CHAPTER 1

INTRODUCTION

1.1 Nonlinear optics

Non-linear optics represents optical phenomena, the beginning of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation in quartz crystal by P. Franken in 1961, shortly after the advent of the laser by Maiman in 1960. Interest in this field has grown continuously since it has significant impact on optical storage technology and integrated optics technology (Bass, 1962 and Williams, 1984).

Nonlinear optics (NLO) is concerned with the interaction of electromagnetic fields (light) in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. The media in which these effects occur are becoming the subject of intense interest, due to their complement properties, such as stability, ease of preparation, compatibility with microelectronic processing methods, mechanical and other properties, as well as their nonlinear optical properties will extremely determine the technological utility of the effect (Williams, 1984). A major advantage of the use of photonics instead of electronics is the possibility to increase the speed of information processes such as photonic switching and optical computing. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. One of the most intensively studied nonlinear optical phenomena is second harmonic generation (SHG), in which incident light at one frequency (ω) is converted into light at twice of that frequency (2ω). The resulting wavelength is half the incident wavelength and hence it is possible to store information with a higher density. Second-order NLO properties can only be observed in materials lacking a center of symmetry since the second-order NLO coefficient is a third-order tensor which in centrosymmetric system all the tensor components equal zero. So, an important point in designing new organic materials for SHG is to introduce noncentrosymmetry in crystal structures.

Electrooptic modulators have traditionally employed ferroelectric inorganic crystals, such as lithium niobate ($LiNbO_3$) or potassium dihydrogenphosphate (KDP), which are formed at high temperatures. However, organic NLO materials offer better several advantages in performance, such as higher nonlinear susceptibilities, higher modulation rates, ultrafast response times, lower dielectric constants, better processability characteristics and a remarkable resistance to optical damage, when compared to the inorganic materials (Nie, 1993). The theory of nonlinear optics has been described thoroughly by Chemla and Zyss (Chemla and Zyss, 1987) and by Williams (Williams, 1984) and will be shortly summarized.

1.1.1 Theory of nonlinear optics

When an oscillating external electromagnetic field (light), experiences a bulk material, there is a perturbation of its charged species in the material (ions or electrons) and therefore of its polarity, expressed by Eq. (1.1):

$$P \;=\; P_0 + P_{ind} \;=\; P_0 + \chi^{(1)}E \qquad\qquad (1.1)$$

In this equation, P_0 is the intrