24—C25	-0.3 (2)
C8—C9—C10—C11	-8.7 (2)	O1—C24—C25—C26	-179.62 (14)
C9—C10—C11—C12	-177.83 (15)	C23—C24—C25—C26	0.2 (2)
C10—C11—C12—C13	-177.82 (16)	C22—C21—C26—C25	-0.9 (2)
C10—C11—C12—C17	3.2 (3)	S1—C21—C26—C25	178.29 (12)
C17—C12—C13—C14	-0.3 (2)	C24—C25—C26—C21	0.4 (2)
C11—C12—C13—C14	-179.40 (15)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1W—H1W \cdots O2 ⁱ	0.84	2.04	2.875 (3)	169
O1W—H2W \cdots O4 ⁱⁱ	0.85	2.10	2.926 (2)	161
C7—H7A \cdots O3 ⁱⁱⁱ	0.93	2.49	3.015 (3)	116
C8—H8A \cdots O3 ⁱⁱⁱ	0.93	2.57	3.049 (3)	113
C20—H20A \cdots O4 ^{iv}	0.96	2.46	3.325 (2)	151
C23—H23A \cdots O1W ^v	0.93	2.44	3.365 (2)	176
C26—H26A \cdots O4	0.93	2.56	2.921 (2)	104

C27—H27A...O1W ^{vi}	0.96	2.58	3.160 (3)	119
C27—H27A...O1 ^{vii}	0.96	2.55	3.282 (2)	133
C16—H16A...Cg1 ^{iv}	0.93	2.81	3.6513 (19)	151

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x, -y+1/2, z-1/2$; (iii) $-x+1, y+1/2, -z+3/2$; (iv) $-x+1, -y+1, -z+1$; (v) $x, -y-1/2, z+1/2$; (vi) $-x+2, y-1/2, -z+3/2$; (vii) $-x+2, -y-1, -z+2$.

Fig. 1

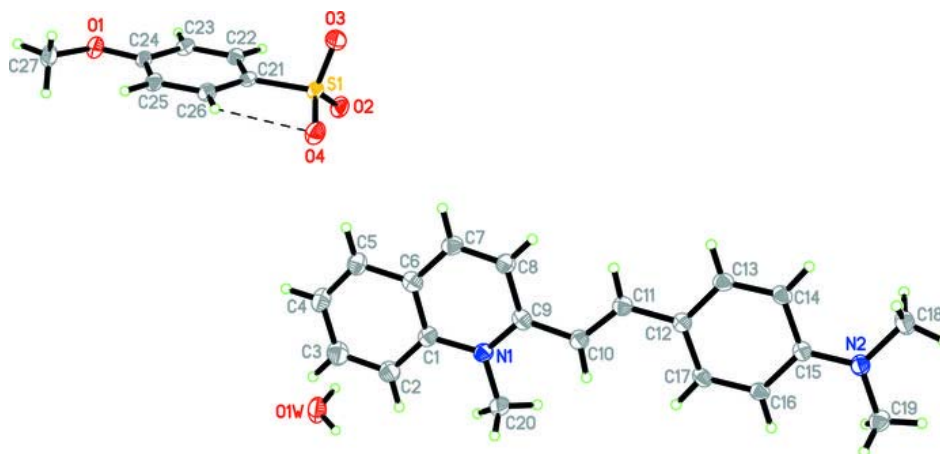
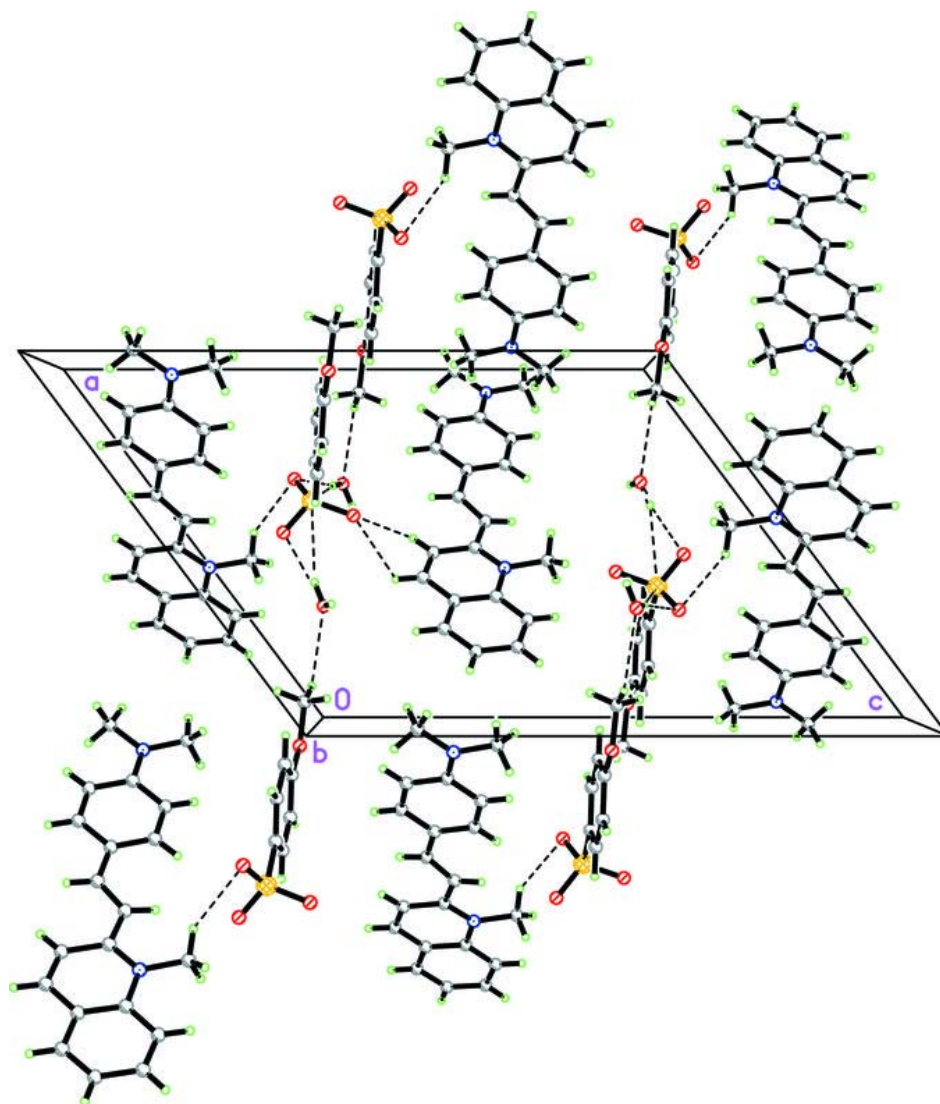


Fig. 2



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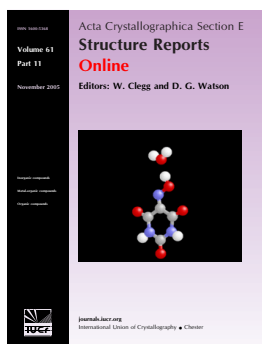
Editors: W. Clegg and D. G. Watson

(*E*)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium iodide sesquihydrate

Suchada Chantrapromma, Thawanrat Kobkeatthawin, Kullapa Chanawanno, Chatchanok Karalai and Hoong-Kun Fun

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(E)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium iodide sesquihydrate

Suchada Chantrapromma,^{a*} Thawanrat Kobkeatthawin,^a Kullapa Chanawanno,^a Chatchanok Karalai^a and Hoong-Kun Fun^{b‡}

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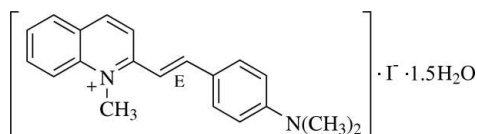
Received 30 March 2008; accepted 16 April 2008

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(C-C) = 0.002$ Å; R factor = 0.029; wR factor = 0.068; data-to-parameter ratio = 34.8.

In the title compound, $C_{20}H_{21}N_2^+I^- \cdot 1.5H_2O$, the cation exists in the *E* configuration and is not planar. The dihedral angle between the quinolinium and dimethylaminophenyl rings is $9.26(6)^\circ$. The O atom of one of the solvent water molecules lies on a twofold rotation axis. In the crystal structure, the cations form one-dimensional zigzag chains along the [001] direction. The cations are linked to water molecules and iodide ions through weak $C-H \cdots O$ and $C-H \cdots I$ interactions, respectively. Water molecules and iodide ions form $O-H \cdots O$ and $O-H \cdots I$ hydrogen bonds, which stabilize the crystal structure. A $C-H \cdots \pi$ interaction is also present.

Related literature

For bond lengths, see: Allen *et al.* (1987). For background to non-linear optical (NLO) materials research, see: Chia *et al.* (1995); Marder *et al.* (1994); Otero *et al.* (2002); Pan *et al.* (1996). For related structures, see for example: Chantrapromma *et al.* (2006, 2007a,b,c,d); Dittrich *et al.* (2003); Jindawong *et al.* (2005); Kobkeatthawin *et al.* (2008); Nogi *et al.* (2000); Sato *et al.* (1999); Umezawa *et al.* (2000).



Experimental

Crystal data

$C_{20}H_{21}N_2^+I^- \cdot 1.5H_2O$
 $M_r = 443.31$

Monoclinic, $C2/c$
 $a = 20.8997(4)$ Å

$b = 10.5941(2)$ Å
 $c = 18.4020(4)$ Å
 $\beta = 113.047(1)^\circ$
 $V = 3749.24(13)$ Å³
 $Z = 8$

Mo $K\alpha$ radiation
 $\mu = 1.72$ mm⁻¹
 $T = 100.0(1)$ K
 $0.52 \times 0.35 \times 0.12$ mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.469$, $T_{\max} = 0.818$

50083 measured reflections
8240 independent reflections
7476 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.068$
 $S = 1.07$
8240 reflections
237 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 1.58$ e Å⁻³
 $\Delta\rho_{\min} = -0.80$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1W-H1W1 \cdots I1^i$	0.85 (3)	2.74 (3)	3.5832 (16)	172 (3)
$O2W-H1W2 \cdots O1W$	0.83 (3)	2.10 (3)	2.9164 (19)	167 (3)
$O1W-H2W1 \cdots I1^{ii}$	0.79 (3)	2.94 (3)	3.7267 (16)	174 (3)
$C3-H3A \cdots O2W^{iii}$	0.93	2.60	3.371 (2)	141
$C7-H7A \cdots I1^{iv}$	0.93	3.04	3.9290 (18)	161
$C17-H17A \cdots I1^{ii}$	0.93	3.01	3.8784 (14)	157
$C2-H2A \cdots Cg1^{ii}$	0.93	3.02	3.7648 (17)	138

Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $x, -y + 1, z - \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; Cg1 is the centroid of the C12–C17 ring.

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: SAINT (Bruker, 2005); program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2479).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
Bruker (2005). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Chantrapromma, S., Jindawong, B., Fun, H.-K. & Patil, P. S. (2007a). *Anal. Sci.* **23**, x81–x82.
Chantrapromma, S., Jindawong, B., Fun, H.-K. & Patil, P. S. (2007b). *Acta Cryst. E* **63**, o2124–o2126.
Chantrapromma, S., Jindawong, B., Fun, H.-K. & Patil, P. S. (2007c). *Acta Cryst. E* **63**, o2321–o2323.
Chantrapromma, S., Jindawong, B., Fun, H.-K., Patil, P. S. & Karalai, C. (2006). *Acta Cryst. E* **62**, o1802–o1804.
Chantrapromma, S., Jindawong, B., Fun, H.-K., Patil, P. S. & Karalai, C. (2007d). *Anal. Sci.* **23**, x27–x28.
Chia, W.-L., Chen, C.-N. & Sheu, H.-J. (1995). *Mater. Res. Bull.* **30**, 1421–1430.

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- Dittrich, Ph., Bartlome, R., Montemezzani, G. & Günter, P. (2003). *Appl. Surf. Sci.* **220**, 88–95.
- Jindawong, B., Chantrapromma, S., Fun, H.-K. & Karalai, C. (2005). *Acta Cryst.* **E61**, o3237–o3239.
- Kobkeatthawin, T., Ruanwas, P., Chantrapromma, S. & Fun, H.-K. (2008). *Acta Cryst.* **E64**, o642–o643.
- Marder, S. R., Perry, J. W. & Yakymyhyn, C. P. (1994). *Chem. Mater.* **6**, 1137–1147.
- Nogi, K., Anwar, U., Tsuji, K., Duan, X.-M., Okada, S., Oikawa, H., Matsuda, H. & Nakanishi, H. (2000). *Nonlinear Optics*, **24**, 35–40.
- Otero, M., Herranz, M. A., Seoane, C., Martín, N., Garín, J., Orduna, J., Alcalá, R. & Villacampa, B. (2002). *Tetrahedron*. **58**, 7463–7475.
- Pan, F., Knöpfle, G., Bosshard, Ch., Follonier, S., Spreiter, R., Wong, M. S. & Günter, P. (1996). *Appl. Phys. Lett.* **69**, 13–15.
- Sato, N., Rikukawa, M., Sanui, K. & Ogata, N. (1999). *Synth. Met.* **101**, 132–133.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Umezawa, H., Tsuji, K., Usman, A., Duan, X.-M., Okada, S., Oikawa, H. & Matsuda, H. (2000). *Nonlinear Optics*, **24**, 73–78.

supplementary materials

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(E)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium iodide sesquihydrate

S. Chantrapromma, T. Kobkeathawin, K. Chanawanno, C. Karalai and H.-K. Fun

Comment

Organic molecules with large π systems have been extensively used in attempts to obtain non-linear optical (NLO) materials (Chia *et al.*, 1995; Dittrich *et al.*, 2003; Marder *et al.*, 1994; Nogi *et al.*, 2000; Otero *et al.*, 2002; Pan *et al.*, 1996; Sato *et al.*, 1999). We have previously synthesized and crystallized several ionic organic salts of quinolinium derivatives which have a conjugate π system to study their non-linear optical properties (Chantrapromma *et al.*, 2006; 2007a; 2007b; 2007c; 2007d; Jindawong *et al.*, 2005). Previous investigations by Marder *et al.*, 1994, Pan *et al.*, 1996 and Umezawa *et al.*, 2000 reported that 1-methyl-4-(2-(4-(dimethylamino)phenyl)ethenyl)pyridinium *p*-toluenesulfonate (DAST) is a promising second-order NLO material. Based on this information and our previous investigation (Chantrapromma *et al.*, 2007c), we have designed and synthesized the title compound (I) with the replacement of the 3-hydroxy-4-methoxyphenyl ring in the cation of 2-[(*E*)-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium iodide monohydrate which showed second-order NLO properties (Chantrapromma *et al.*, 2007c) by the 4-dimethylaminophenyl ring and its crystal structure was reported here. However since second-order NLO effects are created only when chromophores are arranged in a non-centrosymmetric manner, the title compound, which crystallized in the centrosymmetric space group $C2/c$, does not exhibit any second-order NLO properties.

The asymmetric unit of the title compound consists of one $C_{20}H_{21}N_2^+$ cation, one I^- anion and 1.5 H_2O molecules. The remaining cell contents are generated by symmetry with the O2W atom (symmetry code: $-x, y, 1/2 - z$) lying on a two-fold rotation axis. The cation exists in the *E* configuration with respect to the C10=C11 double bond [1.357 (2) Å] and is not planar as indicated by a dihedral angle of 9.26 (6)° between the quinolinium and the dimethylaminophenyl rings. This value is relatively wider than the corresponding angle (3.41 (7)°) reported for the closely related structure of the 4-methoxybenzenesulfonate salt of the same cation (Kobkeathawin *et al.*, 2008). This may be due to packing effects involving the different counterions. The orientation of the ethenyl unit with respect to the quinolinium and the dimethylaminophenyl rings can be indicated by the torsion angles C8-C9-C10-C11 = 8.5 (2)° and C10-C11-C12-C17 = -1.2 (2)°. The bond lengths and angles are in normal ranges (Allen *et al.*, 1987) and are comparable to those in closely related structures (Chantrapromma *et al.*, 2006; 2007a; 2007b; 2007c; Kobkeathawin *et al.*, 2008).

In the crystal packing (Fig. 2), the cations form one-dimensional zigzag chains along the [0 0 1] direction. Water molecules contribute to an O2W—H1W2 \cdots O1W hydrogen bond. The cations are linked to water molecules and iodide ions through weak C—H \cdots O and C—H \cdots I interactions respectively (Table 1). Water molecules and iodide ions are interconnected by O—H \cdots I hydrogen bonds (O1W—H1W1 \cdots I1 and O1W—H2W1 \cdots I1 symmetry codes: $-x, y, 1/2 - z$ and $x, 1 - y, -1/2 + z$, respectively). The crystal is further stabilized by O—H \cdots O and O—H \cdots I hydrogen bonds together with weak C—H \cdots O and C—H \cdots I interactions. A C2—H2A $\cdots\pi$ interaction to the dimethylaminophenyl ring [C12–C17] was also observed: C2—H2A = 0.93; H2A \cdots Cgⁱ = 3.0219; C2—Cgⁱ = 3.7648 (17) Å; C2—H2A \cdots Cgⁱ = 138°. [Cgⁱ is the centroid of the C12–C17 ring (symmetry code: (i): $x, 1 - y, -1/2 + z$)].

Experimental

The title compound was synthesized by mixing a 1:1:1 molar ratio solution of 1,2-dimethylquinolinium iodide (2.00 g, 7.01 mmol), dimethylaminobenzaldehyde (1.05 g, 7.01 mmol) and piperidine (0.70 g, 7.01 mmol) in hot methanol (50 ml). The resulting solution was refluxed for 6 h under a nitrogen atmosphere. The resulting solid was filtered off, washed with methanol and recrystallized from methanol to give green crystals. Single crystals of the title compound suitable for x-ray structure determination were recrystallized from methanol/ethanol solvent (1:1 v/v) by slow evaporation of the solvent at room temperature after a few weeks. (Mp. 491–493 K).

Refinement

Water hydrogen atoms were located in a difference map and refined isotropically. H atoms attached to C were placed in calculated positions with $d(\text{C—H}) = 0.93 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aromatic and CH, 0.96 \AA , $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$ for CH_3 atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at 0.57 \AA from I1 and the deepest hole is located at 0.46 \AA from I1.

Figures

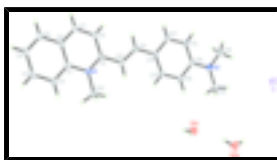


Fig. 1. The asymmetric unit of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. O2W (symmetry code: $-x, y, 1/2 - z$) lies on a two-fold rotation axis.

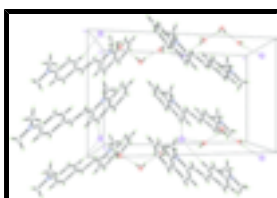


Fig. 2. The crystal packing of (I) viewed along the a axis, showing the one-dimensional zig-zag chains of the cations running along the c direction. The $\text{O—H}\cdots\text{O}$ and $\text{O—H}\cdots\text{I}$ hydrogen bonds and weak $\text{C—H}\cdots\text{O}$ interactions are drawn as dashed lines.

(E)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium iodide sesquihydrate

Crystal data

$\text{C}_{20}\text{H}_{21}\text{N}_2^+\cdot\Gamma\cdot 1.5\text{H}_2\text{O}$

$M_r = 443.31$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 20.8997(4) \text{ \AA}$

$b = 10.5941(2) \text{ \AA}$

$c = 18.4020(4) \text{ \AA}$

$\beta = 113.047(1)^\circ$

$V = 3749.24(13) \text{ \AA}^3$

$Z = 8$

$F_{000} = 1784$

$D_x = 1.571 \text{ Mg m}^{-3}$

Melting point = 491–493 K

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8240 reflections

$\theta = 2.1\text{--}35.0^\circ$

$\mu = 1.72 \text{ mm}^{-1}$

$T = 100.0(1) \text{ K}$

Block, green

$0.52 \times 0.35 \times 0.12 \text{ mm}$

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	8240 independent reflections
Radiation source: fine-focus sealed tube	7476 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.032$
Detector resolution: 8.33 pixels mm^{-1}	$\theta_{\text{max}} = 35.0^\circ$
$T = 100.0(1)$ K	$\theta_{\text{min}} = 2.1^\circ$
ω scans	$h = -33 \rightarrow 33$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$k = -17 \rightarrow 15$
$T_{\text{min}} = 0.469$, $T_{\text{max}} = 0.818$	$l = -29 \rightarrow 28$
50083 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.068$	$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2 + 7.1959P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
8240 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
237 parameters	$\Delta\rho_{\text{max}} = 1.58 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.80 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Experimental. The low-temperature data was collected with the Oxford Cryosystem Cobra low-temperature attachment.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.121463 (5)	0.401312 (10)	0.489877 (6)	0.02205 (3)
N1	0.34849 (6)	0.45765 (12)	-0.04848 (7)	0.0163 (2)

supplementary materials

N2	0.16088 (7)	0.23257 (14)	0.29101 (8)	0.0219 (2)
C1	0.39458 (7)	0.47357 (14)	-0.08616 (8)	0.0173 (2)
C2	0.38630 (8)	0.57284 (16)	-0.13994 (9)	0.0222 (3)
H2A	0.3488	0.6279	-0.1525	0.027*
C3	0.43416 (9)	0.58795 (17)	-0.17383 (10)	0.0249 (3)
H3A	0.4283	0.6533	-0.2096	0.030*
C4	0.49123 (8)	0.50731 (18)	-0.15566 (9)	0.0244 (3)
H4A	0.5234	0.5202	-0.1784	0.029*
C5	0.49965 (8)	0.40906 (16)	-0.10418 (9)	0.0219 (3)
H5A	0.5371	0.3542	-0.0929	0.026*
C6	0.45170 (8)	0.39079 (14)	-0.06823 (8)	0.0183 (2)
C7	0.45974 (8)	0.29187 (16)	-0.01383 (9)	0.0211 (3)
H7A	0.4961	0.2347	-0.0029	0.025*
C8	0.41475 (8)	0.27979 (15)	0.02247 (9)	0.0201 (3)
H8A	0.4206	0.2142	0.0581	0.024*
C9	0.35853 (7)	0.36612 (14)	0.00684 (8)	0.0163 (2)
C10	0.31320 (7)	0.35646 (14)	0.04900 (8)	0.0173 (2)
H10A	0.2735	0.4065	0.0326	0.021*
C11	0.32564 (7)	0.27790 (14)	0.11134 (8)	0.0170 (2)
H11A	0.3652	0.2275	0.1265	0.020*
C12	0.28250 (7)	0.26643 (13)	0.15584 (8)	0.0157 (2)
C13	0.29994 (7)	0.18026 (14)	0.21874 (9)	0.0185 (2)
H13A	0.3396	0.1309	0.2309	0.022*
C14	0.26020 (7)	0.16647 (14)	0.26310 (9)	0.0193 (2)
H14A	0.2730	0.1075	0.3038	0.023*
C15	0.20009 (7)	0.24148 (14)	0.24709 (8)	0.0164 (2)
C16	0.18213 (7)	0.32815 (14)	0.18357 (8)	0.0177 (2)
H16A	0.1428	0.3783	0.1714	0.021*
C17	0.22208 (7)	0.33918 (14)	0.13970 (8)	0.0176 (2)
H17A	0.2088	0.3964	0.0981	0.021*
C18	0.17497 (9)	0.13464 (18)	0.35064 (10)	0.0262 (3)
H18A	0.2231	0.1376	0.3857	0.039*
H18B	0.1646	0.0535	0.3254	0.039*
H18C	0.1465	0.1481	0.3801	0.039*
C19	0.09759 (8)	0.30611 (17)	0.27093 (10)	0.0236 (3)
H19A	0.1078	0.3939	0.2680	0.035*
H19B	0.0792	0.2943	0.3107	0.035*
H19C	0.0640	0.2788	0.2208	0.035*
C20	0.28968 (8)	0.54554 (16)	-0.07022 (10)	0.0223 (3)
H20A	0.2575	0.5167	-0.0483	0.034*
H20B	0.2667	0.5494	-0.1267	0.034*
H20C	0.3064	0.6280	-0.0499	0.034*
O1W	0.03830 (8)	0.54957 (15)	0.13362 (8)	0.0297 (3)
O2W	0.0000	0.6809 (2)	0.2500	0.0385 (5)
H1W2	0.0114 (15)	0.633 (3)	0.2215 (16)	0.044 (8)*
H1W1	0.0030 (16)	0.508 (3)	0.1033 (17)	0.049 (8)*
H2W1	0.0580 (16)	0.564 (3)	0.1055 (18)	0.049 (8)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
II	0.01875 (5)	0.02151 (5)	0.02561 (5)	-0.00453 (3)	0.00840 (4)	-0.00498 (4)
N1	0.0154 (5)	0.0157 (5)	0.0180 (5)	0.0016 (4)	0.0066 (4)	0.0002 (4)
N2	0.0203 (5)	0.0256 (6)	0.0235 (6)	0.0038 (5)	0.0126 (5)	0.0083 (5)
C1	0.0164 (5)	0.0198 (6)	0.0165 (5)	-0.0016 (5)	0.0073 (5)	-0.0020 (5)
C2	0.0190 (6)	0.0242 (7)	0.0236 (6)	0.0016 (5)	0.0086 (5)	0.0041 (5)
C3	0.0233 (7)	0.0289 (8)	0.0229 (7)	-0.0006 (6)	0.0096 (6)	0.0055 (6)
C4	0.0214 (6)	0.0351 (8)	0.0199 (6)	-0.0028 (6)	0.0117 (5)	-0.0010 (6)
C5	0.0180 (6)	0.0282 (7)	0.0205 (6)	0.0022 (5)	0.0088 (5)	-0.0032 (5)
C6	0.0177 (6)	0.0205 (6)	0.0167 (5)	0.0008 (5)	0.0067 (5)	-0.0009 (5)
C7	0.0198 (6)	0.0222 (7)	0.0219 (6)	0.0056 (5)	0.0088 (5)	0.0013 (5)
C8	0.0183 (6)	0.0222 (7)	0.0214 (6)	0.0051 (5)	0.0095 (5)	0.0036 (5)
C9	0.0168 (5)	0.0153 (5)	0.0173 (5)	0.0002 (4)	0.0072 (5)	-0.0001 (4)
C10	0.0182 (6)	0.0172 (6)	0.0185 (6)	-0.0002 (5)	0.0093 (5)	-0.0006 (5)
C11	0.0149 (5)	0.0184 (6)	0.0179 (5)	0.0003 (4)	0.0068 (4)	-0.0001 (5)
C12	0.0149 (5)	0.0160 (5)	0.0162 (5)	-0.0004 (4)	0.0060 (4)	0.0004 (4)
C13	0.0162 (5)	0.0194 (6)	0.0199 (6)	0.0031 (5)	0.0071 (5)	0.0036 (5)
C14	0.0183 (6)	0.0193 (6)	0.0208 (6)	0.0028 (5)	0.0082 (5)	0.0057 (5)
C15	0.0152 (5)	0.0173 (6)	0.0164 (5)	-0.0011 (4)	0.0059 (4)	0.0012 (4)
C16	0.0161 (5)	0.0182 (6)	0.0187 (6)	0.0021 (4)	0.0067 (5)	0.0036 (5)
C17	0.0179 (6)	0.0179 (6)	0.0178 (6)	0.0023 (5)	0.0079 (5)	0.0041 (5)
C18	0.0246 (7)	0.0310 (8)	0.0267 (7)	0.0036 (6)	0.0143 (6)	0.0111 (6)
C19	0.0213 (6)	0.0291 (8)	0.0236 (6)	0.0040 (6)	0.0125 (5)	0.0025 (6)
C20	0.0209 (6)	0.0212 (7)	0.0284 (7)	0.0064 (5)	0.0133 (6)	0.0048 (5)
O1W	0.0271 (6)	0.0340 (7)	0.0266 (6)	0.0012 (5)	0.0092 (5)	0.0014 (5)
O2W	0.0530 (13)	0.0278 (10)	0.0469 (12)	0.000	0.0329 (11)	0.000

Geometric parameters (\AA , $^\circ$)

N1—C9	1.3614 (19)	C11—C12	1.4411 (19)
N1—C1	1.4001 (18)	C11—H11A	0.9300
N1—C20	1.4672 (19)	C12—C13	1.406 (2)
N2—C15	1.3611 (18)	C12—C17	1.408 (2)
N2—C19	1.453 (2)	C13—C14	1.381 (2)
N2—C18	1.454 (2)	C13—H13A	0.9300
C1—C2	1.408 (2)	C14—C15	1.417 (2)
C1—C6	1.412 (2)	C14—H14A	0.9300
C2—C3	1.380 (2)	C15—C16	1.417 (2)
C2—H2A	0.9300	C16—C17	1.3750 (19)
C3—C4	1.397 (2)	C16—H16A	0.9300
C3—H3A	0.9300	C17—H17A	0.9300
C4—C5	1.372 (2)	C18—H18A	0.9600
C4—H4A	0.9300	C18—H18B	0.9600
C5—C6	1.414 (2)	C18—H18C	0.9600
C5—H5A	0.9300	C19—H19A	0.9600
C6—C7	1.413 (2)	C19—H19B	0.9600

supplementary materials

C7—C8	1.356 (2)	C19—H19C	0.9600
C7—H7A	0.9300	C20—H20A	0.9600
C8—C9	1.427 (2)	C20—H20B	0.9600
C8—H8A	0.9300	C20—H20C	0.9600
C9—C10	1.4442 (19)	O1W—H1W1	0.85 (3)
C10—C11	1.357 (2)	O1W—H2W1	0.79 (3)
C10—H10A	0.9300	O2W—H1W2	0.83 (3)
C9—N1—C1	121.43 (12)	C12—C11—H11A	117.4
C9—N1—C20	121.57 (12)	C13—C12—C17	116.83 (12)
C1—N1—C20	116.99 (12)	C13—C12—C11	120.29 (13)
C15—N2—C19	120.78 (13)	C17—C12—C11	122.88 (13)
C15—N2—C18	120.43 (13)	C14—C13—C12	122.22 (13)
C19—N2—C18	118.03 (12)	C14—C13—H13A	118.9
N1—C1—C2	121.28 (13)	C12—C13—H13A	118.9
N1—C1—C6	119.48 (13)	C13—C14—C15	120.47 (13)
C2—C1—C6	119.22 (13)	C13—C14—H14A	119.8
C3—C2—C1	119.55 (15)	C15—C14—H14A	119.8
C3—C2—H2A	120.2	N2—C15—C14	121.92 (13)
C1—C2—H2A	120.2	N2—C15—C16	120.54 (13)
C2—C3—C4	121.53 (15)	C14—C15—C16	117.54 (12)
C2—C3—H3A	119.2	C17—C16—C15	120.92 (13)
C4—C3—H3A	119.2	C17—C16—H16A	119.5
C5—C4—C3	119.73 (14)	C15—C16—H16A	119.5
C5—C4—H4A	120.1	C16—C17—C12	122.01 (13)
C3—C4—H4A	120.1	C16—C17—H17A	119.0
C4—C5—C6	120.29 (14)	C12—C17—H17A	119.0
C4—C5—H5A	119.9	N2—C18—H18A	109.5
C6—C5—H5A	119.9	N2—C18—H18B	109.5
C1—C6—C7	118.76 (13)	H18A—C18—H18B	109.5
C1—C6—C5	119.66 (14)	N2—C18—H18C	109.5
C7—C6—C5	121.58 (14)	H18A—C18—H18C	109.5
C8—C7—C6	120.39 (14)	H18B—C18—H18C	109.5
C8—C7—H7A	119.8	N2—C19—H19A	109.5
C6—C7—H7A	119.8	N2—C19—H19B	109.5
C7—C8—C9	121.03 (14)	H19A—C19—H19B	109.5
C7—C8—H8A	119.5	N2—C19—H19C	109.5
C9—C8—H8A	119.5	H19A—C19—H19C	109.5
N1—C9—C8	118.76 (13)	H19B—C19—H19C	109.5
N1—C9—C10	120.71 (13)	N1—C20—H20A	109.5
C8—C9—C10	120.53 (13)	N1—C20—H20B	109.5
C11—C10—C9	123.26 (13)	H20A—C20—H20B	109.5
C11—C10—H10A	118.4	N1—C20—H20C	109.5
C9—C10—H10A	118.4	H20A—C20—H20C	109.5
C10—C11—C12	125.20 (13)	H20B—C20—H20C	109.5
C10—C11—H11A	117.4	H1W1—O1W—H2W1	102 (3)
C9—N1—C1—C2	-176.27 (14)	C7—C8—C9—N1	3.4 (2)
C20—N1—C1—C2	2.6 (2)	C7—C8—C9—C10	-176.63 (14)
C9—N1—C1—C6	1.9 (2)	N1—C9—C10—C11	-171.48 (14)

C20—N1—C1—C6	-179.27 (14)	C8—C9—C10—C11	8.5 (2)
N1—C1—C2—C3	177.80 (15)	C9—C10—C11—C12	179.05 (14)
C6—C1—C2—C3	-0.3 (2)	C10—C11—C12—C13	179.02 (14)
C1—C2—C3—C4	-0.4 (3)	C10—C11—C12—C17	-1.2 (2)
C2—C3—C4—C5	1.3 (3)	C17—C12—C13—C14	0.0 (2)
C3—C4—C5—C6	-1.4 (2)	C11—C12—C13—C14	179.79 (14)
N1—C1—C6—C7	1.5 (2)	C12—C13—C14—C15	-1.0 (2)
C2—C1—C6—C7	179.65 (14)	C19—N2—C15—C14	-176.95 (15)
N1—C1—C6—C5	-177.92 (13)	C18—N2—C15—C14	-7.2 (2)
C2—C1—C6—C5	0.2 (2)	C19—N2—C15—C16	3.7 (2)
C4—C5—C6—C1	0.6 (2)	C18—N2—C15—C16	173.45 (15)
C4—C5—C6—C7	-178.79 (15)	C13—C14—C15—N2	-178.22 (15)
C1—C6—C7—C8	-2.3 (2)	C13—C14—C15—C16	1.2 (2)
C5—C6—C7—C8	177.06 (15)	N2—C15—C16—C17	178.95 (15)
C6—C7—C8—C9	-0.1 (2)	C14—C15—C16—C17	-0.5 (2)
C1—N1—C9—C8	-4.2 (2)	C15—C16—C17—C12	-0.5 (2)
C20—N1—C9—C8	176.94 (14)	C13—C12—C17—C16	0.7 (2)
C1—N1—C9—C10	175.76 (13)	C11—C12—C17—C16	-179.05 (14)
C20—N1—C9—C10	-3.1 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1W1...I1 ⁱ	0.85 (3)	2.74 (3)	3.5832 (16)	172 (3)
O2W—H1W2...O1W	0.83 (3)	2.10 (3)	2.9164 (19)	167 (3)
O1W—H2W1...I1 ⁱⁱ	0.79 (3)	2.94 (3)	3.7267 (16)	174 (3)
C3—H3A...O2W ⁱⁱⁱ	0.93	2.60	3.371 (2)	141
C7—H7A...I1 ^{iv}	0.93	3.04	3.9290 (18)	161
C17—H17A...I1 ⁱⁱ	0.93	3.01	3.8784 (14)	157
C2—H2A...Cg1 ⁱⁱ	0.93	3.02	3.7648 (17)	138

Symmetry codes: (i) $-x, y, -z+1/2$; (ii) $x, -y+1, z-1/2$; (iii) $-x+1/2, -y+3/2, -z$; (iv) $x+1/2, -y+1/2, z-1/2$.

Fig. 1

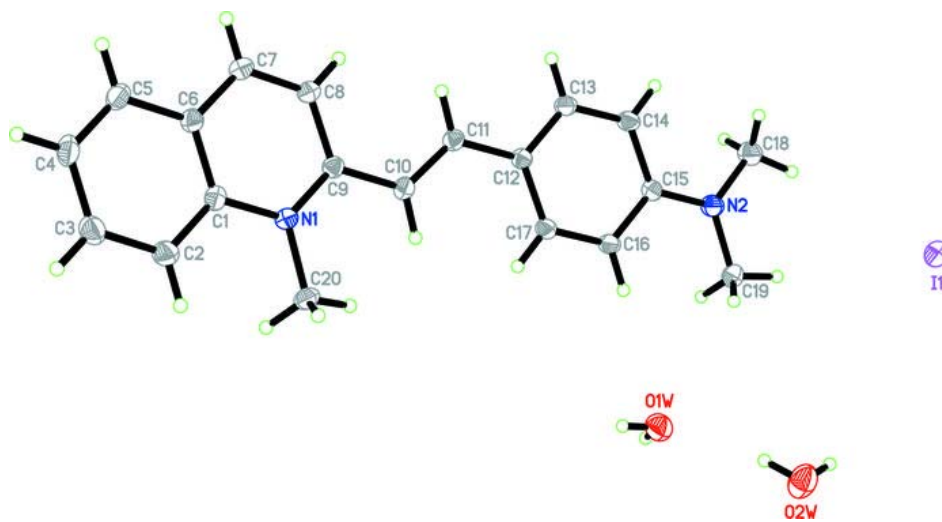
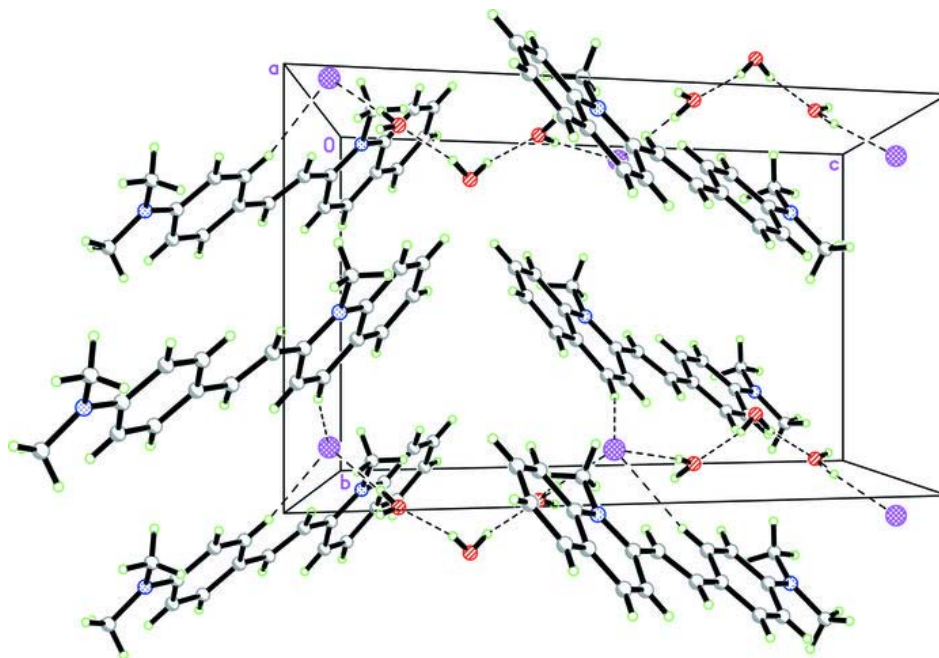


Fig. 2



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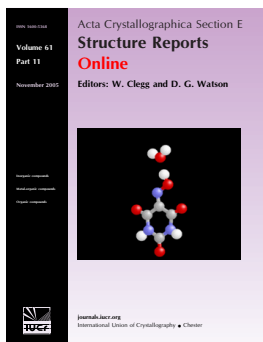
Editors: W. Clegg and D. G. Watson

1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]quinolinium iodide

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1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]-quinolinium iodide¹

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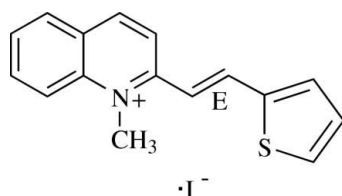
Received 1 July 2008; accepted 4 July 2008

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.023; wR factor = 0.060; data-to-parameter ratio = 24.6.

In the title compound, $\text{C}_{16}\text{H}_{14}\text{NS}^+\text{I}^-$, the cation has an *E* configuration about the $\text{C}=\text{C}$ double bond of the ethylene unit. The dihedral angle between the thiophene ring and the quinolinium ring system is 11.67 (11)°. A weak $\text{C}-\text{H}\cdots\text{S}$ intramolecular interaction involving the thiophene ring generates an *S*(5) ring motif. In the crystal structure, the iodide ion, located between the cations arranged in an antiparallel manner, forms weak $\text{C}-\text{H}\cdots\text{I}$ interactions. The crystal structure is further stabilized by a $\pi-\pi$ interaction between the thiophene and pyridine rings; the centroid-centroid distance is 3.6818 (13) Å.

Related literature

For bond lengths, see: Allen *et al.* (1987). For related literature on hydrogen-bond motifs, see: Bernstein *et al.* (1995). For related structures, see, for example: Chantrapromma *et al.* (2006, 2008); Chantrapromma, Jindawong & Fun (2007); Chantrapromma, Jindawong, Fun & Patil (2007). For background literature on non-linear optical properties, see, for example: Chou *et al.* (1996); Dittrich *et al.* (2003); Drost *et al.* (1995); Morley (1991).



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Experimental

Crystal data

$\text{C}_{16}\text{H}_{14}\text{NS}^+\text{I}^-$
 $M_r = 379.25$
 Triclinic, $P\bar{1}$
 $a = 7.8243$ (1) Å
 $b = 9.6906$ (1) Å
 $c = 10.7633$ (2) Å
 $\alpha = 97.521$ (1)°
 $\beta = 95.338$ (1)°
 $\gamma = 112.758$ (1)°
 $V = 736.82$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 2.30$ mm⁻¹
 $T = 100.0$ (1) K
 $0.58 \times 0.28 \times 0.14$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
 $T_{\min} = 0.346$, $T_{\max} = 0.725$
 17060 measured reflections
 4261 independent reflections
 4118 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.059$
 $S = 1.10$
 4261 reflections
 173 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.90$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C10—H10A \cdots S1	0.93	2.80	3.189 (2)	106
C11—H11A \cdots I1 ⁱ	0.93	3.06	3.934 (2)	157
C16—H16B \cdots I1 ⁱⁱ	0.96	3.06	3.962 (2)	156

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - 1, y, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2311).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, S1–S19.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chantrapromma, S., Jindawong, B. & Fun, H.-K. (2006). *Acta Cryst. E* **62**, o4004–o4006.

- Chantrapromma, S., Jindawong, B. & Fun, H.-K. (2007). *Acta Cryst.* **E63**, o2020–o2022.
- Chantrapromma, S., Jindawong, B., Fun, H.-K. & Patil, P. S. (2007). *Acta Cryst.* **E63**, o2321–o2323.
- Chantrapromma, S., Laksana, C., Ruanwas, P. & Fun, H.-K. (2008). *Acta Cryst.* **E64**, o574–o575.
- Chou, S.-S. P., Sun, D.-J., Huang, J.-Y., Yang, P.-K. & Lin, H.-C. (1996). *Tetrahedron*, **37**, 7279–7282.
- Dittrich, Ph., Bartlome, R., Montemezzani, G. & Günter, P. (2003). *Appl. Surf. Sci.* **220**, 88–95.
- Drost, K. J., Jen, A. K.-J. & Rao, V. P. (1995). *Chemtech*, **25**, 16–25.
- Morley, J. O. (1991). *J. Chem. Soc. Faraday Trans.* **87**, 3009–3013.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

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1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]quinolinium iodide

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Comment

The design and synthesis of conjugated compounds to search for second-order nonlinear optic (NLO) materials have generated extensive interest. From previous reports, both molecular orbital calculations (Morley, 1991) and experimental studies (Drost *et al.*, 1995) have revealed that the products of dipole moment and molecular hyperpolarizability ($\nu\beta$) of thiophene-containing conjugated moieties are superior to that of benzene analogues. Based on this reason we have previously studied the compound containing thiophene unit, namely, 1-methyl-4-[(*E*)-2-(2-thienyl)ethenyl]-pyridinium 4-chlorobenzenesulfonate (Chantrapromma *et al.*, 2008). In this paper we have synthesized the title compound which was designed by the replacement of the cationic 3-hydroxy-4-methoxyphenyl ring that is present in a compound possessing second-harmonic-generation (SHG) properties, 2-[(*E*)-2-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium, iodide monohydrate (Chantrapromma, Jindawong, Fun & Patil, 2007) by the thiophene unit. Herein we report the synthesis and crystal structure of the title compound.

The asymmetric unit of the title compound (Fig. 1) consists of the $C_{16}H_{14}NS^+$ cation and I^- ion. The cation exists in the *E* configuration with respect to the C10=C11 double bond [1.350 (3) Å] and is almost planar with the interplanar angle between the quinolinium and the thiophene ring being 11.67 (11)° and the torsion angles C9–C10–C11–C12 = -178.56 (17)°. The ethenyl unit is co-planar with the thiophene ring as can be indicated by the torsion angles C10–C11–C12–C13 = -179.42 (18)° and C10–C11–C12–S1 = 1.4 (3)°. It is slightly deviated from the quinolinium ring with the torsion angle C8–C9–C10–C11 = -14.2 (3)°. The atom S1 of the thiophene ring contributes to the C—H...S intramolecular weak interaction (Fig. 1 and Table 1) forming S(5) ring motifs (Bernstein *et al.*, 1995). The bond lengths and angles are normal (Allen *et al.*, 1987) and are comparable with closely related structures (Chantrapromma *et al.*, 2006, 2008; Chantrapromma, Jindawong & Fun, 2007; Chantrapromma, Jindawong, Fun & Patil, 2007).

In the crystal packing (Fig. 2), the I^- ion is in between each pair of the two antiparallel cations and is linked with the cations through weak C—H...I interactions. The crystal is stabilized by weak C—H...S and C—H...I interactions (Table 1). A π - π interaction was observed with the $Cg_1...Cg_2$ distance of 3.6818 (13) Å; Cg_1^i and Cg_2^i are the centroids of the S1/C12–C15 and N1/C1/C6–C9 rings, respectively [symmetry code: (i): 1 - x, 1 - y, 1 - z]. The perpendicular distances of Cg_1 on the S1/C12–C15 ring and Cg_2 on the N1/C1/C6–C9 ring are 3.200 and 3.500 Å, respectively

Experimental

2-(2-Thiophenestyryl)-1-methylquinolinium iodide was synthesized by mixing a solution (1:1:1 molar ratio) of 1,2-dimethylquinolinium iodide (2.00 g, 7.0 mmol), 2-thiophenecarboxaldehyde (0.64 ml, 7.0 mmol) and piperidine (0.69 ml, 7.0 mmol) in hot methanol (40 ml). The resulting solution was refluxed for 5 hr under a nitrogen atmosphere. The resultant solid was filtered off and washed with diethyl ether. Brown block-shaped single crystals of the title compound suitable for x-ray structure determination were obtained after recrystallization from methanol by slow evaporation of the solvent at room temperature after a few weeks.

Refinement

All H atoms were placed in calculated positions (C—H = 0.93–0.96 Å) and were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. A rotating group model was used for the methyl group. The highest residual electron density peak is located at 0.75 Å from atom I1 and the deepest hole is located at 0.38 Å from atom S1.

Figures

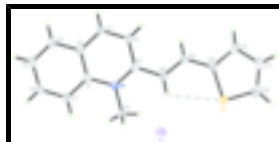


Fig. 1. The title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. The weak C—H...S intramolecular interaction was drawn as a dashed line.

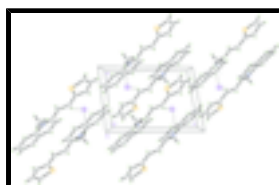


Fig. 2. The packing diagram of the title structure, viewed approximately along the *b* axis. Weak C—H...I interactions were drawn as dashed lines.

1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]quinolinium iodide

Crystal data

$\text{C}_{16}\text{H}_{14}\text{NS}^+\cdot\Gamma^-$	$Z = 2$
$M_r = 379.25$	$F_{000} = 372$
Triclinic, $P\bar{1}$	$D_x = 1.709 \text{ Mg m}^{-3}$
Hall symbol: $-P 1$	Mo $K\alpha$ radiation
$a = 7.8243 (1) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 9.6906 (1) \text{ \AA}$	Cell parameters from 4261 reflections
$c = 10.7633 (2) \text{ \AA}$	$\theta = 2.3\text{--}30.0^\circ$
$\alpha = 97.521 (1)^\circ$	$\mu = 2.30 \text{ mm}^{-1}$
$\beta = 95.338 (1)^\circ$	$T = 100.0 (1) \text{ K}$
$\gamma = 112.758 (1)^\circ$	Block, brown
$V = 736.817 (18) \text{ \AA}^3$	$0.58 \times 0.28 \times 0.14 \text{ mm}$

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	4261 independent reflections
Radiation source: fine-focus sealed tube	4118 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.018$
Detector resolution: $8.33 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 30.0^\circ$
$T = 100.0(1) \text{ K}$	$\theta_{\text{min}} = 2.3^\circ$
ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan	$k = -13 \rightarrow 13$

(SADABS; Bruker, 2005)

$T_{\min} = 0.346$, $T_{\max} = 0.725$

17060 measured reflections

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.059$

$S = 1.10$

4261 reflections

173 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.8519P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 1.50 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.89 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Special details

Experimental. The low-temperature data was collected with the Oxford Cryosystem Cobra low-temperature attachment.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.681003 (17)	0.790360 (14)	0.269777 (12)	0.02186 (5)
S1	0.65928 (8)	0.89200 (6)	0.69144 (6)	0.02828 (11)
N1	0.0896 (2)	0.54762 (17)	0.31586 (15)	0.0162 (3)
C1	-0.0473 (3)	0.4405 (2)	0.21950 (17)	0.0167 (3)
C2	-0.1289 (3)	0.4838 (2)	0.11749 (18)	0.0198 (3)
H2A	-0.0945	0.5863	0.1138	0.024*
C3	-0.2600 (3)	0.3734 (2)	0.02336 (19)	0.0227 (4)
H3A	-0.3128	0.4025	-0.0441	0.027*
C4	-0.3158 (3)	0.2180 (2)	0.02687 (19)	0.0227 (4)
H4A	-0.4034	0.1452	-0.0382	0.027*
C5	-0.2405 (3)	0.1739 (2)	0.12667 (19)	0.0206 (3)
H5A	-0.2781	0.0711	0.1297	0.025*
C6	-0.1062 (3)	0.2843 (2)	0.22486 (18)	0.0180 (3)
C7	-0.0267 (3)	0.2412 (2)	0.32868 (18)	0.0193 (3)

supplementary materials

H7A	-0.0686	0.1391	0.3357	0.023*
C8	0.1112 (3)	0.3491 (2)	0.41844 (18)	0.0180 (3)
H8A	0.1644	0.3198	0.4855	0.022*
C9	0.1745 (2)	0.5058 (2)	0.41052 (17)	0.0161 (3)
C10	0.3282 (3)	0.6203 (2)	0.50081 (18)	0.0175 (3)
H10A	0.3838	0.7174	0.4822	0.021*
C11	0.3950 (3)	0.5929 (2)	0.61089 (17)	0.0174 (3)
H11A	0.3399	0.4946	0.6273	0.021*
C12	0.5444 (3)	0.7036 (2)	0.70463 (18)	0.0177 (3)
C13	0.6158 (3)	0.6721 (2)	0.82202 (19)	0.0217 (4)
H13A	0.5752	0.5776	0.8468	0.026*
C14	0.7577 (3)	0.8091 (3)	0.8930 (2)	0.0282 (4)
H14A	0.8203	0.8145	0.9724	0.034*
C15	0.7946 (3)	0.9321 (3)	0.8350 (2)	0.0300 (4)
H15A	0.8850	1.0285	0.8706	0.036*
C16	0.1413 (3)	0.7112 (2)	0.31385 (19)	0.0211 (3)
H16A	0.1810	0.7677	0.3991	0.032*
H16B	0.0345	0.7250	0.2756	0.032*
H16C	0.2418	0.7471	0.2655	0.032*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
II	0.02044 (7)	0.02041 (7)	0.02481 (7)	0.00758 (5)	0.00089 (5)	0.00842 (5)
S1	0.0287 (3)	0.0207 (2)	0.0312 (3)	0.00775 (19)	-0.0017 (2)	0.00210 (19)
N1	0.0151 (7)	0.0161 (7)	0.0176 (7)	0.0066 (5)	0.0021 (5)	0.0033 (5)
C1	0.0158 (7)	0.0191 (8)	0.0165 (8)	0.0083 (6)	0.0035 (6)	0.0031 (6)
C2	0.0179 (8)	0.0227 (9)	0.0192 (8)	0.0082 (7)	0.0029 (6)	0.0058 (7)
C3	0.0202 (8)	0.0295 (10)	0.0184 (8)	0.0101 (7)	0.0013 (7)	0.0056 (7)
C4	0.0178 (8)	0.0262 (9)	0.0197 (8)	0.0065 (7)	-0.0009 (7)	-0.0006 (7)
C5	0.0188 (8)	0.0193 (8)	0.0213 (8)	0.0068 (7)	0.0007 (7)	-0.0005 (7)
C6	0.0161 (8)	0.0187 (8)	0.0184 (8)	0.0068 (6)	0.0023 (6)	0.0019 (6)
C7	0.0195 (8)	0.0165 (8)	0.0217 (8)	0.0075 (7)	0.0028 (7)	0.0028 (6)
C8	0.0183 (8)	0.0177 (8)	0.0181 (8)	0.0077 (6)	0.0017 (6)	0.0033 (6)
C9	0.0153 (7)	0.0175 (8)	0.0164 (7)	0.0074 (6)	0.0036 (6)	0.0030 (6)
C10	0.0178 (8)	0.0154 (7)	0.0188 (8)	0.0064 (6)	0.0023 (6)	0.0021 (6)
C11	0.0158 (8)	0.0173 (8)	0.0190 (8)	0.0070 (6)	0.0026 (6)	0.0023 (6)
C12	0.0168 (8)	0.0163 (8)	0.0198 (8)	0.0069 (6)	0.0026 (6)	0.0015 (6)
C13	0.0121 (7)	0.0217 (9)	0.0238 (9)	0.0014 (6)	0.0068 (6)	-0.0071 (7)
C14	0.0231 (9)	0.0395 (12)	0.0201 (9)	0.0132 (9)	-0.0010 (7)	0.0002 (8)
C15	0.0263 (10)	0.0248 (10)	0.0295 (11)	0.0056 (8)	-0.0030 (8)	-0.0066 (8)
C16	0.0219 (9)	0.0163 (8)	0.0245 (9)	0.0075 (7)	-0.0003 (7)	0.0051 (7)

Geometric parameters (\AA , $^\circ$)

S1—C15	1.697 (2)	C7—H7A	0.9300
S1—C12	1.7273 (19)	C8—C9	1.421 (2)
N1—C9	1.354 (2)	C8—H8A	0.9300
N1—C1	1.397 (2)	C9—C10	1.446 (3)

N1—C16	1.481 (2)	C10—C11	1.350 (3)
C1—C2	1.410 (3)	C10—H10A	0.9300
C1—C6	1.413 (3)	C11—C12	1.436 (3)
C2—C3	1.377 (3)	C11—H11A	0.9300
C2—H2A	0.9300	C12—C13	1.450 (3)
C3—C4	1.403 (3)	C13—C14	1.420 (3)
C3—H3A	0.9300	C13—H13A	0.9300
C4—C5	1.371 (3)	C14—C15	1.361 (4)
C4—H4A	0.9300	C14—H14A	0.9300
C5—C6	1.412 (3)	C15—H15A	0.9300
C5—H5A	0.9300	C16—H16A	0.9600
C6—C7	1.415 (3)	C16—H16B	0.9600
C7—C8	1.364 (3)	C16—H16C	0.9600
C15—S1—C12	91.58 (11)	N1—C9—C8	119.08 (16)
C9—N1—C1	121.89 (16)	N1—C9—C10	119.79 (16)
C9—N1—C16	119.57 (16)	C8—C9—C10	121.13 (17)
C1—N1—C16	118.53 (15)	C11—C10—C9	123.13 (17)
N1—C1—C2	121.92 (17)	C11—C10—H10A	118.4
N1—C1—C6	118.98 (16)	C9—C10—H10A	118.4
C2—C1—C6	119.09 (17)	C10—C11—C12	125.11 (17)
C3—C2—C1	119.54 (18)	C10—C11—H11A	117.4
C3—C2—H2A	120.2	C12—C11—H11A	117.4
C1—C2—H2A	120.2	C11—C12—C13	124.49 (17)
C2—C3—C4	121.53 (19)	C11—C12—S1	123.74 (15)
C2—C3—H3A	119.2	C13—C12—S1	111.77 (14)
C4—C3—H3A	119.2	C14—C13—C12	108.83 (19)
C5—C4—C3	119.69 (18)	C14—C13—H13A	125.6
C5—C4—H4A	120.2	C12—C13—H13A	125.6
C3—C4—H4A	120.2	C15—C14—C13	114.4 (2)
C4—C5—C6	120.20 (18)	C15—C14—H14A	122.8
C4—C5—H5A	119.9	C13—C14—H14A	122.8
C6—C5—H5A	119.9	C14—C15—S1	113.38 (17)
C5—C6—C1	119.91 (18)	C14—C15—H15A	123.3
C5—C6—C7	121.09 (17)	S1—C15—H15A	123.3
C1—C6—C7	118.99 (17)	N1—C16—H16A	109.5
C8—C7—C6	120.12 (17)	N1—C16—H16B	109.5
C8—C7—H7A	119.9	H16A—C16—H16B	109.5
C6—C7—H7A	119.9	N1—C16—H16C	109.5
C7—C8—C9	120.69 (18)	H16A—C16—H16C	109.5
C7—C8—H8A	119.7	H16B—C16—H16C	109.5
C9—C8—H8A	119.7		
C9—N1—C1—C2	-176.75 (17)	C1—N1—C9—C8	-5.6 (3)
C16—N1—C1—C2	3.6 (3)	C16—N1—C9—C8	173.99 (16)
C9—N1—C1—C6	3.5 (3)	C1—N1—C9—C10	173.83 (16)
C16—N1—C1—C6	-176.05 (16)	C16—N1—C9—C10	-6.6 (2)
N1—C1—C2—C3	178.41 (17)	C7—C8—C9—N1	3.2 (3)
C6—C1—C2—C3	-1.9 (3)	C7—C8—C9—C10	-176.23 (17)
C1—C2—C3—C4	0.5 (3)	N1—C9—C10—C11	166.39 (17)

supplementary materials

C2—C3—C4—C5	0.8 (3)	C8—C9—C10—C11	-14.2 (3)
C3—C4—C5—C6	-0.6 (3)	C9—C10—C11—C12	-178.56 (17)
C4—C5—C6—C1	-0.8 (3)	C10—C11—C12—C13	-179.42 (18)
C4—C5—C6—C7	-179.96 (18)	C10—C11—C12—S1	1.4 (3)
N1—C1—C6—C5	-178.25 (16)	C15—S1—C12—C11	178.33 (17)
C2—C1—C6—C5	2.0 (3)	C15—S1—C12—C13	-0.98 (15)
N1—C1—C6—C7	0.9 (3)	C11—C12—C13—C14	-177.85 (18)
C2—C1—C6—C7	-178.77 (17)	S1—C12—C13—C14	1.5 (2)
C5—C6—C7—C8	175.96 (18)	C12—C13—C14—C15	-1.3 (3)
C1—C6—C7—C8	-3.2 (3)	C13—C14—C15—S1	0.6 (3)
C6—C7—C8—C9	1.2 (3)	C12—S1—C15—C14	0.22 (19)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10A \cdots S1	0.93	2.80	3.189 (2)	106
C11—H11A \cdots I ⁱ	0.93	3.06	3.934 (2)	157
C16—H16B \cdots I ⁱⁱ	0.96	3.06	3.962 (2)	156

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$.

Fig. 1

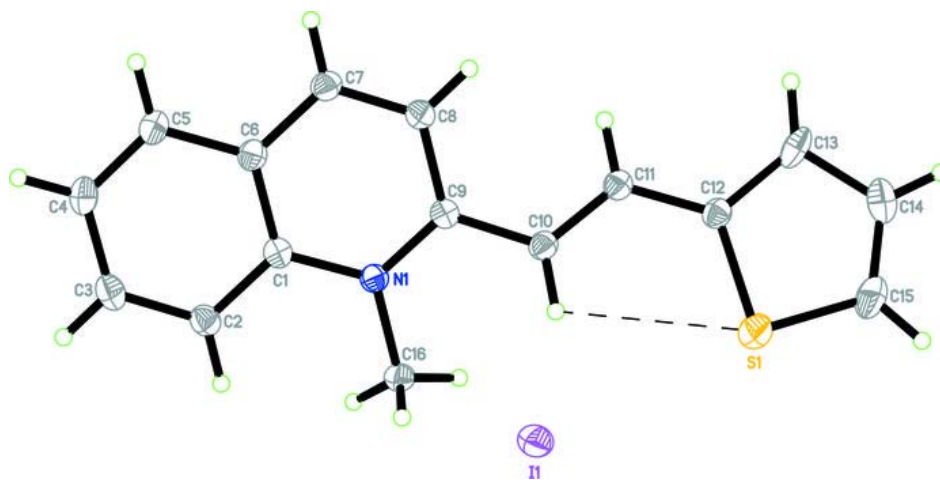
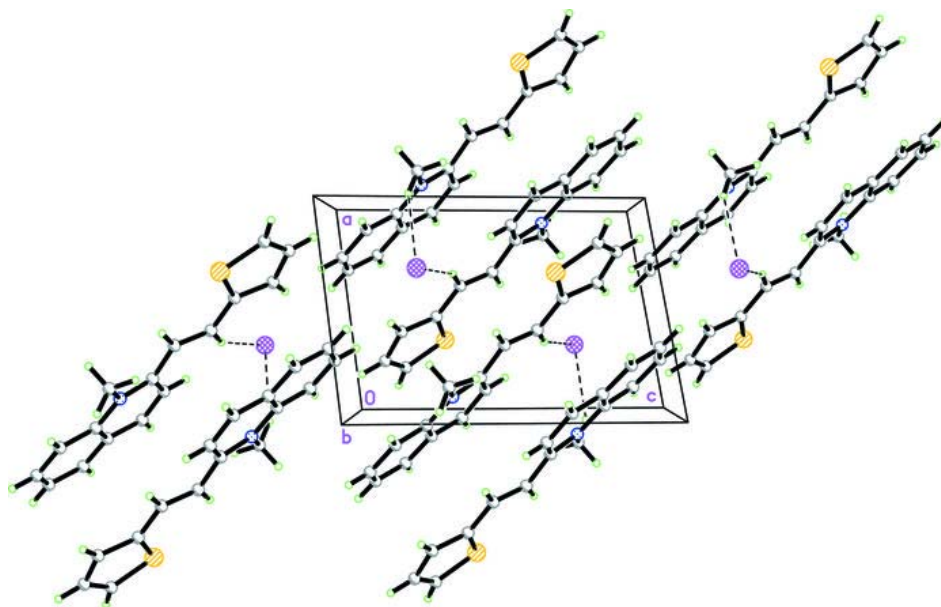


Fig. 2



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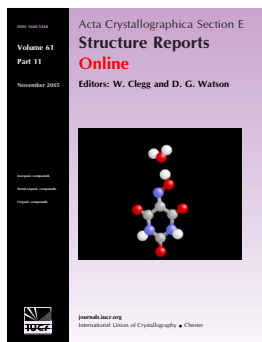
Editors: W.T.A. Harrison, J. Simpson and
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(*E*)-4-[4-(Dimethylamino)styryl]-1-methylpyridinium 4-bromobenzenesulfonate

Suchada Chantrapromma, Patcharaporn Jansrisewangwong, Rusmeenee Musor and Hoong-Kun Fun

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(E)-4-[4-(Dimethylamino)styryl]-1-methylpyridinium 4-bromobenzene-sulfonate¹Suchada Chantrapromma,^{a*} Patcharaporn Jansrisewangwong,^a Rusmeenee Musor^a and Hoong-Kun Fun^{b§}^aCrystal Materials Research Unit, Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, and ^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

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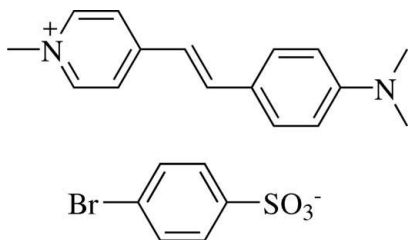
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.046; wR factor = 0.097; data-to-parameter ratio = 24.4.

In the title compound, $\text{C}_{16}\text{H}_{19}\text{N}_2^+ \cdot \text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$, the cation is nearly planar, with a dihedral angle of 3.19 (15)° between the pyridinium and the dimethylaminophenyl rings, and exists in the *trans* configuration. In the crystal packing, the cations and anions are linked into chains parallel to the c axis. These chains are stacked along the b axis. The crystal is stabilized by weak $\text{C}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \pi$ interactions, and a $\pi-\pi$ interaction is also observed with a $\text{Cg} \cdots \text{Cg}$ distance of 3.5675 (19) Å.

Related literature

For background to NLO materials research, see: Chia *et al.* (1995); Sato *et al.* (1999); Nogi *et al.* (2000); Otero *et al.* (2002); Dittrich *et al.* (2003). For related structures, see, for example: Adachi *et al.* (1999); Chantrapromma *et al.* (2006; 2008); Jagannathan *et al.* (2007); Ogawa *et al.* (2008); Rahman *et al.* (2003); Yang *et al.* (2007). For comparison bond lengths, see Allen *et al.* (1987).



¹ This paper is dedicated to the late Her Royal Highness Princess Galyani Vadhana Krom Luang Naradhiwas Rajanagarindra for her patronage of Science in Thailand.

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Experimental*Crystal data*

$\text{C}_{16}\text{H}_{19}\text{N}_2^+ \cdot \text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$
 $M_r = 475.39$
 Monoclinic, Cc
 $a = 10.3712$ (4) Å
 $b = 10.9937$ (5) Å
 $c = 17.9027$ (8) Å
 $\beta = 92.442$ (3)°

$V = 2039.37$ (15) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.15$ mm⁻¹
 $T = 100.0$ (1) K
 $0.49 \times 0.31 \times 0.11$ mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.414$, $T_{\max} = 0.787$

13146 measured reflections
 6479 independent reflections
 4811 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.097$
 $S = 1.02$
 6479 reflections
 265 parameters
 2 restraints

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.01$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.38$ e Å⁻³
 Absolute structure: Flack (1983),
 1997 Friedel pairs
 Flack parameter: 0.024 (7)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{C}2-\text{H}2A \cdots \text{O}1^i$	0.93	2.44	3.366 (4)	175
$\text{C}4-\text{H}4A \cdots \text{O}2^{\text{ii}}$	0.93	2.45	3.375 (4)	175
$\text{C}6-\text{H}6A \cdots \text{O}3^{\text{iii}}$	0.93	2.44	3.175 (4)	136
$\text{C}7-\text{H}7A \cdots \text{O}2^{\text{ii}}$	0.93	2.36	3.285 (4)	173
$\text{C}14-\text{H}14C \cdots \text{O}3^i$	0.96	2.36	3.304 (4)	168
$\text{C}15-\text{H}15A \cdots \text{O}2$	0.96	2.57	3.515 (4)	168
$\text{C}19-\text{H}19A \cdots \text{O}1^{\text{iv}}$	0.93	2.47	3.306 (4)	149
$\text{C}3-\text{H}3A \cdots \text{Cg}3^{\text{ii}}$	0.93	2.76	3.601 (4)	151
$\text{C}14-\text{H}14B \cdots \text{Cg}2^{\text{v}}$	0.96	2.55	3.468 (4)	161

Symmetry codes: (i) $x - 1, -y + 1, z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (v) $x - 1, y, z$. $\text{Cg}2$ and $\text{Cg}3$ are the centroids of the $\text{C}8-\text{C}13$ and $\text{C}17-\text{C}22$ rings.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2136).

References

- Adachi, H., Takanishi, Y., Yabuzaki, J., Mori, Y. & Sasaki, T. (1999). *J. Cryst. Growth*, **158/159**, 568–571.
 Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Bruker (2005). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chantrapromma, S., Kobkeattawin, T., Chanawanno, K., Karalai, C. & Fun, H.-K. (2008). *Acta Cryst.* **E64**, o876–o877.

- Chantrapomma, S., Ruanwas, P., Fun, H.-K. & Patil, P. S. (2006). *Acta Cryst.* **E62**, o5494–o5496.
- Chia, W.-L., Chen, C.-N. & Sheu, H.-J. (1995). *Mater. Res. Bull.* **30**, 1421–1430.
- Dittrich, Ph., Bartlome, R., Montemezzani, G. & Günter, P. (2003). *Appl. Surf. Sci.* **220**, 88–95.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Jagannathan, K., Kalainathan, S., Gnanasekaran, T., Vijayan, N. & Bhagavannarayana, G. (2007). *Cryst. Growth Des.* **7**, 859–863.
- Nogi, K., Anwar, U., Tsuji, K., Duan, X.-M., Okada, S., Oikawa, H., Matsuda, H. & Nakanishi, H. (2000). *Nonlinear Optics*, **24**, 35–40.
- Ogawa, J., Okada, S., Glavcheva, Z. & Nakanishi, H. (2008). *J. Cryst. Growth*, **310**, 836–842.
- Otero, M., Herranz, M. A., Seoane, C., Martín, N., Garín, J., Orduna, J., Alcalá, R. & Villacampa, B. (2002). *Tetrahedron*, **58**, 7463–7475.
- Rahman, A. A., Razak, I. A., Fun, H.-K., Saene, P., Jindawong, B., Chantrapomma, S. & Karalai, C. (2003). *Acta Cryst.* **E59**, o1798–o1800.
- Sato, N., Rikukawa, M., Sanui, K. & Ogata, N. (1999). *Synth. Met.* **101**, 132–133.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Yang, Z., Wörle, M., Mutter, L., Jazbinsek, M. & Günter, P. (2007). *Cryst. Growth Des.* **7**, 83–86.

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(*E*)-4-[4-(Dimethylamino)styryl]-1-methylpyridinium 4-bromobenzenesulfonate

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Comment

Organic crystals with extensive conjugated π systems are attractive candidates for non-linear optic (NLO) studies because of their large NLO coefficients (Chia *et al.*, 1995; Dittrich *et al.*, 2003; Otero *et al.*, 2002; Nogi *et al.*, 2000; Sato *et al.*, 1999). 4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium tosylate (DAST) is one such promising NLO material (Adachi *et al.*, 1999). Previous studies (Dittrich *et al.*, 2003; Nogi *et al.*, 2000; Sato *et al.*, 1999) have shown that DAST and its analogues exhibit second-order non-linear optical properties. To investigate the effect of counter anion on the NLO properties of DAST, the title compound was prepared by changing the counter anion from 4-toluenesulfonate in DAST to 4-bromobenzenesulfonate. The title compound is found to crystallize with the non-centrosymmetric space group *Cc* and therefore has second order nonlinear optical properties.

The asymmetric unit of the title compound (Fig. 1), consists of the $C_{16}H_{19}N_2^+$ cation and $C_6H_4BrO_3S^-$ anion. The cation exists in the *E* configuration with respect to the C6=C7 double bond [1.342 (5) Å] and the cation is nearly planar as indicated by the dihedral angle between the pyridinium and the dimethylaminophenyl rings 3.19 (15)°, and by the torsion angles C4–C5–C6–C7 = 1.0 (5)° and C6–C7–C8–C13 = 2.4 (5)°. Both methyl groups of the dimethylamino group are co-planar with the C8–C13 ring with the torsion angle C15–N2–C11–C10 of 2.3 (5)° and C16–N2–C11–C12 = 1.5 (5)°. The relative arrangement of cation and anion is shown by the angles between the mean plane of the 4-bromophenyl ring and those of the pyridinium and dimethylaminophenyl systems which are 74.81 (16)° and 77.99 (16)°, respectively. The bond lengths and angles are normal (Allen *et al.*, 1987) and the cation bond lengths and angles are comparable with related structures (Chantrapromma *et al.*, 2008).

In the crystal packing, all O atoms of sulfonate group are involved in weak C—H \cdots O interactions (Table 1). The cations and anions are linked by weak C—H \cdots O interactions into chains along the *c* axis and these chains are stacked along the *b* axis (Fig. 2). The crystal structure is further stabilized by a C—H \cdots π interactions (Table 1). π – π interactions with the distance $Cg_1\cdots Cg_2 = 3.5675$ (19) Å (symmetry code $-1/2 + x, -1/2 + y, z$ and $1/2 + x, 1/2 + y, z$) are observed; Cg_1 , Cg_2 and Cg_3 are the centroids of the N1/C1–C5, C8–C13 and C17–C22 rings.

Experimental

(*E*)-4-[4-(Dimethylamino)styryl]-1-methylpyridinium iodide (compound A) was synthesized by mixing a solution (1:1:1 molar ratio) of 1,4-dimethylpyridinium iodide (2.00 g, 8.5 mmol), 4-dimethylaminobenzaldehyde (1.27 g, 8.5 mmol) and piperidine (0.84 ml, 8.5 mmol) in hot methanol (50 ml). The resulting solution was refluxed for 3 h under a nitrogen atmosphere. The resultant solid was filtered off, washed with diethylether to give red solid of compound A (2.86 g, 92%), Mp. 536–537 K). Silver(I) *p*-bromobenzenesulfonate (compound B) was synthesized according to our previously reported procedure (Chantrapromma *et al.*, 2006). The title compound was synthesized by mixing compound A (0.20 g, 0.5 mmol) in hot methanol (25 ml) and a solution of compound B (0.17 g, 0.5 mmol) in hot methanol (50 ml). The mixture immediately yielded a grey precipitate of silver iodide. After stirring the mixture for 30 min, the precipitate of silver iodide was removed

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and the resulting solution was evaporated yielding a red solid. Red plate-shaped single crystals of the title compound suitable for *x*-ray structure determination were recrystallized from methanol by slow evaporation of the solvent at room temperature over several days, Mp. 536–537 K.

Refinement

All H atoms were placed in calculated positions with $d(\text{C—H}) = 0.93 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aromatic and CH, 0.96 \AA , $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$ for CH_3 atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at 0.47 \AA from Br1 and the deepest hole is located at 0.71 \AA from Br1. A total of 1997 Friedel pairs were used to determine the absolute structure.

Figures

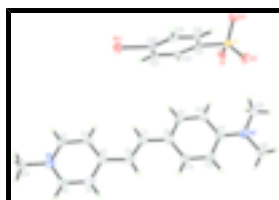


Fig. 1. The asymmetric unit showing 50% probability displacement ellipsoids and the atom-numbering scheme.

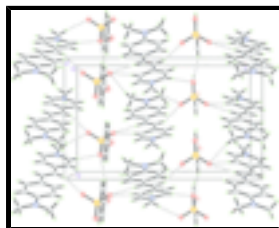


Fig. 2. Crystal packing viewed along the *a* axis. The weak C—H...O interactions are drawn as dashed lines.

(*E*)-4-[4-(Dimethylamino)styryl]-1-methylpyridinium 4-bromobenzenesulfonate

Crystal data

$\text{C}_{16}\text{H}_{19}\text{N}_2^+ \cdot \text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$

$M_r = 475.39$

Monoclinic, *Cc*

Hall symbol: *C* -2yc

$a = 10.3712 (4) \text{ \AA}$

$b = 10.9937 (5) \text{ \AA}$

$c = 17.9027 (8) \text{ \AA}$

$\beta = 92.442 (3)^\circ$

$V = 2039.37 (15) \text{ \AA}^3$

$Z = 4$

$F_{000} = 976$

$D_x = 1.548 \text{ Mg m}^{-3}$

Melting point = 536–537 K

Mo *K* α radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6479 reflections

$\theta = 2.7\text{--}35.0^\circ$

$\mu = 2.15 \text{ mm}^{-1}$

$T = 100.0 (1) \text{ K}$

Plate, red

$0.49 \times 0.31 \times 0.11 \text{ mm}$

Data collection

Bruker SMART APEX2 CCD area-detector
diffractometer

6479 independent reflections

Radiation source: fine-focus sealed tube	4811 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.043$
Detector resolution: 8.33 pixels mm^{-1}	$\theta_{\text{max}} = 35.0^\circ$
$T = 100.0(1)$ K	$\theta_{\text{min}} = 2.7^\circ$
ω scans	$h = -16 \rightarrow 16$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$k = -17 \rightarrow 14$
$T_{\text{min}} = 0.414$, $T_{\text{max}} = 0.787$	$l = -28 \rightarrow 19$
13146 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 0.6614P]$
$wR(F^2) = 0.097$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.001$
6479 reflections	$\Delta\rho_{\text{max}} = 1.01 \text{ e } \text{\AA}^{-3}$
265 parameters	$\Delta\rho_{\text{min}} = -1.38 \text{ e } \text{\AA}^{-3}$
2 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1997 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.024 (7)

Special details

Experimental. The low-temperature data was collected with the Oxford Cryosystem Cobra low-temperature attachment.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.36598 (3)	0.77042 (3)	0.68824 (2)	0.02730 (9)
S1	0.98401 (6)	0.80532 (7)	0.66253 (5)	0.01869 (16)
O1	1.0332 (2)	0.6820 (2)	0.65917 (15)	0.0260 (5)
O2	1.0299 (2)	0.8717 (2)	0.72875 (14)	0.0264 (5)
O3	0.9990 (2)	0.8740 (2)	0.59428 (14)	0.0275 (5)
N1	0.1505 (2)	0.3126 (2)	0.93738 (17)	0.0235 (6)

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N2	1.1241 (3)	0.6429 (3)	0.91479 (17)	0.0288 (6)
C1	0.3252 (3)	0.3957 (3)	1.0096 (2)	0.0267 (7)
H1A	0.3595	0.4215	1.0557	0.032*
C2	0.2023 (3)	0.3507 (3)	1.0041 (2)	0.0248 (7)
H2A	0.1538	0.3462	1.0466	0.030*
C3	0.2213 (3)	0.3179 (3)	0.8760 (2)	0.0230 (7)
H3A	0.1854	0.2908	0.8305	0.028*
C4	0.3442 (3)	0.3621 (3)	0.8789 (2)	0.0238 (7)
H4A	0.3909	0.3646	0.8357	0.029*
C5	0.4003 (3)	0.4034 (3)	0.9463 (2)	0.0231 (7)
C6	0.5317 (3)	0.4507 (3)	0.9554 (2)	0.0265 (8)
H6A	0.5609	0.4749	1.0029	0.032*
C7	0.6126 (3)	0.4612 (3)	0.8992 (2)	0.0231 (7)
H7A	0.5821	0.4373	0.8519	0.028*
C8	0.7443 (3)	0.5069 (3)	0.9063 (2)	0.0238 (7)
C9	0.8152 (3)	0.5165 (3)	0.84225 (19)	0.0224 (7)
H9A	0.7775	0.4917	0.7967	0.027*
C10	0.9406 (3)	0.5618 (3)	0.8439 (2)	0.0229 (7)
H10A	0.9842	0.5690	0.7998	0.027*
C11	1.0015 (3)	0.5969 (3)	0.9124 (2)	0.0225 (7)
C12	0.9307 (3)	0.5851 (3)	0.9777 (2)	0.0260 (7)
H12A	0.9690	0.6066	1.0237	0.031*
C13	0.8055 (3)	0.5421 (3)	0.9742 (2)	0.0250 (7)
H13A	0.7608	0.5363	1.0179	0.030*
C14	0.0170 (3)	0.2686 (3)	0.9326 (2)	0.0298 (8)
H14A	0.0039	0.2197	0.8885	0.045*
H14B	-0.0409	0.3367	0.9302	0.045*
H14C	0.0007	0.2206	0.9760	0.045*
C15	1.1928 (3)	0.6611 (3)	0.8465 (2)	0.0295 (8)
H15A	1.1404	0.7084	0.8119	0.044*
H15B	1.2110	0.5835	0.8246	0.044*
H15C	1.2722	0.7032	0.8579	0.044*
C16	1.1872 (3)	0.6788 (3)	0.9852 (2)	0.0304 (8)
H16A	1.1782	0.6151	1.0213	0.046*
H16B	1.1480	0.7518	1.0030	0.046*
H16C	1.2771	0.6932	0.9781	0.046*
C17	0.8138 (3)	0.7927 (3)	0.6710 (2)	0.0176 (6)
C18	0.7402 (3)	0.8978 (3)	0.6780 (2)	0.0192 (7)
H18A	0.7809	0.9732	0.6797	0.023*
C19	0.6080 (3)	0.8917 (3)	0.6823 (2)	0.0209 (7)
H19A	0.5594	0.9624	0.6858	0.025*
C20	0.5489 (3)	0.7790 (3)	0.6814 (2)	0.0207 (6)
C21	0.6187 (3)	0.6722 (3)	0.6750 (2)	0.0220 (7)
H21A	0.5774	0.5970	0.6743	0.026*
C22	0.7524 (3)	0.6800 (3)	0.6696 (2)	0.0191 (7)
H22A	0.8008	0.6094	0.6649	0.023*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01676 (11)	0.03575 (17)	0.02948 (18)	-0.00106 (18)	0.00199 (10)	-0.0056 (2)
S1	0.0163 (3)	0.0187 (4)	0.0211 (4)	0.0010 (2)	0.0013 (3)	0.0020 (3)
O1	0.0167 (9)	0.0242 (12)	0.0375 (16)	-0.0007 (8)	0.0055 (10)	0.0016 (11)
O2	0.0198 (10)	0.0342 (13)	0.0251 (14)	-0.0022 (9)	-0.0010 (9)	-0.0054 (11)
O3	0.0247 (10)	0.0308 (13)	0.0270 (14)	-0.0007 (9)	0.0021 (9)	0.0068 (10)
N1	0.0221 (12)	0.0201 (13)	0.0287 (18)	0.0065 (10)	0.0035 (12)	0.0037 (12)
N2	0.0305 (13)	0.0347 (16)	0.0212 (16)	-0.0087 (12)	0.0001 (12)	-0.0013 (14)
C1	0.0304 (15)	0.0215 (16)	0.028 (2)	0.0070 (12)	-0.0003 (14)	-0.0023 (14)
C2	0.0302 (15)	0.0235 (16)	0.0210 (19)	0.0080 (12)	0.0049 (14)	0.0013 (14)
C3	0.0269 (14)	0.0220 (16)	0.0197 (19)	0.0052 (12)	-0.0011 (13)	0.0028 (13)
C4	0.0249 (14)	0.0245 (16)	0.0223 (19)	0.0063 (12)	0.0044 (12)	0.0034 (14)
C5	0.0235 (13)	0.0176 (14)	0.0285 (19)	0.0062 (11)	0.0033 (13)	0.0004 (14)
C6	0.0229 (14)	0.0271 (17)	0.030 (2)	0.0064 (12)	0.0001 (14)	-0.0039 (15)
C7	0.0247 (14)	0.0203 (15)	0.0240 (19)	0.0036 (11)	-0.0007 (13)	-0.0008 (13)
C8	0.0245 (14)	0.0215 (15)	0.025 (2)	0.0047 (11)	0.0022 (13)	-0.0003 (14)
C9	0.0281 (14)	0.0203 (15)	0.0185 (18)	0.0035 (11)	-0.0031 (13)	-0.0020 (13)
C10	0.0265 (14)	0.0208 (15)	0.0214 (19)	0.0036 (11)	0.0017 (13)	-0.0004 (13)
C11	0.0284 (14)	0.0164 (14)	0.0228 (19)	0.0018 (11)	0.0008 (13)	0.0023 (13)
C12	0.0308 (15)	0.0245 (17)	0.0224 (19)	0.0005 (12)	-0.0014 (14)	-0.0009 (14)
C13	0.0277 (15)	0.0258 (16)	0.0217 (19)	0.0003 (12)	0.0023 (13)	-0.0035 (14)
C14	0.0250 (14)	0.0274 (16)	0.037 (2)	0.0018 (13)	0.0038 (14)	0.0079 (16)
C15	0.0299 (15)	0.0315 (18)	0.027 (2)	-0.0053 (13)	-0.0018 (14)	0.0038 (16)
C16	0.0354 (17)	0.0309 (18)	0.024 (2)	-0.0066 (14)	-0.0055 (15)	-0.0007 (16)
C17	0.0174 (12)	0.0168 (14)	0.0186 (18)	0.0008 (10)	0.0004 (12)	-0.0001 (12)
C18	0.0182 (12)	0.0177 (16)	0.0215 (19)	-0.0021 (11)	0.0002 (12)	-0.0015 (13)
C19	0.0229 (14)	0.0202 (16)	0.0197 (18)	0.0029 (11)	0.0012 (12)	-0.0028 (13)
C20	0.0167 (12)	0.0293 (16)	0.0160 (17)	0.0013 (12)	0.0003 (11)	-0.0020 (14)
C21	0.0230 (14)	0.0181 (16)	0.025 (2)	-0.0009 (11)	-0.0009 (13)	-0.0004 (14)
C22	0.0226 (14)	0.0150 (15)	0.0197 (19)	0.0036 (11)	-0.0001 (13)	0.0039 (13)

Geometric parameters (\AA , $^\circ$)

Br1—C20	1.909 (3)	C9—H9A	0.9300
S1—O3	1.450 (3)	C10—C11	1.409 (5)
S1—O1	1.451 (2)	C10—H10A	0.9300
S1—O2	1.455 (2)	C11—C12	1.413 (5)
S1—C17	1.784 (3)	C12—C13	1.380 (4)
N1—C3	1.349 (4)	C12—H12A	0.9300
N1—C2	1.355 (4)	C13—H13A	0.9300
N1—C14	1.466 (4)	C14—H14A	0.9600
N2—C11	1.367 (4)	C14—H14B	0.9600
N2—C16	1.451 (4)	C14—H14C	0.9600
N2—C15	1.455 (5)	C15—H15A	0.9600
C1—C2	1.367 (5)	C15—H15B	0.9600
C1—C5	1.405 (5)	C15—H15C	0.9600

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C1—H1A	0.9300	C16—H16A	0.9600
C2—H2A	0.9300	C16—H16B	0.9600
C3—C4	1.363 (4)	C16—H16C	0.9600
C3—H3A	0.9300	C17—C18	1.392 (4)
C4—C5	1.393 (5)	C17—C22	1.393 (4)
C4—H4A	0.9300	C18—C19	1.378 (4)
C5—C6	1.461 (4)	C18—H18A	0.9300
C6—C7	1.342 (5)	C19—C20	1.382 (5)
C6—H6A	0.9300	C19—H19A	0.9300
C7—C8	1.455 (4)	C20—C21	1.387 (5)
C7—H7A	0.9300	C21—C22	1.396 (4)
C8—C9	1.393 (5)	C21—H21A	0.9300
C8—C13	1.402 (5)	C22—H22A	0.9300
C9—C10	1.391 (4)		
O3—S1—O1	113.63 (15)	C10—C11—C12	117.7 (3)
O3—S1—O2	112.50 (15)	C13—C12—C11	121.0 (3)
O1—S1—O2	113.53 (14)	C13—C12—H12A	119.5
O3—S1—C17	104.72 (14)	C11—C12—H12A	119.5
O1—S1—C17	106.37 (13)	C12—C13—C8	121.6 (3)
O2—S1—C17	105.09 (15)	C12—C13—H13A	119.2
C3—N1—C2	119.8 (3)	C8—C13—H13A	119.2
C3—N1—C14	120.8 (3)	N1—C14—H14A	109.5
C2—N1—C14	119.4 (3)	N1—C14—H14B	109.5
C11—N2—C16	120.8 (3)	H14A—C14—H14B	109.5
C11—N2—C15	120.8 (3)	N1—C14—H14C	109.5
C16—N2—C15	118.3 (3)	H14A—C14—H14C	109.5
C2—C1—C5	120.8 (3)	H14B—C14—H14C	109.5
C2—C1—H1A	119.6	N2—C15—H15A	109.5
C5—C1—H1A	119.6	N2—C15—H15B	109.5
N1—C2—C1	120.5 (3)	H15A—C15—H15B	109.5
N1—C2—H2A	119.7	N2—C15—H15C	109.5
C1—C2—H2A	119.7	H15A—C15—H15C	109.5
N1—C3—C4	121.6 (3)	H15B—C15—H15C	109.5
N1—C3—H3A	119.2	N2—C16—H16A	109.5
C4—C3—H3A	119.2	N2—C16—H16B	109.5
C3—C4—C5	120.3 (3)	H16A—C16—H16B	109.5
C3—C4—H4A	119.8	N2—C16—H16C	109.5
C5—C4—H4A	119.8	H16A—C16—H16C	109.5
C4—C5—C1	117.0 (3)	H16B—C16—H16C	109.5
C4—C5—C6	124.4 (3)	C18—C17—C22	119.2 (3)
C1—C5—C6	118.6 (3)	C18—C17—S1	119.4 (2)
C7—C6—C5	123.9 (3)	C22—C17—S1	121.4 (2)
C7—C6—H6A	118.1	C19—C18—C17	121.0 (3)
C5—C6—H6A	118.1	C19—C18—H18A	119.5
C6—C7—C8	125.4 (3)	C17—C18—H18A	119.5
C6—C7—H7A	117.3	C18—C19—C20	119.0 (3)
C8—C7—H7A	117.3	C18—C19—H19A	120.5
C9—C8—C13	117.2 (3)	C20—C19—H19A	120.5
C9—C8—C7	118.8 (3)	C19—C20—C21	121.8 (3)

C13—C8—C7	124.0 (3)	C19—C20—Br1	119.0 (2)
C10—C9—C8	122.4 (3)	C21—C20—Br1	119.1 (2)
C10—C9—H9A	118.8	C20—C21—C22	118.5 (3)
C8—C9—H9A	118.8	C20—C21—H21A	120.8
C9—C10—C11	120.0 (3)	C22—C21—H21A	120.8
C9—C10—H10A	120.0	C17—C22—C21	120.5 (3)
C11—C10—H10A	120.0	C17—C22—H22A	119.7
N2—C11—C10	120.7 (3)	C21—C22—H22A	119.7
N2—C11—C12	121.6 (3)		
C3—N1—C2—C1	0.7 (5)	C9—C10—C11—C12	-0.5 (4)
C14—N1—C2—C1	-177.9 (3)	N2—C11—C12—C13	177.9 (3)
C5—C1—C2—N1	0.0 (5)	C10—C11—C12—C13	-0.8 (5)
C2—N1—C3—C4	-0.7 (5)	C11—C12—C13—C8	0.9 (5)
C14—N1—C3—C4	177.9 (3)	C9—C8—C13—C12	0.3 (5)
N1—C3—C4—C5	0.0 (5)	C7—C8—C13—C12	-179.9 (3)
C3—C4—C5—C1	0.7 (4)	O3—S1—C17—C18	-61.5 (3)
C3—C4—C5—C6	179.1 (3)	O1—S1—C17—C18	177.9 (3)
C2—C1—C5—C4	-0.7 (5)	O2—S1—C17—C18	57.2 (3)
C2—C1—C5—C6	-179.2 (3)	O3—S1—C17—C22	117.4 (3)
C4—C5—C6—C7	1.0 (5)	O1—S1—C17—C22	-3.2 (3)
C1—C5—C6—C7	179.4 (3)	O2—S1—C17—C22	-123.8 (3)
C5—C6—C7—C8	-179.5 (3)	C22—C17—C18—C19	-1.0 (5)
C6—C7—C8—C9	-177.8 (3)	S1—C17—C18—C19	178.0 (3)
C6—C7—C8—C13	2.4 (5)	C17—C18—C19—C20	1.5 (5)
C13—C8—C9—C10	-1.7 (5)	C18—C19—C20—C21	-1.1 (5)
C7—C8—C9—C10	178.5 (3)	C18—C19—C20—Br1	179.5 (3)
C8—C9—C10—C11	1.8 (5)	C19—C20—C21—C22	0.2 (5)
C16—N2—C11—C10	-179.9 (3)	Br1—C20—C21—C22	179.6 (3)
C15—N2—C11—C10	2.3 (5)	C18—C17—C22—C21	0.1 (5)
C16—N2—C11—C12	1.5 (5)	S1—C17—C22—C21	-178.9 (3)
C15—N2—C11—C12	-176.4 (3)	C20—C21—C22—C17	0.4 (5)
C9—C10—C11—N2	-179.2 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2A...O1 ⁱ	0.93	2.44	3.366 (4)	175
C4—H4A...O2 ⁱⁱ	0.93	2.45	3.375 (4)	175
C6—H6A...O3 ⁱⁱⁱ	0.93	2.44	3.175 (4)	136
C7—H7A...O2 ⁱⁱ	0.93	2.36	3.285 (4)	173
C14—H14C...O3 ⁱ	0.96	2.36	3.304 (4)	168
C15—H15A...O2	0.96	2.57	3.515 (4)	168
C19—H19A...O1 ^{iv}	0.93	2.47	3.306 (4)	149
C3—H3A...Cg3 ⁱⁱ	0.93	2.76	3.601 (4)	151
C14—H14B...Cg2 ^v	0.96	2.55	3.468 (4)	161
C16—H16A...Cg3 ^{vi}	0.93	2.98	3.446 (4)	111

supplementary materials

Symmetry codes: (i) $x-1, -y+1, z+1/2$; (ii) $x-1/2, y-1/2, z$; (iii) $x-1/2, -y+3/2, z+1/2$; (iv) $x-1/2, y+1/2, z$; (v) $x-1, y, z$; (vi) $x+1/2, -y+3/2, z+1/2$.

Fig. 1

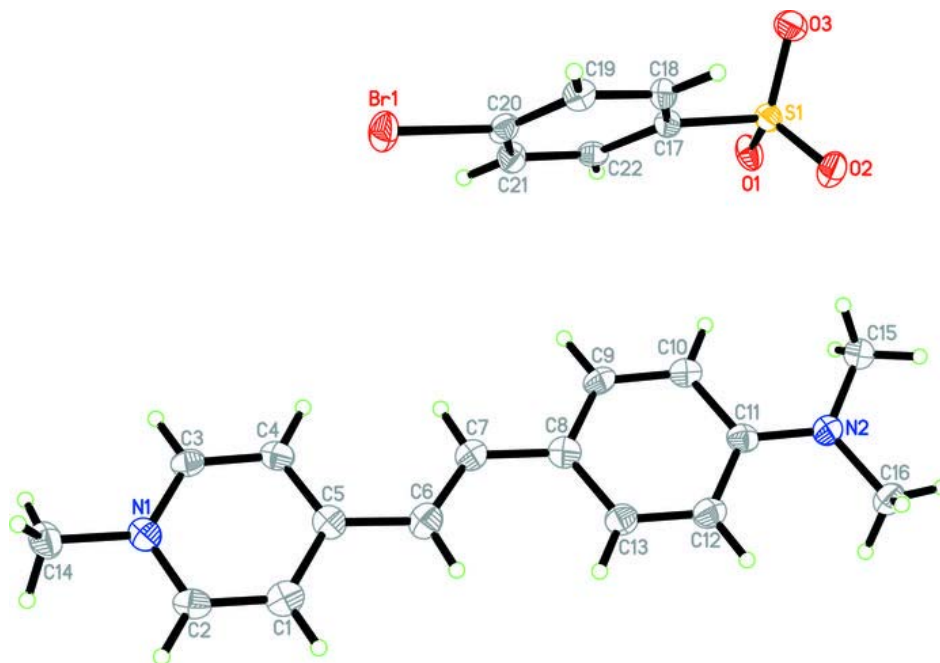
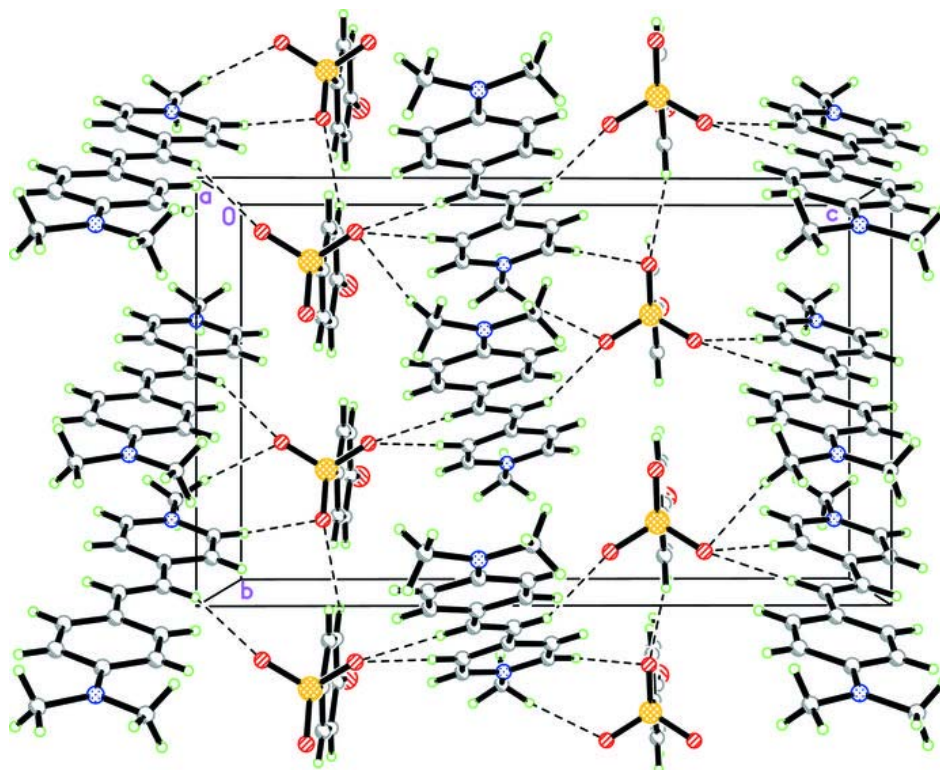


Fig. 2



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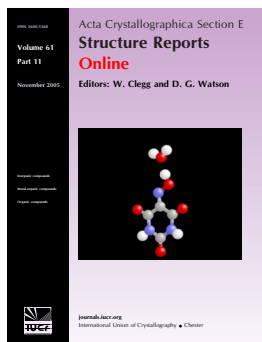
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1-Methyl-4-[(*E*)-2-(2-thienyl)ethenyl]pyridinium 4-methylbenzenesulfonate

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Chatchanok Karalai

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1-Methyl-4-[(*E*)-2-(2-thienyl)ethenyl]-pyridinium 4-methylbenzenesulfonate¹

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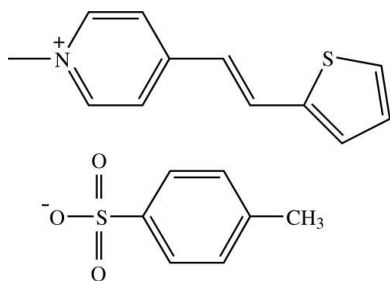
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Key indicators: single-crystal X-ray study; *T* = 100 K; mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$; *R* factor = 0.051; *wR* factor = 0.148; data-to-parameter ratio = 20.2.

In the title compound, $\text{C}_{12}\text{H}_{12}\text{NS}^+\cdot\text{C}_7\text{H}_7\text{O}_3\text{S}^-$, the cation exists in an *E* configuration with respect to the ethenyl $\text{C}=\text{C}$ bond. The cation is essentially planar with a dihedral angle of $1.94 (10)^\circ$ between the pyridinium and thiophene rings. The benzene ring of the anion makes dihedral angles of $75.23 (10)$ and $76.83 (10)^\circ$, respectively, with the pyridinium and thiophene rings. In the crystal structure, cations and anions form alternate layers parallel to the *bc* plane. Within each layer, both cations and anions are arranged into chains directed along the *b* axis. The cation chain and the anion chain are interconnected by weak $\text{C}-\text{H}\cdots\text{O}$ interactions into a three-dimensional network. The crystal structure is further stabilized by $\text{C}-\text{H}\cdots\pi$ interactions.

Related literature

For bond lengths, see: Allen *et al.* (1987). For related literature on hydrogen-bond motifs, see: Bernstein *et al.* (1995). For related structures, see, for example: Chantrapromma, Jindawong & Fun (2007); Chantrapromma, Jindawong, Fun & Patil (2007); Chantrapromma *et al.* (2008); Lakshmanaperumal *et al.* (2002, 2004); Rahman *et al.* (2003); Ruanwas *et al.* (2008); Usman *et al.* (2000, 2001).



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Experimental

Crystal data

$\text{C}_{12}\text{H}_{12}\text{NS}^+\cdot\text{C}_7\text{H}_7\text{O}_3\text{S}^-$
M_r = 373.49
Triclinic, *P* $\bar{1}$
a = 9.2947 (1) Å
b = 9.6144 (1) Å
c = 10.7790 (1) Å
 α = 87.817 (1) $^\circ$
 β = 64.702 (1) $^\circ$
 γ = 88.712 (1) $^\circ$
V = 870.21 (1) Å^3
Z = 2
Mo *K* α radiation
 μ = 0.32 mm^{-1}
T = 100.0 (1) K
0.36 × 0.35 × 0.18 mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)
T_{min} = 0.893, *T_{max}* = 0.945
18024 measured reflections
4606 independent reflections
4122 reflections with *I* > 2 σ (*I*)
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.148$
S = 1.04
4606 reflections
228 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.98 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.71 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å , $^\circ$).

<i>D</i> — <i>H</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i> ⋯ <i>A</i>
C2—H2A⋯O3 ⁱ	0.93	2.31	3.219 (3)	166
C3—H3A⋯O1 ⁱⁱ	0.93	2.49	3.168 (2)	130
C6—H6A⋯O2	0.93	2.56	3.378 (3)	147
C11—H11A⋯O1 ⁱⁱⁱ	0.93	2.54	3.303 (3)	139
C12—H12A⋯O1 ⁱ	0.96	2.52	3.455 (3)	165
C12—H12C⋯O1 ⁱⁱ	0.96	2.47	3.341 (3)	151
C15—H15A⋯O2 ^{iv}	0.93	2.42	3.272 (2)	152
C17—H17A⋯O3 ⁱ	0.93	2.43	3.202 (2)	141
C4—H4A⋯Cg1 ^v	0.93	2.62	3.431 (2)	145
C10—H10A⋯Cg1 ^{vi}	0.93	2.95	3.666 (3)	135

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z+1$; (iii) $-x+1, -y+2, -z$; (iv) $-x+1, -y+1, -z$; (v) $-x, -y+1, -z+1$; (vi) $x-1, y+1, z$. Cg1 is the centroid of the C13–C18 benzene ring.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2338).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chantrapromma, S., Jindawong, B. & Fun, H.-K. (2007). *Acta Cryst.* **E63**, o2020–o2022.

- Chantrapomma, S., Jindawong, B., Fun, H.-K. & Patil, P. S. (2007). *Acta Cryst.* **E63**, o2321–o2323.
- Chantrapomma, S., Laksana, C., Ruanwas, P. & Fun, H.-K. (2008). *Acta Cryst.* **E64**, o574–o575.
- Lakshmanaperumal, C. K., Arulchakkaravarthi, A., Balamurugan, N., Santhanaraghavan, P. & Ramasamy, P. (2004). *J. Cryst. Growth*, **265**, 260–265.
- Lakshmanaperumal, C. K., Arulchakkaravarthi, A., Rajesh, N. P., Santhana Raghavan, P., Huang, Y. C., Ichimura, M. & Ramasamy, P. (2002). *J. Cryst. Growth*, **240**, 212–217.
- Rahman, A. A., Razak, I. A., Fun, H.-K., Saene, P., Jindawong, B., Chantrapomma, S. & Karalai, C. (2003). *Acta Cryst.* **E59**, o1798–o1800.
- Ruanwas, P., Kobkeatthawin, T., Chantrapomma, S., Fun, H.-K. & Karalai, C. (2008). *Acta Cryst.* **E64**, o1453–o1454.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Usman, A., Kosuge, H., Okada, S., Oikawa, H. & Nakanishi, H. (2001). *Jpn. J. Appl. Phys.* **40**, 4213–4216.
- Usman, A., Okada, S., Oikawa, H. & Nakanishi, H. (2000). *Chem. Mater.* **12**, 1162–1170.

supplementary materials

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1-Methyl-4-[(*E*)-2-(2-thienyl)ethenyl]pyridinium 4-methylbenzenesulfonate

S. Chantrapromma, P. Ruanwas, H.-K. Fun and C. Karalai

Comment

Pyridinium derivatives have been found to have nonlinear optical properties (Lakshmanaperumal *et al.*, 2002, 2004; Usman *et al.*, 2000, 2001). We have previously synthesized and crystallized several compounds of pyridinium and quinolinium derivatives to study their non-linear optical properties (Chantrapromma, Jindawong & Fun, 2007; Chantrapromma, Jindawong, Fun & Patil, 2007; Chantrapromma *et al.*, 2008; Ruanwas *et al.*, 2008). As part of our research on nonlinear optic materials, the title compound was synthesized.

The asymmetric unit of the title compound consists of the $C_{12}H_{12}NS^+$ cation and the $C_7H_7O_3S^-$ anion. The cation exists in an *E* configuration with respect to the ethenyl C=C bond [C6=C7 = 1.346 (3) Å]. The cation is essentially planar with a dihedral angle between the pyridinium and thiophene rings of 1.94 (10)°. The orientation of the anion with respect to the cation can be indicated by the interplanar angles between the benzene ring [C13–C18] with the pyridinium [C1–C5/N1] and thiophene [C8–C11/S1] rings of 75.23 (10) and 76.83 (10)°, respectively. The ethenyl unit is nearly coplanar with the pyridinium and thiophene rings with the torsion angles C4–C5–C6–C7 = 3.0 (3)° and C6–C7–C8–S1 = -3.7 (3)°. The atom O3 of the sulfonate and the S1 atom of the thiophene contribute to the weak intramolecular C—H···O and C—H···S interactions (Fig. 1 and Table 1), forming S(5) ring motifs (Bernstein *et al.*, 1995). The bond lengths and angles are normal (Allen *et al.*, 1987) and are comparable with closely related structures (Chantrapromma, Jindawong & Fun, 2007; Chantrapromma, Jindawong, Fun & Patil, 2007; Chantrapromma *et al.*, 2008; Ruanwas *et al.*, 2008).

All the O atoms of 4-methylbenzenesulfonate anion are involved in the C—H···O weak interactions (Table 1). In the crystal packing (Fig. 2), the cations and anions form alternate layers parallel to the *bc* plane. Within each layer both cations and anions are arranged into chains directed along the *b* axis. The cations and anions chains are interconnected by C—H···O weak interactions into a three dimensional network. The crystal structure is further stabilized by the C4—H4A··· π and C10—H10A··· π interactions (Table 1); C_{g1} is the centroid of the C13–C18 benzene ring.

Experimental

The title compound was synthesized by mixing 4-(2-thiophenestyryl)-1-methylpyridinium iodide (0.1 g, 0.3 mmol) which was prepared in a similar manner to that previously reported (Chantrapromma *et al.*, 2008) in hot methanol (40 ml) and *p*-toluenesulfonate (0.09 g, 0.3 mmol) in hot methanol (30 ml) (Rahman *et al.*, 2003). The mixture immediately yielded a yellow solid of silver iodide. After stirring the mixture for 30 min, the precipitate of silver iodide was removed and the resulting solution was evaporated and the green-yellow solid was obtained. Yellow block-shaped single crystals of the title compound suitable for *x*-ray structure determination were recrystallized from the methanol/ethanol (1:1 *v/v*) solvent by slow evaporation of the solvent at room temperature after several weeks (m.p. 507–509 K).

Refinement

All H atoms could have been discerned in a difference Fourier map. Nevertheless, all the H atoms attached to the carbon atoms were constrained in a riding motion approximation with $C_{\text{aryl}}\text{—H} = 0.93$ and $C_{\text{methyl}}\text{—H} = 0.96$ Å. The U_{iso} values were constrained to be $1.5U_{\text{eq}}$ of the carrier atom for methyl H atoms and $1.2U_{\text{eq}}$ for the remaining H atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at 1.01 Å from C6 and the deepest hole is located at 0.33 Å from S1.

Figures

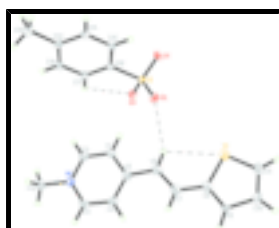


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. The weak C—H···O and C—H···S interactions are drawn as dashed lines.

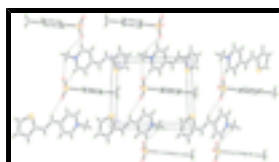


Fig. 2. The packing diagram of the title compound, viewed along the *c* axis. The weak C—H···O and C—H···S interactions are drawn as dashed lines.

1-Methyl-4-[(*E*)-2-(2-thienyl)ethenyl]pyridinium 4-methylbenzenesulfonate

Crystal data

$C_{12}H_{12}NS^+ \cdot C_7H_7O_3S^-$

$M_r = 373.49$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 9.2947$ (1) Å

$b = 9.6144$ (1) Å

$c = 10.7790$ (1) Å

$\alpha = 87.817$ (1)°

$\beta = 64.702$ (1)°

$\gamma = 88.712$ (1)°

$V = 870.214$ (15) Å³

$Z = 2$

$F_{000} = 392$

$D_x = 1.425$ Mg m⁻³

Melting point = 507–509 K

Mo *K* α radiation

$\lambda = 0.71073$ Å

Cell parameters from 4606 reflections

$\theta = 2.4\text{--}29.0^\circ$

$\mu = 0.32$ mm⁻¹

$T = 100.0$ (1) K

Block, yellow

$0.36 \times 0.35 \times 0.18$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

4606 independent reflections

4122 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

Detector resolution: 8.33 pixels mm⁻¹
 $T = 100.0(1)$ K
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.893$, $T_{\max} = 0.945$
 18024 measured reflections

$\theta_{\max} = 29.0^\circ$
 $\theta_{\min} = 2.4^\circ$
 $h = -12 \rightarrow 12$
 $k = -13 \rightarrow 13$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.149$
 $S = 1.04$
 4606 reflections
 228 parameters
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0809P)^2 + 1.1333P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.98 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.71 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none

Special details

Experimental. The data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.15733 (7)	0.99833 (6)	0.16005 (6)	0.02891 (16)
S2	0.55035 (5)	0.58728 (4)	0.20813 (4)	0.01428 (13)
O1	0.69298 (18)	0.61236 (15)	0.08113 (15)	0.0220 (3)
O2	0.40517 (17)	0.63620 (15)	0.19977 (15)	0.0194 (3)
O3	0.56449 (18)	0.63482 (14)	0.32920 (14)	0.0196 (3)
N1	-0.0092 (2)	0.50151 (17)	0.75333 (17)	0.0169 (3)
C1	0.1573 (2)	0.6066 (2)	0.5395 (2)	0.0221 (4)
H1A	0.2574	0.6145	0.4662	0.026*
C2	0.1351 (2)	0.5142 (2)	0.6456 (2)	0.0208 (4)

supplementary materials

H2A	0.2199	0.4597	0.6437	0.025*
C3	-0.1335 (2)	0.5809 (2)	0.7588 (2)	0.0195 (4)
H3A	-0.2317	0.5721	0.8342	0.023*
C4	-0.1159 (2)	0.6742 (2)	0.6539 (2)	0.0206 (4)
H4A	-0.2025	0.7279	0.6586	0.025*
C5	0.0314 (2)	0.6894 (2)	0.5397 (2)	0.0196 (4)
C6	0.0632 (2)	0.7841 (2)	0.4220 (2)	0.0220 (4)
H6A	0.1643	0.7827	0.3497	0.026*
C7	-0.0453 (3)	0.8733 (2)	0.4121 (2)	0.0235 (4)
H7A	-0.1461	0.8719	0.4849	0.028*
C8	-0.0211 (3)	0.9713 (2)	0.2998 (2)	0.0225 (4)
C9	-0.1401 (2)	1.0515 (2)	0.29383 (19)	0.0151 (3)
H9A	-0.2454	1.0489	0.3591	0.018*
C10	-0.0793 (3)	1.1440 (2)	0.1689 (2)	0.0247 (4)
H10A	-0.1417	1.2086	0.1474	0.030*
C11	0.0787 (3)	1.1230 (2)	0.0896 (2)	0.0262 (4)
H11A	0.1367	1.1709	0.0070	0.031*
C12	-0.0343 (3)	0.3981 (2)	0.8657 (2)	0.0241 (4)
H12A	0.0649	0.3795	0.8710	0.036*
H12B	-0.0740	0.3134	0.8479	0.036*
H12C	-0.1099	0.4341	0.9510	0.036*
C13	0.4960 (2)	0.1137 (2)	0.2619 (2)	0.0178 (4)
C14	0.5220 (2)	0.1820 (2)	0.1374 (2)	0.0179 (4)
H14A	0.5273	0.1303	0.0643	0.021*
C15	0.5401 (2)	0.3257 (2)	0.12029 (19)	0.0161 (3)
H15A	0.5573	0.3694	0.0367	0.019*
C16	0.5323 (2)	0.40335 (18)	0.22945 (18)	0.0141 (3)
C17	0.5046 (2)	0.33792 (19)	0.35510 (19)	0.0158 (3)
H17A	0.4983	0.3899	0.4283	0.019*
C18	0.4864 (2)	0.1940 (2)	0.3702 (2)	0.0174 (4)
H18A	0.4674	0.1505	0.4543	0.021*
C19	0.4833 (3)	-0.0423 (2)	0.2771 (3)	0.0260 (4)
H19A	0.3967	-0.0675	0.3632	0.039*
H19B	0.5807	-0.0809	0.2744	0.039*
H19C	0.4644	-0.0779	0.2034	0.039*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0231 (3)	0.0296 (3)	0.0285 (3)	0.0008 (2)	-0.0063 (2)	0.0060 (2)
S2	0.0174 (2)	0.0119 (2)	0.0122 (2)	0.00110 (15)	-0.00523 (17)	0.00122 (15)
O1	0.0223 (7)	0.0188 (7)	0.0167 (7)	-0.0017 (5)	-0.0007 (6)	0.0020 (5)
O2	0.0224 (7)	0.0171 (6)	0.0200 (7)	0.0047 (5)	-0.0105 (6)	0.0004 (5)
O3	0.0284 (7)	0.0151 (6)	0.0183 (7)	0.0020 (5)	-0.0129 (6)	-0.0014 (5)
N1	0.0175 (7)	0.0161 (7)	0.0172 (7)	0.0001 (6)	-0.0076 (6)	-0.0002 (6)
C1	0.0187 (9)	0.0242 (10)	0.0180 (9)	-0.0016 (7)	-0.0028 (7)	-0.0009 (7)
C2	0.0163 (8)	0.0210 (9)	0.0229 (10)	0.0035 (7)	-0.0062 (7)	-0.0033 (7)
C3	0.0150 (8)	0.0234 (9)	0.0190 (9)	0.0000 (7)	-0.0061 (7)	-0.0007 (7)

C4	0.0182 (9)	0.0221 (9)	0.0235 (10)	0.0023 (7)	-0.0112 (8)	0.0002 (7)
C5	0.0252 (9)	0.0169 (9)	0.0181 (9)	-0.0040 (7)	-0.0104 (8)	0.0005 (7)
C6	0.0215 (9)	0.0222 (10)	0.0205 (9)	-0.0015 (7)	-0.0074 (8)	0.0003 (7)
C7	0.0218 (9)	0.0251 (10)	0.0218 (10)	-0.0018 (8)	-0.0077 (8)	0.0010 (8)
C8	0.0275 (10)	0.0195 (9)	0.0225 (10)	-0.0024 (8)	-0.0127 (8)	0.0015 (7)
C9	0.0091 (7)	0.0229 (9)	0.0135 (8)	0.0019 (6)	-0.0051 (6)	-0.0011 (7)
C10	0.0281 (10)	0.0218 (10)	0.0280 (11)	-0.0013 (8)	-0.0162 (9)	0.0061 (8)
C11	0.0295 (11)	0.0243 (10)	0.0242 (10)	-0.0038 (8)	-0.0115 (9)	0.0076 (8)
C12	0.0322 (11)	0.0195 (9)	0.0224 (10)	-0.0001 (8)	-0.0137 (9)	0.0034 (8)
C13	0.0158 (8)	0.0145 (8)	0.0243 (9)	0.0013 (6)	-0.0098 (7)	0.0004 (7)
C14	0.0181 (8)	0.0169 (9)	0.0187 (9)	0.0016 (7)	-0.0079 (7)	-0.0030 (7)
C15	0.0167 (8)	0.0172 (9)	0.0139 (8)	0.0014 (6)	-0.0061 (7)	0.0001 (6)
C16	0.0147 (8)	0.0123 (8)	0.0141 (8)	0.0012 (6)	-0.0051 (6)	0.0004 (6)
C17	0.0172 (8)	0.0160 (8)	0.0142 (8)	0.0013 (6)	-0.0069 (7)	0.0007 (6)
C18	0.0172 (8)	0.0165 (9)	0.0190 (9)	0.0000 (6)	-0.0086 (7)	0.0043 (7)
C19	0.0313 (11)	0.0141 (9)	0.0367 (12)	-0.0006 (8)	-0.0186 (10)	0.0020 (8)

Geometric parameters (Å, °)

S1—C11	1.707 (2)	C9—C10	1.484 (3)
S1—C8	1.715 (2)	C9—H9A	0.9300
S2—O2	1.4569 (15)	C10—C11	1.362 (3)
S2—O3	1.4574 (14)	C10—H10A	0.9300
S2—O1	1.4587 (14)	C11—H11A	0.9300
S2—C16	1.7769 (18)	C12—H12A	0.9600
N1—C3	1.351 (2)	C12—H12B	0.9600
N1—C2	1.352 (3)	C12—H12C	0.9600
N1—C12	1.479 (3)	C13—C18	1.394 (3)
C1—C2	1.367 (3)	C13—C14	1.398 (3)
C1—C5	1.400 (3)	C13—C19	1.504 (3)
C1—H1A	0.9300	C14—C15	1.391 (3)
C2—H2A	0.9300	C14—H14A	0.9300
C3—C4	1.371 (3)	C15—C16	1.393 (3)
C3—H3A	0.9300	C15—H15A	0.9300
C4—C5	1.403 (3)	C16—C17	1.393 (3)
C4—H4A	0.9300	C17—C18	1.393 (3)
C5—C6	1.458 (3)	C17—H17A	0.9300
C6—C7	1.346 (3)	C18—H18A	0.9300
C6—H6A	0.9300	C19—H19A	0.9600
C7—C8	1.447 (3)	C19—H19B	0.9600
C7—H7A	0.9300	C19—H19C	0.9600
C8—C9	1.357 (3)		
C11—S1—C8	92.72 (11)	C11—C10—C9	112.07 (19)
O2—S2—O3	112.96 (8)	C11—C10—H10A	124.0
O2—S2—O1	113.06 (9)	C9—C10—H10A	124.0
O3—S2—O1	113.19 (9)	C10—C11—S1	111.84 (17)
O2—S2—C16	105.46 (9)	C10—C11—H11A	124.1
O3—S2—C16	105.73 (9)	S1—C11—H11A	124.1
O1—S2—C16	105.54 (8)	N1—C12—H12A	109.5

supplementary materials

C3—N1—C2	120.63 (17)	N1—C12—H12B	109.5
C3—N1—C12	118.95 (17)	H12A—C12—H12B	109.5
C2—N1—C12	120.41 (17)	N1—C12—H12C	109.5
C2—C1—C5	120.85 (18)	H12A—C12—H12C	109.5
C2—C1—H1A	119.6	H12B—C12—H12C	109.5
C5—C1—H1A	119.6	C18—C13—C14	118.08 (18)
N1—C2—C1	120.52 (18)	C18—C13—C19	121.03 (18)
N1—C2—H2A	119.7	C14—C13—C19	120.87 (18)
C1—C2—H2A	119.7	C15—C14—C13	121.46 (18)
N1—C3—C4	120.49 (18)	C15—C14—H14A	119.3
N1—C3—H3A	119.8	C13—C14—H14A	119.3
C4—C3—H3A	119.8	C14—C15—C16	119.38 (17)
C3—C4—C5	120.62 (18)	C14—C15—H15A	120.3
C3—C4—H4A	119.7	C16—C15—H15A	120.3
C5—C4—H4A	119.7	C15—C16—C17	120.27 (17)
C1—C5—C4	116.87 (18)	C15—C16—S2	119.07 (14)
C1—C5—C6	117.82 (18)	C17—C16—S2	120.61 (14)
C4—C5—C6	125.30 (19)	C16—C17—C18	119.45 (17)
C7—C6—C5	123.75 (19)	C16—C17—H17A	120.3
C7—C6—H6A	118.1	C18—C17—H17A	120.3
C5—C6—H6A	118.1	C17—C18—C13	121.35 (18)
C6—C7—C8	126.6 (2)	C17—C18—H18A	119.3
C6—C7—H7A	116.7	C13—C18—H18A	119.3
C8—C7—H7A	116.7	C13—C19—H19A	109.5
C9—C8—C7	122.8 (2)	C13—C19—H19B	109.5
C9—C8—S1	112.58 (16)	H19A—C19—H19B	109.5
C7—C8—S1	124.57 (17)	C13—C19—H19C	109.5
C8—C9—C10	110.76 (17)	H19A—C19—H19C	109.5
C8—C9—H9A	124.6	H19B—C19—H19C	109.5
C10—C9—H9A	124.6		
C3—N1—C2—C1	-0.7 (3)	C8—C9—C10—C11	1.8 (3)
C12—N1—C2—C1	177.87 (19)	C9—C10—C11—S1	-0.7 (3)
C5—C1—C2—N1	-0.3 (3)	C8—S1—C11—C10	-0.32 (19)
C2—N1—C3—C4	1.0 (3)	C18—C13—C14—C15	0.9 (3)
C12—N1—C3—C4	-177.58 (19)	C19—C13—C14—C15	-177.44 (18)
N1—C3—C4—C5	-0.3 (3)	C13—C14—C15—C16	0.0 (3)
C2—C1—C5—C4	0.9 (3)	C14—C15—C16—C17	-0.8 (3)
C2—C1—C5—C6	-179.05 (19)	C14—C15—C16—S2	-178.34 (14)
C3—C4—C5—C1	-0.6 (3)	O2—S2—C16—C15	69.43 (16)
C3—C4—C5—C6	179.3 (2)	O3—S2—C16—C15	-170.67 (14)
C1—C5—C6—C7	-177.1 (2)	O1—S2—C16—C15	-50.48 (17)
C4—C5—C6—C7	3.0 (3)	O2—S2—C16—C17	-108.10 (16)
C5—C6—C7—C8	178.9 (2)	O3—S2—C16—C17	11.80 (18)
C6—C7—C8—C9	175.6 (2)	O1—S2—C16—C17	131.99 (16)
C6—C7—C8—S1	-3.7 (3)	C15—C16—C17—C18	0.7 (3)
C11—S1—C8—C9	1.40 (18)	S2—C16—C17—C18	178.16 (14)
C11—S1—C8—C7	-179.3 (2)	C16—C17—C18—C13	0.3 (3)
C7—C8—C9—C10	178.64 (19)	C14—C13—C18—C17	-1.0 (3)
S1—C8—C9—C10	-2.0 (2)	C19—C13—C18—C17	177.30 (18)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C2—H2A···O3 ⁱ	0.93	2.31	3.219 (3)	166
C3—H3A···O1 ⁱⁱ	0.93	2.49	3.168 (2)	130
C6—H6A···O2	0.93	2.56	3.378 (3)	147
C11—H11A···O1 ⁱⁱⁱ	0.93	2.54	3.303 (3)	139
C12—H12A···O1 ⁱ	0.96	2.52	3.455 (3)	165
C12—H12C···O1 ⁱⁱ	0.96	2.47	3.341 (3)	151
C15—H15A···O2 ^{iv}	0.93	2.42	3.272 (2)	152
C17—H17A···O3 ⁱ	0.93	2.43	3.202 (2)	141
C4—H4A···Cg1 ^v	0.93	2.62	3.431 (2)	145
C10—H10A···Cg1 ^{vi}	0.93	2.95	3.666 (3)	135

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z+1$; (iii) $-x+1, -y+2, -z$; (iv) $-x+1, -y+1, -z$; (v) $-x, -y+1, -z+1$; (vi) $x-1, y+1, z$.

Fig. 1

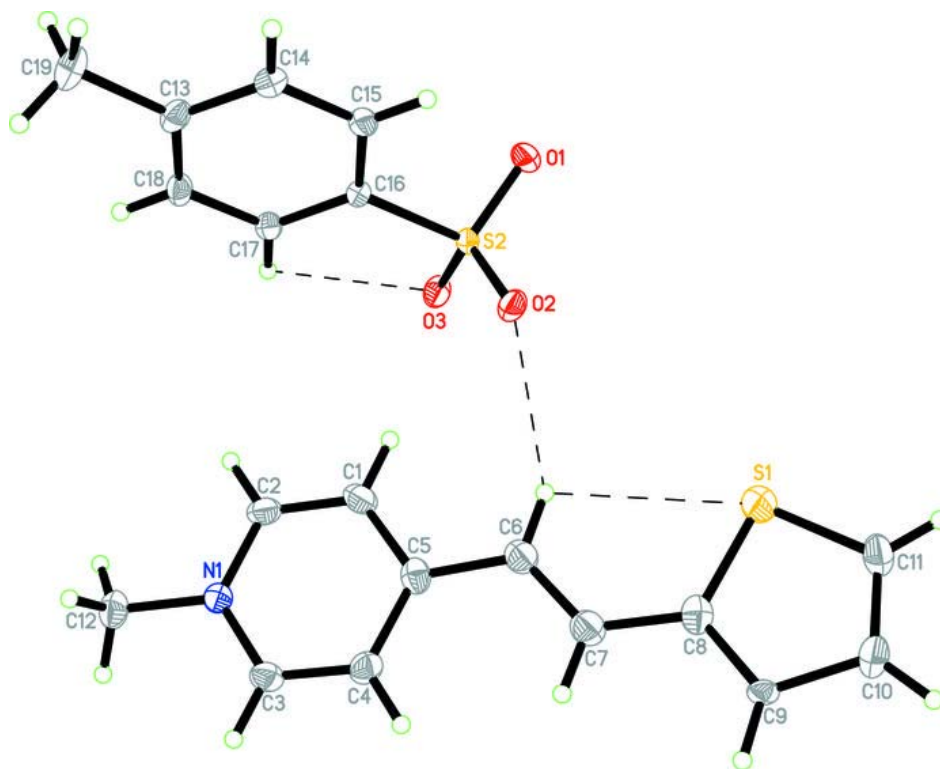
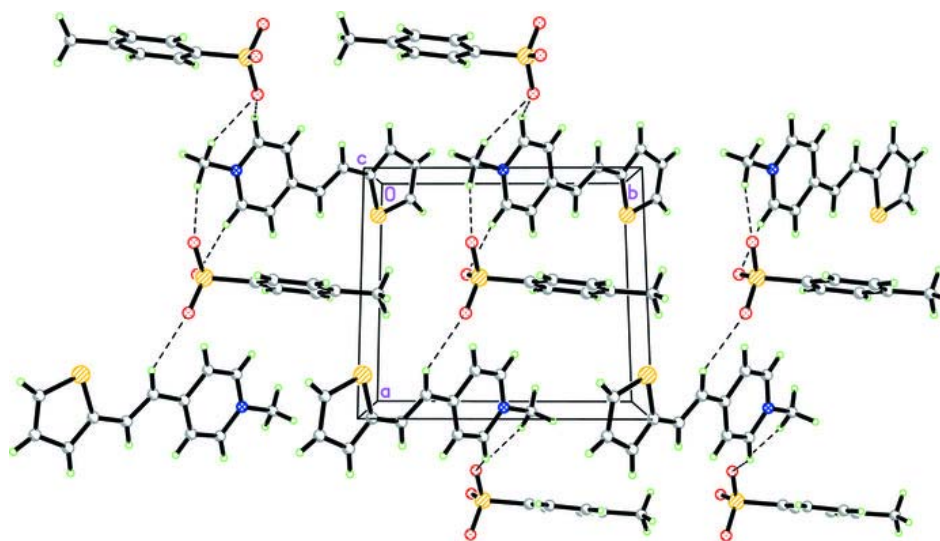


Fig. 2



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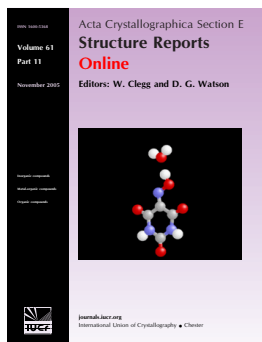
Editors: W.T.A. Harrison, J. Simpson and
M. Weil

1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]quinolinium 4-bromobenzenesulfonate

Hoong-Kun Fun, Thawanrat Kobkeatthawin and Suchada Chantrapromma

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1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]-quinolinium 4-bromobenzenesulfonate

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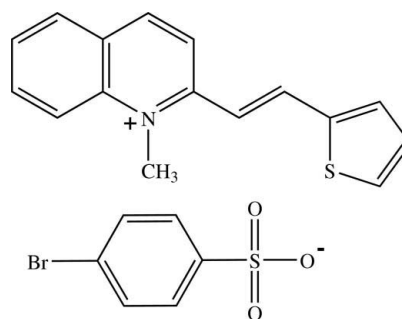
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.035; wR factor = 0.089; data-to-parameter ratio = 22.2.

In the title compound, $\text{C}_{16}\text{H}_{14}\text{NS}^+ \cdot \text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$, the cation exists in an *E* configuration and is essentially planar, the dihedral angle between the quinolinium and thiophene rings being $3.45(9)^\circ$. The anion is inclined to the cation with dihedral angles of $75.43(8)$ and $72.03(11)^\circ$, respectively between the benzene ring and the quinolinium and thiophene rings. In the crystal, the cations and anions are arranged individually into separate chains along the *c* axis. The cation chains are stacked in an antiparallel manner along the *a* axis by $\pi \cdots \pi$ interactions with centroid-centroid distances of $3.7257(13)$ and $3.7262(14)$ Å. Weak $\text{C}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \pi$ interactions link the cations and anions into a three-dimensional network. Short $\text{Br} \cdots \text{S}$ [$3.7224(5)$ Å] and $\text{Br} \cdots \text{O}$ [$3.4267(16)$ Å] contacts are also observed.

Related literature

For bond-length data, see: Allen *et al.* (1987). For background to non-linear optical materials research, see: Chantrapromma *et al.* (2009*a,b*), Fun *et al.* (2009); Raimundo *et al.* (2002). For related structures, see: Chantrapromma *et al.* (2006); Ruanwas *et al.* (2008). For the stability of the temperature controller used in the data collection, see Cosier & Glazer, (1986).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{14}\text{NS}^+ \cdot \text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$
 $M_r = 488.41$
 Monoclinic, $P2_1/c$
 $a = 7.9026(1)$ Å
 $b = 18.8211(2)$ Å
 $c = 13.4816(1)$ Å
 $\beta = 93.292(1)^\circ$
 $V = 2001.89(4)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.29$ mm⁻¹
 $T = 100$ K
 $0.34 \times 0.32 \times 0.24$ mm

Data collection

Bruker APEXII CCD area detector
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.511$, $T_{\max} = 0.612$
 51446 measured reflections
 5827 independent reflections
 5163 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.089$
 $S = 1.12$
 5827 reflections
 263 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 1.18$ e Å⁻³
 $\Delta\rho_{\min} = -0.46$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$Cg4$ is the centroid of the C17–C22 benzene ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C3–H3A \cdots O3 ⁱ	0.93	2.51	3.409 (3)	162
C7–H7A \cdots O1 ⁱⁱ	0.93	2.47	3.241 (3)	140
C8–H8A \cdots O2 ⁱⁱⁱ	0.93	2.29	3.218 (3)	175
C10–H10A \cdots S1	0.93	2.77	3.185 (2)	108
C11–H11A \cdots O2 ⁱⁱⁱ	0.93	2.31	3.238 (3)	176
C15–H15A \cdots O3 ^{iv}	0.93	2.40	3.265 (3)	154
C16–H16B \cdots O1 ^v	0.96	2.43	3.321 (3)	155
C17–H17A \cdots O1	0.93	2.54	2.915 (3)	105
C20–H20A \cdots O1 ^{vi}	0.93	2.32	3.242 (3)	172
C13–H13A \cdots Cg4 ⁱⁱⁱ	0.93	2.57	3.434 (2)	155

Symmetry codes: (i) $x, y, z + 1$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x - 1, y, z$; (v) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $x + 1, y, z$.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2736).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bruker (2005). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chantrapromma, S., Chanawanno, K. & Fun, H.-K. (2009a). *Acta Cryst. E65*, o1144–o1145.
- Chantrapromma, S., Chanawanno, K. & Fun, H.-K. (2009b). *Acta Cryst. E65*, o3115–o3116.
- Chantrapromma, S., Ruanwas, P., Fun, H.-K. & Patil, P. S. (2006). *Acta Cryst. E62*, o5494–o5496.
- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
- Fun, H.-K., Surasit, C., Chanawanno, K. & Chantrapromma, S. (2009). *Acta Cryst. E65*, o2633–o2634.
- Raimundo, J.-M., Blanchard, P., Planas, N. G., Mercier, N., Rak, I. L., Hierle, R. & Roncali, J. (2002). *J. Org. Chem.* **67**, 205–218.
- Ruanwas, P., Kobkeathawin, T., Chantrapromma, S., Fun, H.-K. & Karalai, C. (2008). *Acta Cryst. E64*, o1453–o1454.
- Sheldrick, G. M. (2008). *Acta Cryst. A64*, 112–122.
- Spek, A. L. (2009). *Acta Cryst. D65*, 148–155.

supplementary materials

Acta Cryst. (2010). E66, o1053-o1054 [doi:10.1107/S1600536810007488]

1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]quinolinium 4-bromobenzenesulfonate

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Comment

During the course of our NLO (non-linear optical) materials research, we have previously reported the crystal structures of the NLO-active compounds (Chantrapromma *et al.*, 2009*a, b*; Fun *et al.*, 2009). With the knowledge that the organic dipolar compounds with extended π systems and having terminal donor and acceptor groups are likely to exhibit large hyperpolarizability (β) (Raimundo *et al.*, 2002), the title compound (I) was designed and synthesized in order to study its NLO properties. Unfortunately (I) crystallizes out in a centrosymmetric $P2_1/c$ space group which precluded the second-order nonlinear optical properties.

The asymmetric unit of the title compound (Fig. 1) consists of the $C_{16}H_{14}NS^+$ cation and $C_6H_4BrO_3S^-$ anion. The cation exists in the *E* configuration with respect to the C10=C11 double bond [1.348 (3) Å] and is essentially planar with the dihedral angle between the quinolinium and the thiophene rings being 3.45 (9)° and the torsion angles C9–C10–C11–C12 = -179.8 (2)°. The ten non-H atoms of quinolinium unit lie on the same plane with an r.m.s. deviation of 0.0184 (2) Å. The relative arrangement of cation and anion is shown by the angles between the mean plane of the 4-bromophenyl ring and those of the quinolinium and thiophene rings which are 75.43 (8)° and 72.03 (11)°, respectively. The bond lengths are normal (Allen *et al.*, 1987) and are comparable with those in related structures (Chantrapromma *et al.*, 2006; Ruanwas *et al.*, 2008).

In the crystal, all O atoms of sulfonate group are involved in weak C—H \cdots O interactions (Table 1). The cations and anions are arranged individually into chains along the *c* axis (Fig. 2). The cation chains are stacked in an antiparallel manner along the *a* axis by π – π interactions with $Cg_1\cdots Cg_2 = 3.7257$ (13) Å (symmetry code: -x, -y, 1-z) and $Cg_1\cdots Cg_3 = 3.7262$ (14) Å (symmetry code: 1-x, -y, 1-z); Cg_1 , Cg_2 and Cg_3 are the centroids of the S1/C12–C15, N1/C1/C6–C9 and C1–C6 rings, respectively. Weak C—H \cdots O and C—H \cdots π interactions (Table 1) link the cations and anions into a three-dimensional network; Cg_4 is the centroid of the C17–C22 benzene ring. Short Br \cdots S [3.7224 (5) Å] and Br \cdots O [3.4267 (16) Å] contacts (symmetry code for both: 1+x, 1/2-y, 1/2+z) are also observed.

Experimental

2-(2-Thiophenestyryl)-1-methylquinolinium iodide (compound A) was synthesized by mixing a solution (1:1:1 molar ratio) of 1,2-dimethylquinolinium iodide (2.00 g, 7.0 mmol), 2-thiophenecarboxaldehyde (0.64 ml, 7.0 mmol) and piperidine (0.69 ml, 7.0 mmol) in hot methanol (40 ml). The resulting solution was refluxed for 5 h under nitrogen atmosphere. The resultant solid was filtered off and washed with diethyl ether. Silver(I)4-bromobenzenesulfonate (compound B) was synthesized according to our previously reported procedure. (Chantrapromma *et al.*, 2006). The title compound was synthesized by mixing compound A (0.10 g, 0.26 mmol) in hot methanol (50 ml) and compound B (0.09 g, 0.26 mmol) in hot methanol (20 ml). The mixture immediately yielded a grey precipitate of silver iodide. After stirring the mixture for ca. 45 min, the precipitate was removed and the resulting solution was evaporated yielding a brown solid. Brown block-shaped single crystals of the title compound suitable for x-ray diffraction analysis were recrystallized from methanol solvent by slow evaporation at room temperature over a few weeks. (Mp. 538–539 K).

Refinement

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with $d(\text{C-H}) = 0.93 \text{ \AA}$ for aromatic and CH and 0.96 \AA for CH_3 atoms. The U_{iso} values were constrained to be $1.5U_{\text{eq}}$ of the carrier atom for methyl H atoms and $1.2U_{\text{eq}}$ for the remaining H atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at 0.75 \AA from Br1 and the deepest hole is located at 0.55 \AA from S1.

Figures

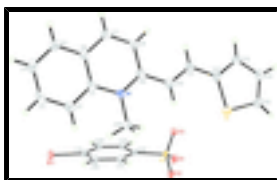


Fig. 1. The molecular structure of the title compound, with 50% probability displacement ellipsoids and the atom-numbering scheme.

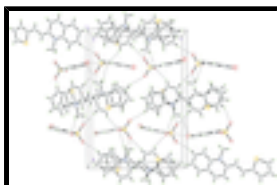


Fig. 2. The crystal packing of the title compound viewed down the a axis. Hydrogen bonds and weak $\text{C—H}\cdots\text{O}$ interactions are shown as dashed lines.

1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]quinolinium 4-bromobenzenesulfonate

Crystal data

$\text{C}_{16}\text{H}_{14}\text{NS}^+ \cdot \text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$

$M_r = 488.41$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 7.9026 (1) \text{ \AA}$

$b = 18.8211 (2) \text{ \AA}$

$c = 13.4816 (1) \text{ \AA}$

$\beta = 93.292 (1)^\circ$

$V = 2001.89 (4) \text{ \AA}^3$

$Z = 4$

$F(000) = 992$

$D_x = 1.620 \text{ Mg m}^{-3}$

Melting point = $538\text{--}539 \text{ K}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5827 reflections

$\theta = 2.2\text{--}30.0^\circ$

$\mu = 2.29 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, brown

$0.34 \times 0.32 \times 0.24 \text{ mm}$

Data collection

Bruker APEXII CCD area detector diffractometer

Radiation source: sealed tube

graphite

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\text{min}} = 0.511$, $T_{\text{max}} = 0.612$

5827 independent reflections

5163 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 2.2^\circ$

$h = -11 \rightarrow 11$

$k = -26 \rightarrow 26$

51446 measured reflections

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.035$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.089$

H-atom parameters constrained

$S = 1.12$

$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 3.2344P]$

5827 reflections

where $P = (F_o^2 + 2F_c^2)/3$

263 parameters

$(\Delta/\sigma)_{\max} = 0.001$

0 restraints

$\Delta\rho_{\max} = 1.18 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.00270 (7)	0.06224 (3)	0.28565 (4)	0.02261 (11)
N1	0.3667 (2)	0.04462 (9)	0.63104 (13)	0.0179 (3)
C1	0.4567 (3)	0.03115 (11)	0.72171 (15)	0.0178 (4)
C2	0.4926 (3)	0.08556 (12)	0.79170 (16)	0.0219 (4)
H2A	0.4584	0.1320	0.7780	0.026*
C3	0.5783 (3)	0.06935 (13)	0.87999 (17)	0.0246 (4)
H3A	0.6020	0.1053	0.9260	0.030*
C4	0.6314 (3)	-0.00053 (14)	0.90275 (17)	0.0257 (5)
H4A	0.6896	-0.0104	0.9631	0.031*
C5	0.5967 (3)	-0.05415 (12)	0.83528 (16)	0.0220 (4)
H5A	0.6308	-0.1004	0.8501	0.026*
C6	0.5094 (3)	-0.03885 (11)	0.74348 (15)	0.0185 (4)
C7	0.4708 (3)	-0.09311 (11)	0.67292 (16)	0.0198 (4)
H7A	0.5081	-0.1393	0.6856	0.024*
C8	0.3799 (3)	-0.07819 (11)	0.58700 (16)	0.0204 (4)

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H8A	0.3542	-0.1143	0.5415	0.025*
C9	0.3237 (3)	-0.00778 (11)	0.56601 (15)	0.0179 (4)
C10	0.2217 (3)	0.00785 (12)	0.47635 (16)	0.0217 (4)
H10A	0.1787	0.0537	0.4692	0.026*
C11	0.1837 (3)	-0.03853 (11)	0.40215 (16)	0.0197 (4)
H11A	0.2259	-0.0845	0.4089	0.024*
C12	0.0821 (3)	-0.02164 (11)	0.31320 (16)	0.0197 (4)
C13	0.0397 (3)	-0.06890 (11)	0.23773 (17)	0.0210 (4)
H13A	0.0709	-0.1166	0.2387	0.025*
C14	-0.0574 (3)	-0.03622 (13)	0.15811 (18)	0.0261 (5)
H14A	-0.0965	-0.0603	0.1010	0.031*
C15	-0.0870 (3)	0.03424 (13)	0.17442 (18)	0.0258 (5)
H15A	-0.1489	0.0635	0.1301	0.031*
C16	0.3192 (3)	0.11898 (12)	0.60670 (18)	0.0254 (5)
H16A	0.3170	0.1256	0.5360	0.038*
H16B	0.4009	0.1507	0.6383	0.038*
H16C	0.2091	0.1288	0.6300	0.038*
Br1	1.28408 (3)	0.278131 (13)	0.464999 (17)	0.02491 (7)
S2	0.66919 (6)	0.23502 (2)	0.13641 (3)	0.01276 (9)
O1	0.51250 (19)	0.23380 (8)	0.18823 (12)	0.0197 (3)
O2	0.6865 (2)	0.29873 (8)	0.07625 (11)	0.0202 (3)
O3	0.7004 (2)	0.16993 (8)	0.08184 (11)	0.0211 (3)
C17	0.8027 (3)	0.25412 (11)	0.32873 (15)	0.0177 (4)
H17A	0.6913	0.2560	0.3474	0.021*
C18	0.9364 (3)	0.26436 (12)	0.39958 (15)	0.0203 (4)
H18A	0.9153	0.2731	0.4656	0.024*
C19	1.1011 (3)	0.26130 (11)	0.36972 (15)	0.0174 (4)
C20	1.1376 (3)	0.24670 (11)	0.27242 (16)	0.0173 (4)
H20A	1.2492	0.2436	0.2544	0.021*
C21	1.0033 (3)	0.23684 (10)	0.20250 (15)	0.0161 (4)
H21A	1.0251	0.2274	0.1367	0.019*
C22	0.8362 (2)	0.24106 (10)	0.23020 (14)	0.0141 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0243 (3)	0.0173 (2)	0.0262 (3)	0.00428 (19)	0.0006 (2)	0.00228 (19)
N1	0.0176 (8)	0.0160 (8)	0.0201 (8)	-0.0014 (6)	0.0019 (6)	-0.0001 (6)
C1	0.0151 (9)	0.0204 (9)	0.0182 (9)	-0.0018 (7)	0.0033 (7)	-0.0004 (7)
C2	0.0207 (10)	0.0209 (10)	0.0243 (10)	-0.0012 (8)	0.0026 (8)	-0.0038 (8)
C3	0.0239 (11)	0.0281 (11)	0.0220 (10)	-0.0047 (9)	0.0020 (8)	-0.0083 (8)
C4	0.0229 (11)	0.0358 (12)	0.0183 (10)	-0.0039 (9)	0.0000 (8)	0.0013 (9)
C5	0.0206 (10)	0.0230 (10)	0.0226 (10)	-0.0011 (8)	0.0026 (8)	0.0053 (8)
C6	0.0170 (9)	0.0211 (10)	0.0177 (9)	-0.0025 (7)	0.0035 (7)	0.0001 (7)
C7	0.0218 (10)	0.0154 (9)	0.0222 (10)	-0.0007 (7)	0.0026 (8)	0.0016 (7)
C8	0.0235 (10)	0.0160 (9)	0.0217 (10)	-0.0026 (8)	0.0013 (8)	-0.0030 (7)
C9	0.0176 (9)	0.0173 (9)	0.0189 (9)	-0.0023 (7)	0.0027 (7)	0.0001 (7)
C10	0.0237 (10)	0.0192 (9)	0.0221 (10)	0.0007 (8)	0.0007 (8)	0.0001 (8)

C11	0.0191 (10)	0.0179 (9)	0.0222 (10)	0.0000 (7)	0.0021 (8)	0.0020 (7)
C12	0.0178 (9)	0.0180 (9)	0.0232 (10)	0.0002 (7)	0.0002 (8)	0.0040 (8)
C13	0.0195 (10)	0.0158 (9)	0.0279 (11)	-0.0001 (7)	0.0024 (8)	0.0010 (8)
C14	0.0260 (11)	0.0250 (11)	0.0266 (11)	-0.0017 (9)	-0.0039 (9)	0.0001 (9)
C15	0.0219 (10)	0.0273 (11)	0.0274 (11)	0.0046 (9)	-0.0056 (8)	0.0065 (9)
C16	0.0293 (11)	0.0152 (9)	0.0310 (11)	-0.0001 (8)	-0.0046 (9)	-0.0004 (8)
Br1	0.02009 (11)	0.03105 (12)	0.02239 (11)	-0.00586 (8)	-0.00934 (8)	0.00605 (8)
S2	0.0121 (2)	0.0129 (2)	0.01296 (19)	-0.00040 (15)	-0.00194 (15)	0.00143 (15)
O1	0.0130 (7)	0.0228 (7)	0.0230 (7)	-0.0007 (5)	-0.0006 (5)	0.0033 (6)
O2	0.0221 (7)	0.0189 (7)	0.0193 (7)	-0.0012 (6)	-0.0031 (6)	0.0072 (6)
O3	0.0228 (7)	0.0187 (7)	0.0211 (7)	0.0018 (6)	-0.0048 (6)	-0.0048 (6)
C17	0.0147 (9)	0.0231 (10)	0.0156 (9)	-0.0020 (7)	0.0022 (7)	0.0008 (7)
C18	0.0206 (10)	0.0269 (10)	0.0132 (8)	-0.0032 (8)	-0.0004 (7)	0.0011 (7)
C19	0.0141 (9)	0.0196 (9)	0.0178 (9)	-0.0032 (7)	-0.0058 (7)	0.0041 (7)
C20	0.0118 (8)	0.0178 (9)	0.0221 (9)	0.0002 (7)	-0.0001 (7)	0.0030 (7)
C21	0.0153 (9)	0.0168 (9)	0.0164 (8)	-0.0001 (7)	0.0016 (7)	0.0003 (7)
C22	0.0138 (8)	0.0123 (8)	0.0160 (8)	-0.0005 (6)	-0.0014 (7)	0.0008 (6)

Geometric parameters (Å, °)

S1—C15	1.705 (2)	C12—C13	1.378 (3)
S1—C12	1.731 (2)	C13—C14	1.423 (3)
N1—C9	1.350 (3)	C13—H13A	0.9300
N1—C1	1.402 (3)	C14—C15	1.367 (3)
N1—C16	1.481 (3)	C14—H14A	0.9300
C1—C6	1.407 (3)	C15—H15A	0.9300
C1—C2	1.410 (3)	C16—H16A	0.9600
C2—C3	1.370 (3)	C16—H16B	0.9600
C2—H2A	0.9300	C16—H16C	0.9600
C3—C4	1.409 (4)	Br1—C19	1.9050 (19)
C3—H3A	0.9300	S2—O1	1.4565 (16)
C4—C5	1.376 (3)	S2—O3	1.4572 (15)
C4—H4A	0.9300	S2—O2	1.4585 (15)
C5—C6	1.412 (3)	S2—C22	1.778 (2)
C5—H5A	0.9300	C17—C22	1.391 (3)
C6—C7	1.417 (3)	C17—C18	1.396 (3)
C7—C8	1.357 (3)	C17—H17A	0.9300
C7—H7A	0.9300	C18—C19	1.385 (3)
C8—C9	1.421 (3)	C18—H18A	0.9300
C8—H8A	0.9300	C19—C20	1.387 (3)
C9—C10	1.444 (3)	C20—C21	1.391 (3)
C10—C11	1.348 (3)	C20—H20A	0.9300
C10—H10A	0.9300	C21—C22	1.395 (3)
C11—C12	1.440 (3)	C21—H21A	0.9300
C11—H11A	0.9300		
C15—S1—C12	91.95 (11)	C12—C13—C14	112.1 (2)
C9—N1—C1	122.04 (18)	C12—C13—H13A	124.0
C9—N1—C16	119.69 (18)	C14—C13—H13A	124.0
C1—N1—C16	118.27 (18)	C15—C14—C13	112.8 (2)

supplementary materials

N1—C1—C6	118.71 (18)	C15—C14—H14A	123.6
N1—C1—C2	121.65 (19)	C13—C14—H14A	123.6
C6—C1—C2	119.6 (2)	C14—C15—S1	112.02 (17)
C3—C2—C1	119.4 (2)	C14—C15—H15A	124.0
C3—C2—H2A	120.3	S1—C15—H15A	124.0
C1—C2—H2A	120.3	N1—C16—H16A	109.5
C2—C3—C4	121.6 (2)	N1—C16—H16B	109.5
C2—C3—H3A	119.2	H16A—C16—H16B	109.5
C4—C3—H3A	119.2	N1—C16—H16C	109.5
C5—C4—C3	119.7 (2)	H16A—C16—H16C	109.5
C5—C4—H4A	120.2	H16B—C16—H16C	109.5
C3—C4—H4A	120.2	O1—S2—O3	113.71 (9)
C4—C5—C6	119.9 (2)	O1—S2—O2	112.89 (9)
C4—C5—H5A	120.0	O3—S2—O2	112.74 (9)
C6—C5—H5A	120.0	O1—S2—C22	106.05 (9)
C1—C6—C5	119.8 (2)	O3—S2—C22	105.82 (9)
C1—C6—C7	119.02 (19)	O2—S2—C22	104.69 (9)
C5—C6—C7	121.1 (2)	C22—C17—C18	119.99 (19)
C8—C7—C6	120.5 (2)	C22—C17—H17A	120.0
C8—C7—H7A	119.8	C18—C17—H17A	120.0
C6—C7—H7A	119.8	C19—C18—C17	118.81 (19)
C7—C8—C9	120.48 (19)	C19—C18—H18A	120.6
C7—C8—H8A	119.8	C17—C18—H18A	120.6
C9—C8—H8A	119.8	C18—C19—C20	122.23 (18)
N1—C9—C8	119.19 (19)	C18—C19—Br1	119.13 (16)
N1—C9—C10	120.16 (19)	C20—C19—Br1	118.64 (15)
C8—C9—C10	120.65 (19)	C19—C20—C21	118.37 (18)
C11—C10—C9	125.4 (2)	C19—C20—H20A	120.8
C11—C10—H10A	117.3	C21—C20—H20A	120.8
C9—C10—H10A	117.3	C20—C21—C22	120.55 (18)
C10—C11—C12	124.4 (2)	C20—C21—H21A	119.7
C10—C11—H11A	117.8	C22—C21—H21A	119.7
C12—C11—H11A	117.8	C17—C22—C21	120.02 (18)
C13—C12—C11	124.9 (2)	C17—C22—S2	121.09 (15)
C13—C12—S1	111.13 (16)	C21—C22—S2	118.77 (15)
C11—C12—S1	123.91 (17)		
C9—N1—C1—C6	2.6 (3)	C9—C10—C11—C12	-179.8 (2)
C16—N1—C1—C6	-177.04 (19)	C10—C11—C12—C13	-178.7 (2)
C9—N1—C1—C2	-176.27 (19)	C10—C11—C12—S1	3.4 (3)
C16—N1—C1—C2	4.1 (3)	C15—S1—C12—C13	0.22 (18)
N1—C1—C2—C3	178.8 (2)	C15—S1—C12—C11	178.3 (2)
C6—C1—C2—C3	0.0 (3)	C11—C12—C13—C14	-178.2 (2)
C1—C2—C3—C4	-0.1 (3)	S1—C12—C13—C14	-0.1 (2)
C2—C3—C4—C5	-0.1 (4)	C12—C13—C14—C15	-0.2 (3)
C3—C4—C5—C6	0.5 (3)	C13—C14—C15—S1	0.3 (3)
N1—C1—C6—C5	-178.50 (18)	C12—S1—C15—C14	-0.3 (2)
C2—C1—C6—C5	0.4 (3)	C22—C17—C18—C19	0.1 (3)
N1—C1—C6—C7	0.4 (3)	C17—C18—C19—C20	-1.6 (3)
C2—C1—C6—C7	179.31 (19)	C17—C18—C19—Br1	178.06 (16)

C4—C5—C6—C1	-0.6 (3)	C18—C19—C20—C21	1.8 (3)
C4—C5—C6—C7	-179.5 (2)	Br1—C19—C20—C21	-177.86 (15)
C1—C6—C7—C8	-2.0 (3)	C19—C20—C21—C22	-0.5 (3)
C5—C6—C7—C8	176.9 (2)	C18—C17—C22—C21	1.2 (3)
C6—C7—C8—C9	0.7 (3)	C18—C17—C22—S2	-174.80 (16)
C1—N1—C9—C8	-3.9 (3)	C20—C21—C22—C17	-1.0 (3)
C16—N1—C9—C8	175.7 (2)	C20—C21—C22—S2	175.11 (15)
C1—N1—C9—C10	176.08 (19)	O1—S2—C22—C17	-9.57 (19)
C16—N1—C9—C10	-4.3 (3)	O3—S2—C22—C17	-130.66 (17)
C7—C8—C9—N1	2.2 (3)	O2—S2—C22—C17	110.03 (17)
C7—C8—C9—C10	-177.8 (2)	O1—S2—C22—C21	174.37 (15)
N1—C9—C10—C11	173.8 (2)	O3—S2—C22—C21	53.28 (18)
C8—C9—C10—C11	-6.2 (3)	O2—S2—C22—C21	-66.04 (17)

Hydrogen-bond geometry (\AA , $^\circ$)

Cg4 is the centroid of the C17—C22 benzene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3A \cdots O3 ⁱ	0.93	2.51	3.409 (3)	162
C7—H7A \cdots O1 ⁱⁱ	0.93	2.47	3.241 (3)	140
C8—H8A \cdots O2 ⁱⁱⁱ	0.93	2.29	3.218 (3)	175
C10—H10A \cdots S1	0.93	2.77	3.185 (2)	108
C11—H11A \cdots O2 ⁱⁱⁱ	0.93	2.31	3.238 (3)	176
C15—H15A \cdots O3 ^{iv}	0.93	2.40	3.265 (3)	154
C16—H16B \cdots O1 ^v	0.96	2.43	3.321 (3)	155
C17—H17A \cdots O1	0.93	2.54	2.915 (3)	105
C20—H20A \cdots O1 ^{vi}	0.93	2.32	3.242 (3)	172
C13—H13A \cdots Cg4 ⁱⁱⁱ	0.93	2.57	3.434 (2)	155

Symmetry codes: (i) $x, y, z+1$; (ii) $-x+1, -y, -z+1$; (iii) $-x+1, y-1/2, -z+1/2$; (iv) $x-1, y, z$; (v) $x, -y+1/2, z+1/2$; (vi) $x+1, y, z$.

Fig. 1

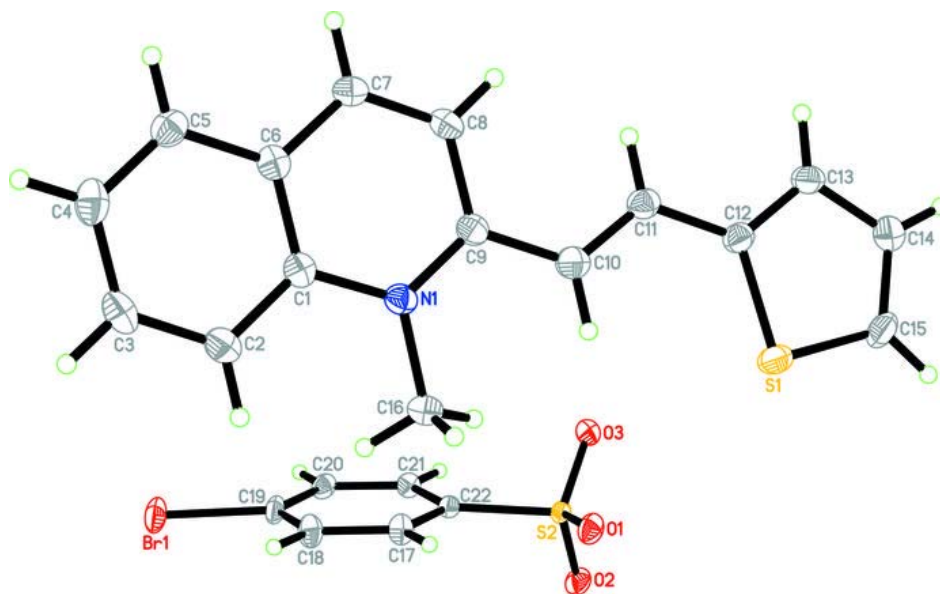
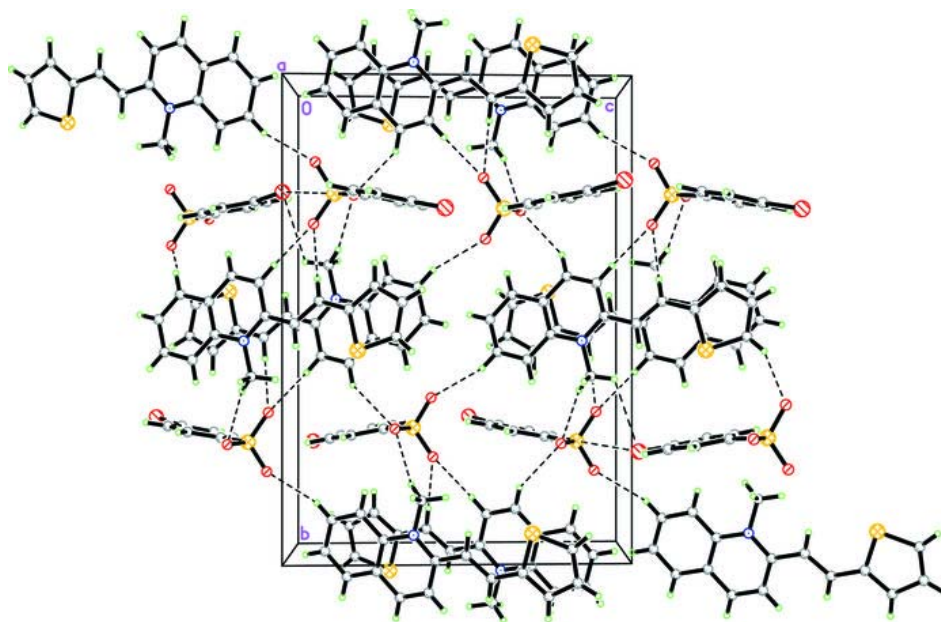


Fig. 2



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Original article

Synthesis, structure and *in vitro* antibacterial activities of new hybrid disinfectants quaternary ammonium compounds: Pyridinium and quinolinium stilbene benzenesulfonates

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ABSTRACT

The series of pyridinium (**1–10**) and quinolinium (**11–20**) stilbene benzenesulfonates have been synthesized and their structures were investigated by UV–vis, FT-IR and ¹H NMR spectroscopy. In addition, compound **5** was also determined by single crystal X-ray diffraction technique. The antibacterial activity of the synthesized compounds against both Gram-positive and Gram-negative bacteria has been determined. The quinolinium derivatives exhibited two very potent characteristic activities, namely, (i) specific activity to Methicillin-Resistant *Staphylococcus aureus* and (ii) with broad band spectrum activity. Compounds **11**, **13** and **14** are the most active showing broad spectrum antibacterial activity against Gram-positive (Methicillin-Resistant *S. aureus*, *S. aureus*, *Bacillus subtilis*, Vancomycin-Resistant *Enterococcus faecalis* and *E. faecalis*) and Gram-negative bacterium (*Shigella sonnei*). The MICs of these compounds were found to be better than that of Benzalkonium chloride (BZK), the commercially used disinfectant.

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1. Introduction

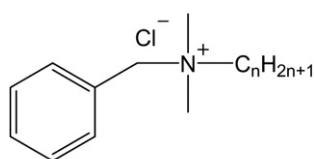
The discovery of an alarming growth rate of bacterial resistance phenomena against common antibacterial agents has limited the use of commercial disinfectants [1]. In the field of synthetic chemistry, numerous studies of the synthesis and antimicrobial characteristics of quaternary ammonium compounds (QACs) have been used since 1935 [2]. Among these compounds, pyridinium and quinolinium salts represent the important groups of chemicals widely used as biocides, drugs and herbicides [3,4]. Disinfectants based on this class are widely used in hospital environments and in the food industry due to their low toxicity to humans and animals and to their wide antimicrobial spectra [5,6]. Benzalkonium chloride (BZK; Fig. 1) is the quaternary ammonium disinfectant which consisted of a mixture of alkylbenzyltrimethylammonium chlorides of various alkyl chain lengths and usually used as a biocide. BZK solutions are rapidly-acting biocidal agents with a moderately long

duration of action. They are mostly active against bacteria, viruses, fungi, and protozoa. Gram-positive bacteria are generally more susceptible to BZK than Gram-negative [7]. However, the allergic problems reported worldwide [8,9] and the BZK-resistant bacteria [10–14] have restricted the use of this agent.

Among the various structure types of QAC, stilbene derivative seem to be an effective candidate according to the literature which suggested that the aminated stilbenes possess some pharmacological properties and biological role in plant defense against pathogens [15]. Moreover, introducing new molecular parameters such as heteroatoms [16], chemical functions [17,18] and aromatics [19] may lead to potential compounds which can overcome the increasing resistance phenomenon. There are numerous reports on antibacterial agents containing dimethylamino [20,21] and ethoxy [22,23] groups so these two groups were applied to our designed compounds.

In addition, the well-known antibacterial drugs sulfonamides also represented wide application in synthetic bioactive compounds for a long period of time [24,25]. These interesting features of QAC and sulfonamides led us to design and synthesize the hybrid disinfectant between QAC (pyridinium and quinolinium

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$n = 8, 10, 12, 14, 16, 18$

Fig. 1. The structure of the well-known quaternary ammonium disinfectant Benzalkonium chloride (BZK).

stilbene) and sulfonamide-like skeletons in order to study their antibacterial activities.

In this study, the series of twenty pyridinium (**1–10**) and quinolinium (**11–20**) stilbene benzenesulfonates (see Fig. 2) were designed and synthesized on the basis of the combination of two efficient chemophores which were (i) stilbene-QAC and (ii) sulfonamide-like structures. The purpose of this investigation was to elucidate the influence of the presence of pyridinium and quinolinium rings, as well as the ethoxy and dimethylamino substituents in the phenyl ring on the antibacterial activities of these compounds in order to acquire further information on the structural characteristics enhancing their activities. The antibacterial activities of the compounds have been screened *in vitro* against the tested pathogenic bacteria by microliter plate colorimetric assay.

2. Chemistry

2.1. Materials

Melting points were determined on the Fisher-Johns melting point apparatus. UV–vis spectra were obtained in the methanol solutions with a SPECORD S100 (Analytikjena) spectrometer in the range of 200–800 nm. FT-IR spectra were recorded in the 4000–400 cm^{-1} region with a PerkinElmer FT-IR System Spectrum BX spectrophotometer using KBr pellets. Elemental analyses were performed with a CE Instruments Flash 1112 Series EA CHNS-O Analyzer and were consistent with theoretical values within $\pm 0.4\%$.

^1H NMR spectra were recorded on a 300 MHz Bruker FT-NMR Ultra Shield™ spectrometers in DMSO- d_6 and CDCl_3 mixed solvent with TMS as the internal standard. Chemical shifts are reported in δ (ppm) and coupling constants (J) are expressed in Hertz.

All chemicals and solvents used for the synthesis were of reagent grade and used as received.

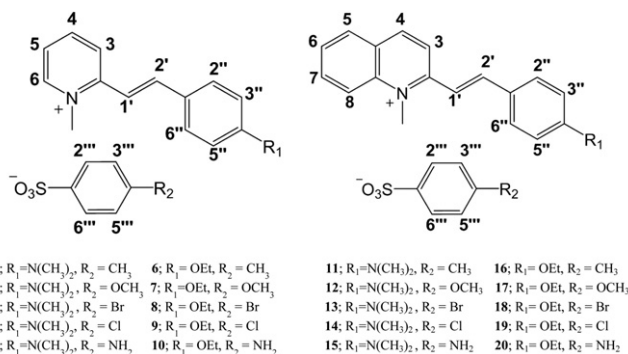


Fig. 2. Structure and ^1H designation of the synthesized pyridinium (**1–10**) and quinolinium (**11–20**) stilbene benzenesulfonates.

2.2. Synthesis of all pyridinium and quinolinium stilbene derivatives

The synthesis of compounds **PAM**, **PET**, **QAM**, **QET** and **1–20** are as following (Fig. 3).

2.2.1. (*E*)-2-(4-(dimethylamino)styryl)-1-methylpyridinium iodide (**PAM**)

(*E*)-2-(4-ethoxystyryl)-1-methylquinolinium iodide was synthesized by mixing a solution (1:1:1 mole ratio) of 1,2-dimethylpyridinium iodide (2.00 g, 8.5 mmol) which was synthesized by the previous method [26], 4-dimethylaminobenzaldehyde (1.27 g, 8.5 mmol) and piperidine (0.84 ml, 8.5 mmol) in hot methanol. The resulting red solution was refluxed for 6 h under nitrogen atmosphere. The resultant red solid was filtered off, washed with diethyl ether, dried *in vacuo* and purified by recrystallization. M.p. 273–274 °C, 1.92 g (61%) yield. UV (CH_3OH) λ_{max} (nm): 202.0, 219.0, 281.0, 461.0; IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{C}}$; 1559 s, $\nu_{\text{C}-\text{N}}$; 1370 s; ^1H NMR (d_6 -DMSO mixed with CDCl_3): δ 4.20 (s, 1- CH_3), 8.17 ($d, J = 7.5$, H-3), 8.27 ($d, J = 7.5$, H-4), 7.54 ($d, J = 7.5$, H-5), 8.63 ($d, J = 7.5$, H-6), 7.06 ($d, J = 15.6$, H-1'), 7.71 ($d, J = 15.6$, H-2'), 7.55 ($d, J = 8.4$, H-2'', H-6''), 6.60 ($d, J = 8.4$, H-3'', H-5''), 2.95 (s, N-(CH_3) $_2$). Anal. calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_2$: C, 52.47; H, 5.23; N, 7.65. Found: C, 52.31; H, 5.18; N, 7.88.

2.2.1.1. (*E*)-2-(4-(dimethylamino)styryl)-1-methylpyridinium 4-methylbenzenesulfonate (**1**). A 0.26 g (0.71 mmol) solution of **PAM** in hot methanol (50 ml) was mixed with 0.20 g (0.71 mmol) of silver (I) 4-methylbenzenesulfonate in hot methanol (50 ml). The mixture turned to deep red and cloudy immediately. After stirring for 30 min, the precipitate of silver iodide was filtered and the filtrate was evaporated to give a deep red solid. The resultant yellow solid was filtered off, washed with diethyl ether, dried *in vacuo* and purified by recrystallization. M.p. 195–196 °C, 0.21 g (71%) yield. UV (CH_3OH) λ_{max} (nm): 202.0, 219.0, 284.0, 462.0; IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{C}}$; 1591 s, $\nu_{\text{C}-\text{N}}$; $\nu_{\text{S}=\text{O}}$; 1195 s; 1440 s; ^1H NMR (d_6 -DMSO mixed with CDCl_3): δ 4.34 (s, 1- CH_3), 8.28 ($d, J = 7.2$, H-3), 8.25 ($t, J = 7.2$, H-4), 7.73 ($d, J = 7.2$, H-5), 8.78 ($d, J = 7.2$, H-6), 7.77 ($d, J = 15.3$, H-1'), 7.13 ($d, J = 15.3$, H-2'), 7.65 ($d, J = 7.5$, H-2'', H-6''), 7.10 ($d, J = 7.5$, H-3'', H-5''), 3.10 (s, N-(CH_3) $_2$), 7.70 ($d, J = 7.8$, H-2''', H-6''''), 6.70 ($d, J = 7.8$, H-3''', H-5'''), 2.32 (s, 4'''- CH_3). Anal. calcd. for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_3\text{S}$: C, 67.29; H, 6.38; N, 6.82; S, 7.82; O, 11.69. Found: C, 67.09; H, 6.48; N, 7.00; S, 7.72; O, 11.71.

Compounds **2–5** were synthesized with identical procedure of **1** by replacing silver (I) 4-methylbenzenesulfonate with silver (I) 4-methoxybenzenesulfonate (for **2**), silver (I) 4-bromobenzenesulfonate (for **3**), silver (I) 4-chlorobenzenesulfonate (for **4**), and silver (I) 4-aminobenzenesulfonate (for **5**). All of the resulting solids were further purified by recrystallization whereas silver (I) 4-substituted-benzenesulfonates were synthesized according to previously reported procedure [26–29].

2.2.1.2. (*E*)-2-(4-(dimethylamino)styryl)-1-methylpyridinium 4-methoxybenzenesulfonate (**2**). M.p. 175–176 °C, 0.25 g (89%) yield. UV (CH_3OH) λ_{max} (nm): 202.0, 229.0, 273.0, 461.0; IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{C}}$; 1596 s, $\nu_{\text{C}-\text{N}}$; 1207 s, $\nu_{\text{S}=\text{O}}$; 1189 s; ^1H NMR (d_6 -DMSO mixed with CDCl_3): δ 4.33 (s, 1- CH_3), 8.40 ($d, J = 8.1$, H-3), 8.29 ($t, J = 8.1$, H-4), 7.70 ($d, J = 8.1$, H-5), 8.77 ($d, J = 8.1$, H-6), 7.20 ($d, J = 15.6$, H-1'), 7.85 ($d, J = 15.6$, H-2'), 7.65 ($d, J = 8.7$, H-2'', H-6''), 7.64 ($d, J = 8.7$, H-3'', H-5''), 3.08 (s, N-(CH_3) $_2$), 6.81 ($d, J = 8.1$, H-2''', H-6''''), 6.74 ($d, J = 8.1$, H-3''', H-5'''), 3.78 (s, 4'''- OCH_3). Anal. calcd. for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4\text{S}$: C, 64.77; H, 6.14; N, 6.57; S, 7.52; O, 15.00. Found: C, 64.84; H, 6.20; N, 6.55; S, 7.50; O, 14.91.

2.2.1.3. (*E*)-2-(4-(dimethylamino)styryl)-1-methylpyridinium 4-bromobenzenesulfonate (**3**). M.p.(decompose) 280–281 °C, 0.25 g

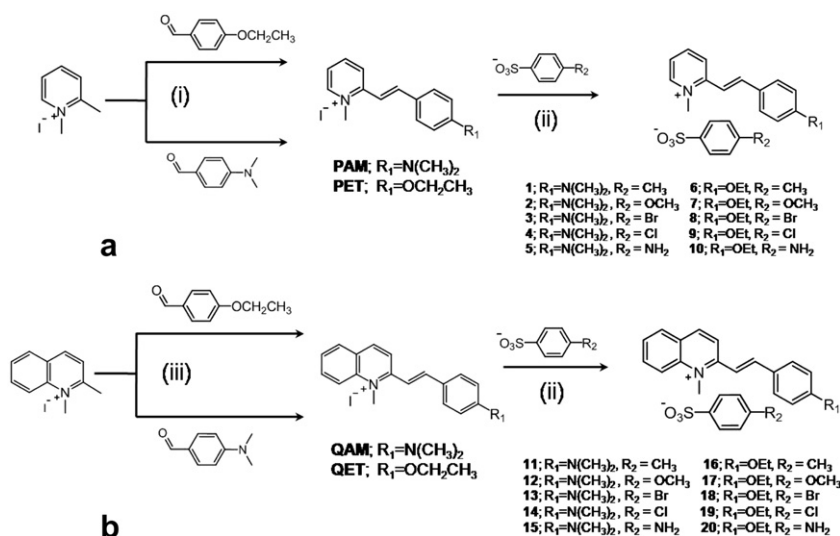


Fig. 3. Synthesis scheme of pyridinium stilbene derivatives (a) and quinolinium stilbene derivatives (b); (i)=MeOH, reflux, 50–55 °C, 4 h, N₂ atmosphere (**PET**) and 6 h (**PAM**), (ii)=MeOH, stir, 50 °C, 0.5 h (iii)=MeOH, reflux, 50–55 °C, 6 h, N₂ atmosphere (both **QET** and **QAM**).

(91%) yield. UV (CH₃OH) λ_{max} (nm): 203.0, 223.0, 461.0; IR (KBr, cm⁻¹): $\nu_{\text{C}=\text{C}}$; 1636 s, $\nu_{\text{C}-\text{N}}$; 1191 s, $\nu_{\text{S}} = \text{O}$; 1191 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.30 (s, 1-CH₃), 8.17 (d, *J* = 7.5, H-3), 8.17 (d, *J* = 7.5, H-4), 7.54 (d, *J* = 7.5, H-5), 8.66 (d, *J* = 7.5, H-6), 7.02 (d, *J* = 15.6, H-1'), 7.71 (d, *J* = 15.6, H-2'), 7.49 (d, *J* = 8.4, H-2'', H-6''), 6.60 (d, *J* = 8.4, H-3'', H-5''), 2.94 (s, N-(CH₃)₂), 7.56 (d, *J* = 8.7, H-2''', H-6'''), 6.82 (d, *J* = 8.7, H-3''', H-5'''). Anal. calcd. for C₂₂H₂₃BrN₂O₃S: C, 55.58; H, 4.88; N, 5.89; S, 6.74; O, 10.10. Found: C, 55.42; H, 4.89; N, 5.89; S, 6.70; O, 10.21.

2.2.1.4. (E)-2-(4-(dimethylamino)styryl)-1-methylpyridinium 4-chlorobenzenesulfonate (4). M.p. 243–244 °C, 0.22 g (79%) yield. UV (CH₃OH) λ_{max} (nm): 201.0, 223.0, 284.0, 462.0; IR (KBr, cm⁻¹): $\nu_{\text{C}=\text{C}}$; 1683 s, $\nu_{\text{C}-\text{N}}$; 1198 s, $\nu_{\text{S}} = \text{O}$; 1198 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.35 (s, 1-CH₃), 8.24 (d, *J* = 8.1, H-3), 8.30 (t, *J* = 8.1, H-4), 7.70 (t, *J* = 8.1, H-5), 8.74 (d, *J* = 8.1, H-6), 7.77 (d, *J* = 15.6, H-1'), 7.12 (d, *J* = 15.6, H-2'), 7.64 (d, *J* = 8.7, H-2'', H-6''), 6.73 (d, *J* = 8.7, H-3'', H-5''), 3.11 (s, N-(CH₃)₂), 7.78 (d, *J* = 8.4, H-2''', H-6'''), 7.28 (d, *J* = 8.4, H-3''', H-5'''). Anal. calcd. for C₂₂H₂₃ClN₂O₃S: C, 61.31; H, 5.38; N, 6.50; S, 7.44; O, 11.14. Found: C, 61.35; H, 5.36; N, 6.43; S, 7.49; O, 11.12.

2.2.1.5. (E)-2-(4-(dimethylamino)styryl)-1-methylpyridinium 4-aminobenzenesulfonate (5). M.p. 257–258 °C, 0.19 g (66%) yield. UV (CH₃OH) λ_{max} (nm): 204.0, 253.0, 461.0; IR (KBr, cm⁻¹): $\nu_{\text{C}=\text{C}}$; 1611 s, $\nu_{\text{C}-\text{N}}$; 1297 s, $\nu_{\text{S}} = \text{O}$; 1195 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.32 (s, 1-CH₃), 8.42 (d, *J* = 8.7, H-3), 8.31 (t, *J* = 8.7, H-4), 7.69 (d, *J* = 8.7, H-5), 8.77 (d, *J* = 8.7, H-6), 7.87 (d, *J* = 15.9, H-1'), 7.22 (d, *J* = 15.9, H-2'), 7.69 (d, *J* = 8.4, H-2'', H-6''), 7.37 (d, *J* = 8.4, H-3'', H-5''), 3.07 (s, N-(CH₃)₂), 6.75 (d, *J* = 8.1, H-2''', H-6'''), 6.48 (d, *J* = 8.1, H-3''', H-5'''). Anal. calcd. for C₂₂H₂₅N₃O₃S: C, 64.21; H, 6.12; N, 10.22; S, 7.79; O, 11.66. Found: C, 64.31; H, 6.09; N, 10.18; S, 7.90; O, 11.52.

2.2.2. (E)-2-(4-ethoxystyryl)-1-methylpyridinium iodide (**PET**)

(E)-2-(4-ethoxystyryl)-1-methylpyridinium iodide was synthesized by mixing a solution (1:1:1 mole ratio) of 1,2-dimethylpyridinium iodide (2.00 g, 8.5 mmol) which was synthesized by the previous method [26], 4-ethoxybenzaldehyde (1.16 ml, 8.5 mmol) and piperidine (0.84 ml, 8.5 mmol) in hot methanol. The resulting deep yellow solution was refluxed for 4 h under nitrogen atmosphere. The resultant yellow solid was filtered off, washed with

diethyl ether, dried in vacuo and purified by recrystallization. M.p. 208–210 °C, 2.08 g (66%) yield. UV (CH₃OH) λ_{max} (nm): 202.0, 218.0, 366.0; IR (KBr, cm⁻¹): $\nu_{\text{C}=\text{C}}$; 1601 s, $\nu_{\text{C}} = \text{O}$; 1237 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.44 (s, 1-CH₃), 8.40 (d, *J* = 8.7, H-3), 8.46 (t, *J* = 8.7, H-4), 7.74 (t, *J* = 8.7, H-5), 8.95 (d, *J* = 8.7, H-6), 7.41 (d, *J* = 15.9, H-1'), 7.85 (d, *J* = 15.9, H-2'), 7.80 (d, *J* = 8.7, H-2'', H-6''), 6.98 (d, *J* = 8.7, H-3'', H-5''), 4.12 (q, *J* = 6.9, O-CH₂), 1.43 (t, *J* = 6.9, CH₃). Anal. calcd. for C₁₆H₁₈INO: C, 52.33; H, 4.94; N, 3.81; O, 4.36. Found: C, 52.28; H, 4.92; N, 3.92; O, 4.30.

2.2.2.1. (E)-2-(4-ethoxystyryl)-1-methylpyridinium 4-methylbenzenesulfonate (6). A 0.22 g (0.58 mmol) solution of **PET** in hot methanol (50 ml) was mixed with 0.20 g (0.58 mmol) of silver (I) 4-methylbenzenesulfonate in hot methanol (50 ml). The mixture turned to yellow and cloudy immediately. After stirring for 30 min, the precipitate of silver iodide was filtered and the filtrate was evaporated to give a yellow solid. The resultant yellow solid was filtered off, washed with diethyl ether, dried in vacuo and purified by recrystallization. M.p. 171–172 °C, 0.26 g (88%) yield. UV (CH₃OH) λ_{max} (nm): 202.0, 246.0, 366.0; IR (KBr, cm⁻¹): $\nu_{\text{C}=\text{C}}$; 1597 s, $\nu_{\text{C}} = \text{O}$; 1220 s, $\nu_{\text{S}} = \text{O}$; 1180 s; δ ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.44 (s, 1-CH₃), 8.42 (d, *J* = 8.4, H-3), 8.49 (t, *J* = 8.4, H-4), 7.78 (t, *J* = 8.4, H-5), 8.98 (d, *J* = 8.4, H-6), 7.41 (d, *J* = 15.9, H-1'), 7.85 (d, *J* = 15.9, H-2'), 7.80 (d, *J* = 8.7, H-2'', H-6''), 6.98 (d, *J* = 8.7, H-3'', H-5''), 4.13 (q, *J* = 6.9, O-CH₂), 1.41 (t, *J* = 6.9, CH₃), 7.79 (d, *J* = 8.7, H-2''', H-6'''), 6.98 (d, *J* = 8.7, H-3''', H-5'''), 2.32 (s, 4'''-CH₃). Anal. calcd. for C₂₃H₂₅NO₄S: C, 67.14; H, 6.12; N, 3.40; S, 7.79; O, 15.55. Found: C, 66.11; H, 6.09; N, 3.41; S, 7.81; O, 15.58.

Compounds **7–10** were synthesized with identical procedure of **6** by replacing silver (I) 4-methylbenzenesulfonate with silver (I) 4-methoxybenzenesulfonate (for **7**), silver (I) 4-bromobenzenesulfonate (for **8**), silver (I) 4-chlorobenzenesulfonate (for **9**), and silver (I) 4-aminobenzenesulfonate (for **10**). All of the resulting solids were further purified by recrystallization.

2.2.2.2. (E)-2-(4-ethoxystyryl)-1-methylpyridinium 4-methoxybenzenesulfonate (7). M.p. 153–155 °C, 0.21 g (72%) yield. UV (CH₃OH) λ_{max} (nm): 202.0, 230.0, 271.0, 366.0; IR (KBr, cm⁻¹): $\nu_{\text{C}=\text{C}}$; 1618 s, $\nu_{\text{C}} = \text{O}$; 1230 s, $\nu_{\text{S}} = \text{O}$; 1183 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.40 (s, 1-CH₃), 8.46 (d, *J* = 8.4, H-3), 8.40 (t, *J* = 8.4, H-4), 7.78 (d, *J* = 8.4, H-5), 8.90 (d, *J* = 8.4, H-6), 7.41 (d, *J* = 15.9, H-1'), 7.85 (d, *J* = 15.9, H-2'), 7.66 (d, *J* = 8.4, H-2'', H-6''), 6.97 (d, *J* = 8.4, H-3''',

$C_{26}H_{27}N_3O_3S$: C, 67.65; H, 5.90; N, 9.10; S, 6.95; O, 10.40. Found: C, 67.64; H, 5.89; N, 9.08; S, 6.96; O, 10.43.

2.2.4. (*E*)-2-(4-ethoxystyryl)-1-methylquinolinium iodide (**QET**)

(*E*)-2-(4-ethoxystyryl)-1-methylquinolinium iodide was synthesized by mixing a solution (1:1:1 mole ratio) of 1,2-dimethylquinolinium iodide (2.00 g, 7.0 mmol) which was synthesized by the previous method [29], 4-ethoxybenzaldehyde (4.32 ml, 7.0 mmol) and piperidine (0.69 ml, 7.0 mmol) in hot methanol. The resulting red solution was refluxed for 6 h under nitrogen atmosphere. The resultant orange-brown solid was filtered off, washed with diethyl ether, dried in vacuo and purified by recrystallization. M.p. 219–221 °C, 2.20 g (68%) yield. UV (CH₃OH) λ_{max} (nm): 217.5, 252.8, 314.1, 416.2; IR (KBr, cm⁻¹): $\nu_{C=C}$; 1605 s, $\nu_{C=O}$; 1233 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.60 (s, 1-CH₃), 1.42 (t, *J* = 7.2, CH₃), 4.15 (q, *J* = 7.2, OCH₂), 8.50 (d, *J* = 9.0, H-3), 8.93 (d, *J* = 9.0, H-4), 8.27 (d, *J* = 7.5, H-5), 7.90 (t, *J* = 7.5, H-6), 8.15 (t, *J* = 7.5, H-7), 8.45 (d, *J* = 7.5, H-8), 7.74 (d, *J* = 15.6, H-1'), 7.95 (d, *J* = 15.6, H-2'), 7.89 (d, *J* = 8.7, H-2'', H-6''), 7.02 (d, *J* = 8.7, H-3'', H-5''). Anal. calcd. for C₂₀H₂₀INO: C, 57.57; H, 4.83; N, 3.36; O, 3.83. Found: C, 57.45; H, 4.89; N, 3.37; O, 3.79.

2.2.4.1. (*E*)-2-(4-ethoxystyryl)-1-methylquinolinium 4-methylbenzenesulfonate (**16**). A 0.24 g (0.58 mmol) solution of **QET** in hot methanol (50 ml) was mixed with 0.20 g (0.58 mmol) of silver (I) 4-methylbenzenesulfonate in hot methanol (50 ml). The mixture turned to brown and cloudy immediately. After stirring for 30 min, the precipitate of silver iodide was filtered and the filtrate was evaporated to give a yellow solid. The resultant yellow solid was filtered off, washed with diethyl ether, dried in vacuo and purified by recrystallization. M.p. 219–221 °C, 0.14 g (54%) yield. UV (CH₃OH) λ_{max} (nm): 202.7, 217.6, 256.2, 413.9; IR (KBr) ν (cm⁻¹): $\nu_{C=C}$; 1605 s, $\nu_{C=O}$; 1233 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.52 (s, 1-CH₃), 1.39 (t, *J* = 7.2, CH₃), 4.09 (q, *J* = 7.2, OCH₂), 8.42 (d, *J* = 9.0, H-3), 8.85 (d, *J* = 9.0, H-4), 8.22 (d, *J* = 7.5, H-5), 7.83 (t, *J* = 7.5, H-6), 8.08 (t, *J* = 7.5, H-7), 8.05 (d, *J* = 7.5, H-8), 7.70 (d, *J* = 15.9, H-1'), 7.89 (d, *J* = 15.9, H-2'), 7.88 (d, *J* = 8.7, H-2'', H-6''), 6.95 (d, *J* = 8.7, H-3'', H-5''), 7.04 (d, *J* = 7.8, H-2''', H-6'''), 7.58 (d, *J* = 7.8, H-3''', H-5'''), 2.25 (s, 4'''-CH₃). Anal. calcd. for C₂₇H₂₇NO₄S: C, 70.25; H, 5.90; N, 3.03; S, 6.95; O, 13.87. Found: C, 70.20; H, 5.88; N, 3.01; S, 7.10; O, 13.81.

Compounds **17–20** were synthesized with identical procedure of **16** by replacing silver (I) 4-methylbenzenesulfonate with silver (I) 4-methoxybenzenesulfonate (for **17**), silver (I) 4-bromobenzenesulfonate (for **18**), silver (I) 4-chlorobenzenesulfonate (for **19**), and silver (I) 4-aminobenzenesulfonate (for **20**). All of the resulting solids were further purified by recrystallization.

2.2.4.2. (*E*)-2-(4-ethoxystyryl)-1-methylquinolinium 4-methoxybenzenesulfonate (**17**). M.p. 256–257 °C, 0.26 g (80%) yield. UV (CH₃OH) λ_{max} (nm): 330.3, 413.1; IR (KBr, cm⁻¹): $\nu_{C=C}$; 1571 s, $\nu_{C=O}$; 1219 s, $\nu_{S=O}$; 1163 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.60 (s, 1-CH₃), 1.45 (t, *J* = 7.2, CH₃), 4.15 (q, *J* = 7.2, OCH₂), 8.47 (d, *J* = 9.0, H-3), 8.89 (d, *J* = 9.0, H-4), 8.25 (d, *J* = 7.5, H-5), 7.89 (t, *J* = 7.5, H-6), 8.18 (t, *J* = 7.5, H-7), 8.40 (d, *J* = 7.5, H-8), 7.70 (d, *J* = 15.6, H-1'), 8.09 (d, *J* = 15.6, H-2'), 7.85 (d, *J* = 8.7, H-2'', H-6''), 7.70 (d, *J* = 8.7, H-3'', H-5''), 7.01 (d, *J* = 7.8, H-2''', H-6'''), 6.80 (d, *J* = 7.8, H-3''', H-5'''), 3.78 (s, 4'''-OCH₃). Anal. calcd. for C₂₇H₂₇NO₅S: C, 67.90; H, 5.70; N, 2.93; S, 6.72; O, 16.75. Found: C, 67.92; H, 5.66; N, 2.90; S, 6.70; O, 16.82.

2.2.4.3. (*E*)-2-(4-ethoxystyryl)-1-methylquinolinium 4-bromobenzenesulfonate (**18**). M.p. 249–251 °C, 0.24 g (72%) yield. UV (CH₃OH) λ_{max} (nm): 221.0, 255.5, 413.9; IR (KBr, cm⁻¹): $\nu_{C=C}$; 1591 s, $\nu_{C=O}$; 1223 s, $\nu_{S=O}$; 1168 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.60 (s, 1-CH₃), 1.43 (t, *J* = 7.1, CH₃), 4.15 (q, *J* = 7.1, OCH₂), 8.48 (d, *J* = 9.0, H-3), 8.89 (d, *J* = 9.0, H-4), 8.25 (d, *J* = 7.5, H-5), 7.87 (t, *J* = 7.5, H-6), 8.09 (t, *J* = 7.5, H-7), 8.44 (d, *J* = 7.5, H-8), 7.72 (d, *J* = 15.6, H-1'), 8.03 (d,

J = 15.6, H-2'), 7.84 (d, *J* = 8.7, H-2'', H-6''), 6.98 (d, *J* = 8.7, H-3'', H-5''), 7.41 (d, *J* = 8.4, H-2''', H-6'''), 7.60 (d, *J* = 8.4, H-3''', H-5'''). Anal. calcd. for C₂₆H₂₄BrNO₄S: C, 59.32; H, 4.60; N, 2.66; S, 6.08; O, 12.16. Found: C, 59.29; H, 4.58; N, 2.60; S, 6.01; O, 12.32.

2.2.4.4. (*E*)-2-(4-ethoxystyryl)-1-methylquinolinium 4-chlorobenzenesulfonate (**19**). M.p. 254–256 °C, 0.26 g (84%) yield. UV (CH₃OH) λ_{max} (nm): 228.7, 268.4, 410.2; IR (KBr, cm⁻¹): $\nu_{C=C}$; 1590 s, $\nu_{C=O}$; 1224 s, $\nu_{S=O}$; 1152 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.60 (s, 1-CH₃), 1.46 (t, *J* = 7.2, CH₃), 4.18 (q, *J* = 7.2, OCH₂), 8.45 (d, *J* = 9.0, H-3), 8.90 (d, *J* = 9.0, H-4), 8.28 (d, *J* = 7.8, H-5), 7.91 (t, *J* = 7.8, H-6), 8.12 (t, *J* = 7.8, H-7), 8.41 (d, *J* = 7.8, H-8), 7.72 (d, *J* = 15.9, H-1'), 8.10 (d, *J* = 15.9, H-2'), 7.88 (d, *J* = 8.7, H-2'', H-6''), 7.00 (d, *J* = 8.7, H-3'', H-5''), 7.30 (d, *J* = 8.7, H-2''', H-6'''), 7.74 (d, *J* = 8.7, H-3''', H-5'''). Anal. calcd. for C₂₆H₂₄ClNO₄S: C, 64.79; H, 5.02; N, 2.90; S, 6.65; O, 13.28. Found: C, 64.70; H, 5.17; N, 2.68; S, 6.60; O, 13.45.

2.2.4.5. (*E*)-2-(4-ethoxystyryl)-1-methylquinolinium 4-aminobenzenesulfonate (**20**). M.p. (decompose) 242–244 °C, 0.21 g (64%) yield. UV (CH₃OH) λ_{max} (nm): 204.0, 248.0, 302.0, 412.0; IR (KBr, cm⁻¹): $\nu_{C=C}$; 1588 s, $\nu_{C=O}$; 1221 s, $\nu_{S=O}$; 1150 s; ¹H NMR (*d*₆-DMSO mixed with CDCl₃): δ 4.65 (s, 1-CH₃), 8.83 (d, *J* = 8.3, H-3), 8.39 (d, *J* = 8.3, H-4), 7.90 (t, *J* = 8.3, H-5), 8.19 (t, *J* = 8.3, H-6), 8.23 (t, *J* = 8.3, H-7), 8.24 (d, *J* = 8.3, H-8), 7.66 (d, *J* = 15.6, H-1'), 8.01 (d, *J* = 15.6, H-2'), 7.89 (d, *J* = 8.7, H-2'', H-6''), 7.01 (d, *J* = 8.7, H-3'', H-5''), 7.01 (d, *J* = 7.8, H-2''', H-6'''), 7.85 (d, *J* = 7.8, H-3''', H-5'''), 4.34 (br s, 4'''-NH₂). Anal. calcd. for C₂₆H₂₆N₂O₄S: C, 67.50; H, 5.67; N, 6.06; S, 6.93; O, 13.84. Found: C, 67.44; H, 5.88; N, 6.01; S, 6.81; O, 13.86.

All ¹H NMR spectra were available as supplementary materials.

2.3. Crystal structure determination

In addition, single crystals of compound **5** were obtained by recrystallization from methanol and further determined by X-ray diffraction analysis. Crystallographic data were collected on a Bruker SMART APEXII CCD area-detector diffractometer with a graphite monochromated Mo-K α radiation (λ = 0.71073 Å) at 100.0(1) K with the Oxford Cryosystem Cobra low-temperature attachment. The collected data were reduced using SAINT and the empirical absorption corrections were performed using SADABS program [30]. The structures were solved by direct methods and refined by least-squares using the SHELXTL [31] software package. The crystallographic data, selected bond lengths, bond angles and torsion angles for compound **5** were listed in Tables 1 and 2, respectively. The hydrogen bonding geometries were listed in Table 3. X-ray ORTEP diagram and packing diagram of compound **5** are shown in Figs. 6 and 7, respectively.

3. Antibacterial assay

All of the purified compounds were tested against both Gram-positive bacteria i.e. *B. subtilis*, *E. faecalis*, *S. aureus*, Methicillin-Resistant *S. aureus* and Vancomycin-Resistant *E. faecalis* and Gram-negative bacteria i.e. *Pseudomonas aeruginosa*, *Salmonella typhi* and *S. sonnei*. Bacteria *S. typhi*, *S. sonnei*, *B. subtilis* and *P. aeruginosa* were obtained from culture collection, Department of Industrial Biotechnology and Department of Pharmacognosy and Botany, Prince of Songkla University. Methicillin-Resistant *S. aureus* (MRSA) ATCC 43300, Vancomycin-Resistant *E. faecalis* (VRE) ATCC 51299, *S. aureus* TISTR517 and *E. faecalis* TISTR459 were obtained from Microbial Research Center (MIRCEN), Bangkok, Thailand. The antimicrobial assay employed was the colorimetric microdilution broth technique using RPMI1640 medium and Alamar Blue as an indicator. Microbial inoculation were prepared as suspension in RPMI1640 medium and mixed with 1% 100 \times Alamar Blue indicator. The cell suspension was

Table 1
Crystal data and structure refinement parameters for the compound **5**.

Chemical formula: C ₁₆ H ₁₉ N ₂ ·C ₆ H ₆ NO ₃ S·H ₂ O
Formula weight: 429.53
Crystal system: monoclinic
Space group: P2 ₁ /c Z = 2
a = 6.9229(6) Å
b = 12.6106(10) Å
c = 11.9705(10) Å
β = 94.849(6)°
V = 1041.31(15) Å ³
D _{calc} = 1.370 g cm ⁻³
μ(Mo–Kα) = 0.190 mm ⁻¹
T = 100.0(1) K
F(000) = 456
Crystal size = 0.53 × 0.33 × 0.25 mm ³
θ range for data collection 2.35–35.00°
R = 0.1151
R _w = 0.3534
No. of unique data measured = 8910
No. of observed data with I ≥ 2σ(I) = 8910
No. of parameters = 275
Goodness-of-fit = 1.104
(Δρ) _{max} = 2.502 e. Å ⁻³
(Δρ) _{min} = -2.551 e. Å ⁻³
Measurements; Bruker APEX2 CCD diffractometer
Program system: Apex2
Structure determination; direct method (SHELXTL) ¹¹
Refinement: full-matrix least-squares
CCDC759537 contains the supplementary crystallographic data for this paper.
These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif .

then transferred into a 96-well microliter plate (100 μl/well except for first row which contained 190 μl/well). Sample (10 μl) dissolved in DMSO at a concentration of 25 mg/ml was added to each well of the first row and mixed well with a micropipette. Half of the mixtures of cell suspension and compounds in the first rows were then transferred to the next well in the second row to perform a half-fold dilution. The dilution process was repeated as a sequence until the compounds were diluted 128 times in the last row. The excess 100 μl of the mixture in the last row was discarded. The plates were incubated at 37 °C for 8–12 h. The antimicrobial activity was determined as the MIC value which was the least concentration of the compound that could inhibit the change of Alamar Blue indicator from blue to red. All assays were repeated at least three times [32].

4. Result and discussion

4.1. Synthesis of all pyridinium and quinolinium stilbene derivatives

4.1.1. FT-IR and UV–vis spectroscopy

The (*E*)-2-(4-ethoxystyryl)-1-methylpyridinium iodide (**PET**) was conventionally prepared by refluxing the mixture of 1,2-

Table 2
Selected bond lengths (Å), bond angles (°) and torsion angles (°) of compound **5**.

N2–C11	1.367(7)	O1W–H1W1	0.8501
N2–C15	1.471(8)	O1W–H2W1	0.8500
N1–C1	1.346(7)	S1–O1	1.446(4)
N1–C5	1.357(7)	S1–O2	1.459(5)
N1–C14	1.483(8)	S1–O3	1.474(4)
C6–C7	1.351(8)	S1–C17	1.773(5)
C11–N2–C16	120.5(5)	C15–N2–C16	119.9(5)
C5–N1–C1	121.9(5)	O1–S1–O2	112.9(3)
C5–N1–C14	120.6(5)	O1–S1–C17	106.6(3)
C4–C5–C6–C7	-4.7(9)	C16–N2–C11–C10	-174.5(5)
C5–C6–C7–C8	-179.3(6)	C15–N2–C11–C12	1.0(8)
C6–C7–C8–C13	-1.3(10)		

Table 3
Hydrogen bonding geometry (Å, °) of compound **5**.

D–H A	D–H	H...A	D...A	D–H...A
O1W–H1W1...O3	0.85	1.97	2.822(7)	180
O1W–H2W1...O1 ⁱ	0.85	2.04	2.849(7)	158
N3–H3B–O2 ⁱⁱ	0.86	2.44	3.193(8)	147
N3–H3C–O3 ⁱⁱⁱ	0.86	2.21	3.041(7)	163
C1–H1A–O1W ^{iv}	0.93	2.14	3.038(7)	162
C14–H14C–O3	0.96	2.58	3.398(8)	143
C19–H19A–O2 ⁱⁱ	0.93	2.48	3.286(7)	145
C21–H21A–O2 ⁱⁱⁱ	0.93	2.59	3.495(7)	163
C22–H22A–O3	0.93	2.58	2.957(7)	105
C3–H3A...Cg ₇ ^v	0.93	2.76	3.519(7)	140
C12–H12A...Cg ₇	0.93	2.76	3.601(5)	150

Symmetry codes: (i) 1 + x, y, z; (ii) -x, ½ + y, 1 - z; (iii) 1 - x, ½ + y, 1 - z; (iv) 1 - x, -½ + y, -z; (v) x, y, -1 + z. Cg₇ is the centroid of C17–C22 ring.

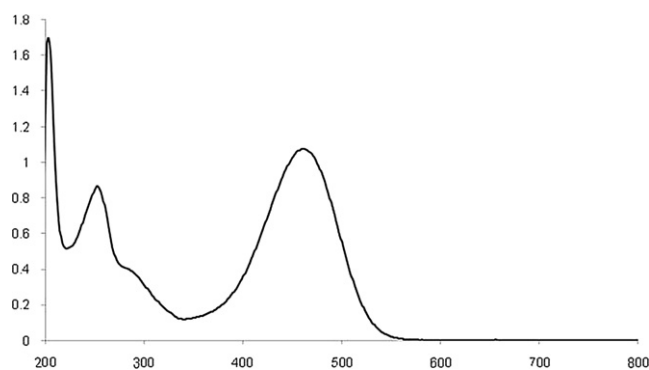
dimethylpyridinium iodide, 4-ethoxybenzaldehyde and piperidine for 4 h in methanol. The product could be easily purified by recrystallization from methanol or ethanol [33]. All three stilbene iodide derivatives (**PAM**, **QAM** and **QET**) were achieved from the same synthesis method. The structures of all compounds were confirmed by UV–vis absorption spectra, IR, and ¹H NMR data.

The UV–vis absorption spectra were made using methanol in the wavelength range of 200–800 nm. The UV–vis absorption spectrum of **5** was shown in Fig. 4. It should be mentioned that analysis of UV–vis spectra revealed *trans*-configuration for all obtained compounds since *trans*-stilbenes exhibit the values of λ_{max} in the range 290–360 nm [34,35]. The UV–vis spectra of quinolinium derivatives in methanol showed absorption bands between 200 and 415 nm. The position of the absorption maximum (ca. 415 nm) ascribed to the π–π* transition of the quinolinium ring.

IR spectra of all compounds have been investigated in the frequency range 400–4000 cm⁻¹ and shown typical aromatic absorption i.e. for compound **5** (Fig. 5), there were resonance conjugated unsaturated stretching modes in the chromophore (C=C at 1611 cm⁻¹) and C–N at 1297 cm⁻¹. The peak found at 1195 cm⁻¹ wave number pertains to S=O bond of sulfonate.

4.1.2. Crystallographic study

The crystallographic-information file for the monohydrated of compound **5** has been deposited in the Cambridge Crystallographic Data Center as CCDC759537. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**Fig. 4.** UV–vis spectrum of compound **5** in CH₃OH.

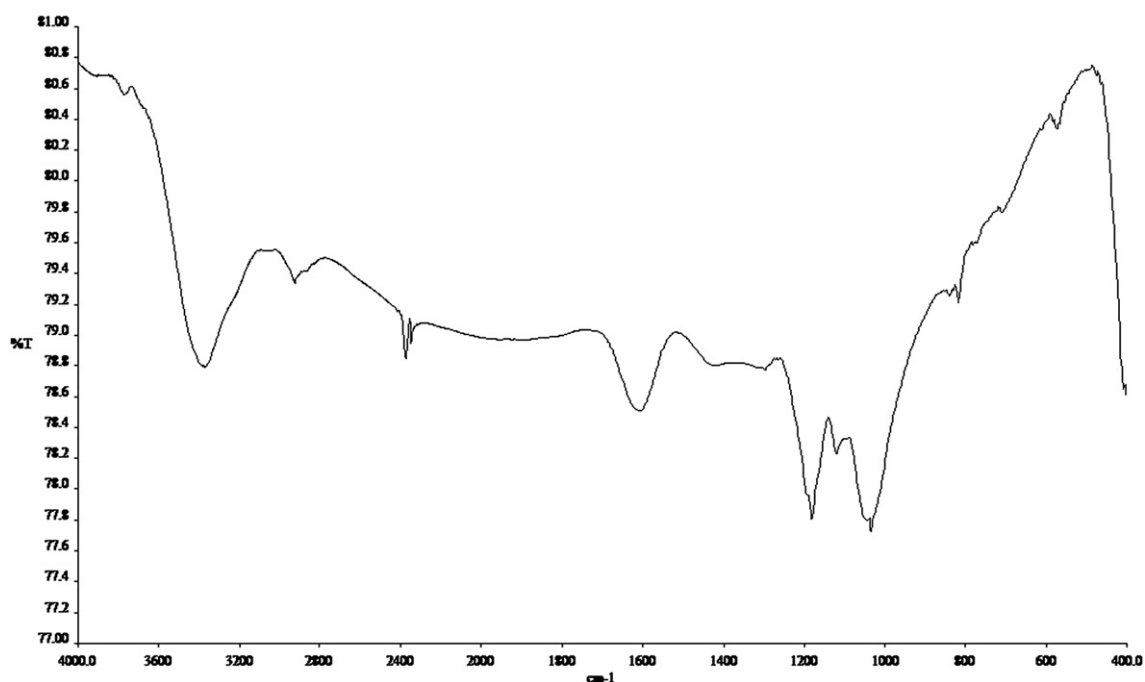


Fig. 5. FT-IR spectrum of compound 5.

The crystallographic and experimental parameters used for data collection and determination of the structure are given in Table 1. All non-hydrogen atoms were refined anisotropically. All H atoms were positioned geometrically and allowed to ride on their parent atoms, with $N-H = 0.86 \text{ \AA}$, $O-H = 0.85 \text{ \AA}$, $C-H = 0.93 \text{ \AA}$ for aromatic and CH and 0.96 \AA for CH_3 atoms. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. The molecular structure and atom numbering of compound 5 are shown in Fig. 6, and the crystal packing is presented in Fig. 7. The selected bond lengths, bond angles and selected torsion angles were listed in Table 2. Compound 5 crystallizes in the $P2_1/c$ space group with $Z = 2$. The asymmetric unit of the title compound consists of a $C_{16}H_{19}N_2^+$ cation, a $C_6H_6NO_3S^-$ anion and one H_2O molecule (Fig. 6). This crystal is a twin with the ratio for the two twin components obtained by least-squares structure refinement being $0.639(6):0.361(6)$. The molecule exists in *trans*-configuration as indicated by the torsion angle $C5-C6-C7-C8 = -179.3(6)^\circ$ and slightly twisted with the dihedral angle between the pyridinium and the phenyl ring ($C8-C13$) being $7.3(3)^\circ$. It can be found that the carbon-carbon

bond lengths of 5 are basically intermediate between typical C–C single (1.45 \AA) and C=C double (1.35 \AA) bonds. The dimethylamino is co-planar with the attached phenyl ring in which one methyl group is slightly deviated as indicated by torsion angles $C15-N2-C11-C10 = 1.0(8)^\circ$ and $C16-N2-C11-C12 = 5.1(8)^\circ$. The anion is inclined to the cation with the dihedral angles between the benzene ring of the anion and pyridinium and benzene rings of the cation being $88.0(3)$ and $81.7(3)^\circ$, respectively.

In the crystal packing as shown in Fig. 7, the cations are linked with water molecules by weak $C1-H1A...O1W$ interaction (symmetry code; $1-x, -\frac{1}{2}+y, -z$) whereas the anions are linked with water molecules by $O1W-H1W1...O3$ (symmetry code; x, y, z) and $O1W-H2W1...O1$ (symmetry code; $1+x, y, z$) hydrogen bonds (Table 3). The molecules are linked into two-dimensional network parallel to the *ab* plane by $C-H...O$ and $N-H...O$ hydrogen bonds and $C-H...π$ interactions (Table 3). The crystal structure is further stabilized by $C-H...π$ interactions involving pyridinium and anionic benzene rings with the $C3-H3A...Cg_1$ and $C12-H12A...Cg_1$ (Table 3, symmetry code; $x, y, -1+z$ and x, y, z respectively); Cg_1 is the centroid of $C17-C22$ ring.

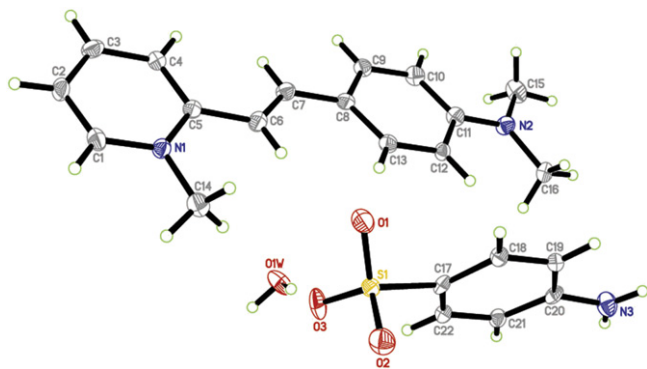


Fig. 6. The ORTEP plot of compound 5 showing the atom numbering scheme. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

4.2. Biological results

The antibacterial activity results showed that these synthesized hybrid disinfectants exhibited interesting antibacterial activity in which all compounds were active against at least one of the tested strains and none of the compounds was totally inactive. The results suggested that this combination concept could lead to the potent antibacterial agents which can be easily modified by the variation of stilbene-QAC moiety or benzenesulfonate parts. The MIC values have proved that all compounds were active against MRSA and the main reason for the antibacterial activity in these hybrid compounds were related to the types of QAC-head groups.

Our antibacterial study (Table 4) showed that these compounds were more effective against Gram-positive than Gram-negative bacteria as generally found which may be due to the “intrinsic resistance” of Gram-negative bacteria [36,37]. In general,

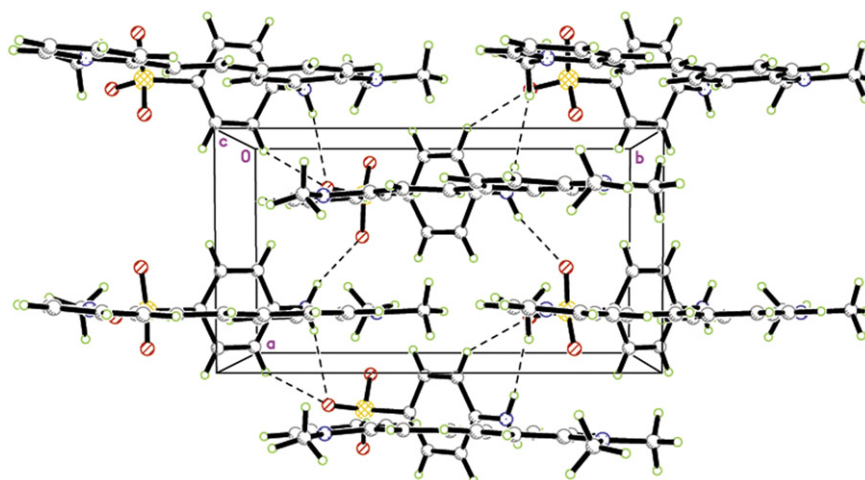


Fig. 7. The crystal packing of compound 5, viewed down the *c*-axis. Hydrogen bonds are shown as dashed lines.

quaternary ammonium halides such as 1-alkylpyridinium halides exhibit strong bacteriostatic activity against Gram-positive bacteria rather than those against Gram-negative bacteria [38]. In this study, the QAC-headgroups which are pyridinium and quinolinium, seem to be the key factor to the activity. The quinolinium headgroup-containing compounds exhibited more potent activity, especially against MRSA, than that of the pyridinium headgroup-containing compounds (see Table 4). Fig. 8 clearly showed the higher activity

against MRSA ($1/\log\text{MIC}_{\text{MRSA}}$) of quinolinium (**11–20**) compared with pyridinium (**1–10**) derivatives.

The quinolinium derivatives (**11–20**) showed the better activity against Gram-positive than Gram-negative bacteria. Compounds **11**, **13** and **14** showed similar activity and were the most active compounds with the MICs value = 2.34 $\mu\text{g}/\text{ml}$ against all tested Gram-positive bacteria and were better than that of the standard references BZK and vancomycin. For the tested results against

Table 4
Antibacterial activity of the synthesized compounds **PAM**, **PET**, **QAM**, **QET** and **1–20**.

Compound	MIC ($\mu\text{g}/\text{ml}$)							
	Gram-positive bacteria				Gram-negative bacteria			
	MRSA*	<i>S. aureus</i>	<i>B. subtilis</i>	VRE**	<i>E. faecalis</i>	<i>P. aeruginosa</i>	<i>S. typhi</i>	<i>S. sonnei</i>
PAM ^a	37.5	300	300	300	300	300	300	300
1	37.5	300	150	300	300	150	300	300
2	75	150	150	150	150	150	150	150
3	75	–	–	–	–	–	–	–
4	37.5	–	300	150	–	300	300	–
5	37.5	–	–	300	–	–	–	–
PET ^b	37.5	–	–	–	–	–	–	300
6	37.5	150	300	300	150	37.5	150	150
7	150	–	–	–	–	–	–	–
8	18.75	–	–	–	–	–	300	300
9	75	–	–	–	–	–	–	–
10	75	–	–	–	–	–	–	–
QAM ^c	9.37	18.75	9.37	4.68	18.75	300	300	4.68
11	2.34	2.34	2.34	2.34	2.34	300	300	2.34
12	2.34	–	75	150	150	–	–	150
13	2.34	2.34	2.34	2.34	2.34	300	300	2.34
14	2.34	2.34	2.34	2.34	2.34	300	300	2.34
15	2.34	75	18.75	18.75	75	150	75	75
QET ^d	2.34	–	37.5	37.5	75	–	–	150
16	2.34	–	9.37	37.5	37.5	–	–	150
17	2.34	–	18.75	18.75	75	–	–	150
18	2.34	300	18.75	18.75	37.5	–	–	75
19	2.34	–	75	150	75	–	–	300
20	4.68	37.5	37.5	75	37.5	–	75	75
BZK	9.37	<2.34	150	9.37	9.37	300	9.37	–
Vancomycin	<2.34	9.37	2.34	2.34	9.375	2.34	2.34	2.34

– No activity was observed up to 300 $\mu\text{g}/\text{mL}$.

* Methicillin-Resistant *S. aureus* ATCC 43300.

** Vancomycin-Resistant *E. faecalis* ATCC 51299.

^a (*E*)-2-(4-(dimethylamino)styryl)-1-methylpyridinium iodide.

^b (*E*)-2-(4-ethoxystyryl)-1-methylpyridinium iodide.

^c (*E*)-2-(4-(dimethylamino)styryl)-1-methylquinolinium iodide.

^d (*E*)-2-(4-ethoxystyryl)-1-methylquinolinium iodide.

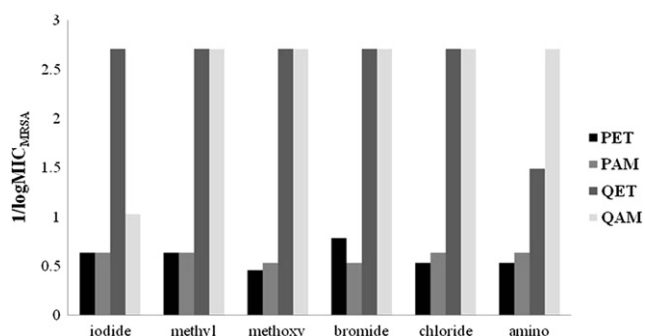


Fig. 8. The comparison of antimicrobial activities between pyridinium and quinolinium stilbenes salts against Methicillin-Resistant *S. aureus* ATCC 43300.

Gram-negative bacteria, compounds **11**, **13** and **14** were very active only against *S. sonnei* (MICs = 2.34 $\mu\text{g}/\text{ml}$) while all quinolinium derivatives were inactive against the rest Gram-negative bacteria (*P. aeruginosa* and *S. typhi*).

While comparing between two quinolinium derivatives series i.e. compounds **11–15** (dimethylamino-containing compounds) and compounds **16–20** (ethoxy-containing compounds), the results showed that both series showed the desirable activity with a bit different characteristic in which compounds **11–15** showed broad band spectrum against the tested Gram-positive and one Gram-negative (*S. sonnei*) whereas compounds **16–20** showed the very specific activity against only MRSA.

The pyridinium derivatives (**1–5** and **6–10** series) showed moderate to low activity against MRSA and low activity against the rest Gram-positive bacteria (*S. aureus*, *B. subtilis*, *E. faecalis* and Vancomycin-Resistant *E. faecalis*). These compounds were inactive against all tested Gram-negative bacteria (MICs > 150 $\mu\text{g}/\text{ml}$). While comparing between the two pyridinium derivatives series i.e. **1–5** and **6–10** series, it was found that the activity of **1–5** series was better than that of **6–10** which might be due to the presence of the dimethylamino group which was able to enhance the activity compared to the effect of the methoxy group in the **6–10** series.

All pyridinium derivatives (**1–10**) were less potent than the standard BZK and vancomycin so it might be concluded that the pyridinium-QAC-headgroup was not the promising molecular parameter for this hybrid antibacterial agents. However, compounds **1**, **2** and **6** were the most active compounds among the pyridinium derivatives with MIC values ranging from 37.5 to 300 $\mu\text{g}/\text{ml}$ for the Gram-positive antibacterial activity.

From the antibacterial activity results (Table 4) it was seen that when the benzenesulfonate moiety was introduced (in **1–20**) in place of I^- (in **PAM**, **PET**, **QAM**, **QET**) the activity were clearly changed with the MIC values changing from 9.37 $\mu\text{g}/\text{ml}$ in **QAM** to 2.34 $\mu\text{g}/\text{ml}$ in compound **11**. The introduction of 4-substituted-benzenesulfonate part seems to promote the activity by 2–4 times only in quinolinium derivatives (**11–20**), especially in compounds **11**, **13** and **14**. However, the introduction of 4-substituted-benzenesulfonate moiety did not significantly enhance the antibacterial activity for the pyridinium derivatives as displayed by the comparison the antibacterial activity between iodide-containing and 4-substituted-benzenesulfonate-containing compounds for example, by changing from iodide (in **PET**) to 4-methylbenzenesulfonate (in compound **6**). The comparative antibacterial activity against MRSA can also be found in compounds **PAM** and compound **1** (see Table 4).

5. Conclusion

The new class of hybrid disinfectants were synthesized and reported in this study. The structural characterizations of the

synthesized compounds were made by the spectroscopic methods. The structure of compound **5** was also confirmed by single crystal X-ray diffraction studies. All compounds showed the antibacterial activities as expected and the quinolinium derivatives displayed more potent activity than that of the pyridinium derivatives against the bacteria tested, whereas the dimethylamino-containing series exhibited better activity than ethoxy-containing series. The hybrid between quinolinium-QAC and sulfonamide-like structures showed good antibacterial activity. Among all compounds, **11–15** are wide-spectrum antibacterial substances while compounds **16–20** showed very specific activity against MRSA. For the wide-spectrum antibacterial substances, compounds **11**, **13** and **14** are the most active compounds which indicated the dominant antibacterial effect of quinolinium-QAC-headgroup and dimethylamino group.

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Appendix. Supplementary data

Crystallographic data of compound **5** has been deposited at the CCDC as supplementary data, CCDC No. 759537. Copies of the data were available at CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ejmech.2010.06.014](https://doi.org/10.1016/j.ejmech.2010.06.014).

References

- [1] D. Dembereinyamba, K.-S. Kim, S. Choi, S.-Y. Park, H. Lee, C.-J. Kim, I.-D. Yoo, *Bioorg. Med. Chem.* 12 (2004) 853–857.
- [2] S.S. Block, *Disinfection, Sterilization, and Preservation*, fifth ed. Lippincott Williams & Wilkins, Philadelphia, U.S.A., 2001.
- [3] J. Pernak, J. Kalewska, H. Ksycifiska, J. Cybulski, *Eur. J. Med. Chem.* 36 (2001) 899–907.
- [4] E. Fiscaro, M. Barbieri, E. Pelizzetti, P.J. Savarino, *Chem. Soc. Faraday Trans.* 87 (1991) 2983–2987.
- [5] A.O. de Souza, C. Fabio, S. Galetti, L. Célio Silva, B. Bicalho, M.M. Parma, S. F. Fonseca, A.J. Marsaioli, Angela C.L.B. Trindade, R.P.F. Gil, F.S. Bezerra, M. Andrade-Neto, C. Maria, F. de Oliveira, *Quim. Nova* 30 (2007) 1563–1566.
- [6] T. Maeda, Y. Manabe, M. Yamamoto, M. Yoshida, K. Okazaki, H. Nagamune, H. Kourai, *Chem. Pharm. Bull.* 47 (1999) 1020–1023.
- [7] J. Reuda, J.A. Lázaro, J. Duchá, *Rev. Sci. Tech.* 22 (2003) 1097–1104.
- [8] D.A. Basketter, M. Marriott, N.J. Gilmour, I.R. White, *Contact Derm.* 50 (2004) 213–217.
- [9] B.H. Lee, S.-H. Kim, *Korean J. Int. Med.* 22 (2007) 244–248.
- [10] M. Braoudaki, A.C. Hilton, *Int. J. Antimicrob. Agents* 25 (2005) 31–37.
- [11] Y. Sakagami, H. Yokoyama, H. Nishimura, Y. Ose, T. Tashima, *Appl. Environ. Microbiol.* 55 (1989) 2036–2040.
- [12] H. Nikaido, *Biochim. Biophys. Acta* 433 (1976) 118–132.
- [13] H. Nikaido, T. Nakae, *Adv. Microb. Physiol.* 20 (1979) 163–250.
- [14] E. Bore, M. Hébraud, I. Chafsey, C. Chambon, C. Skjæret, B. Moen, T. Møretvø, Ø. Langsrud, K. Rudi1, S. Langsrud, *Microbiology* 153 (2007) 935–946.
- [15] E. Wyrzykiewicz, M. Wendzonka, B. Kędzia, *Eur. J. Med. Chem.* 41 (2006) 519–525.
- [16] A. Skrzypczak, B. Brycki, I. Mirska, J. Pernak, *Eur. J. Med. Chem.* 32 (1997) 661–668.
- [17] M. Diz, A. Manresa, A. Pinazo, P. Erra, M.R. Infante, *J. Chem. Soc. Perkin Trans.* 2 (1994) 1871–1876.
- [18] M. Pavlikova, Y. Lacko, F. Devinsky, D. Mlynarcik, *Coll. Czech. Chem. Comm.* 60 (1995) 1213–1227.
- [19] J. Pernak, I. Mirska, R. Kmiecik, *Eur. J. Med. Chem.* 34 (1999) 765–771.
- [20] M. Wainwright, *J. Antimicrob. Chemother.* 47 (2001) 1–13.

- [21] M. Spasova, N. Manolova, D. Paneva, R. Mincheva, P. Dubois, I. Rashkov, V. Maximova, D. Danchev, *Biomacromolecules* 11 (2010) 151–159.
- [22] A.R. Martin, F.L. Rose, *Biochem. J.* 39 (1945) 91–95.
- [23] P.M. Sivakumar, G. Sheshayan, M. Doble, *Chem. Biol. Drug Des.* 72 (2008) 303–313.
- [24] G. Domagk, *Klin. Wschr* 16 (1937) 1412–1418.
- [25] O.W. Barlow, *Proc. Soc. Exp. Biol. Med.* 37 (1937) 315.
- [26] S. Chantrapromma, T. Suwanwong, H.-K. Fun, *Acta. Crystallogr.* E63 (2007) o821–o823.
- [27] S. Chantrapromma, K. Chanawanno, H.-K. Fun, *Acta. Crystallogr.* E65 (2009) o1884–o1885.
- [28] S. Chantrapromma, P. Ruanwas, H.-K. Fun, C. Karalai, *Acta. Crystallogr.* E64 (2008) o2072–o2073.
- [29] S. Chantrapromma, P. Rodwatcharapiban, H.-K. Fun, *Acta. Crystallogr.* E62 (2006) o5689–o5691.
- [30] Bruker, APEX2 (Version 2.1–4), SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2005.
- [31] G.M. Sheldrick, *Acta. Crystallogr.* A64 (2008) 112–122.
- [32] A. Kanjana-Opas, Ph.D. Thesis, University of California, San Diego, 2002.
- [33] C. Laksana, P. Ruanwas, S. Chantrapromma, H.-K. Fun, *Acta. Crystallogr.* E64 (2008) o145–o146.
- [34] H.W. Thompson, P. Torkington, *J. Chem. Soc.* 184 (1945) 640–645.
- [35] M. Oki, H. Kunimoto, *Spectrochim. Acta* 19 (1963) 1463–1471.
- [36] A.R.M. Cutheon, S.M. Ellis, R.E.W. Hancock, G.H.N. Towers, *J. Ethnopharmacol.* 37 (1992) 213–223.
- [37] N.V. Loginova, T.V. Kovalchuk, R.A. Zheldakova, N.P. Osipovich, V.L. Sorokin, G. I. Polozov, G.A. Ksedzova, G.K. Glushonak, A.A. Chernyavskaya, O.I. Shadyro, *Bioorg. Med. Chem. Lett.* 16 (2006) 5403–5407.
- [38] H. Kourai, H. Takechi, M. Kume, K. Takeichi, I. Shibasaki, *J. Antibact. Antifung. Agents* 14 (1986) 55–63.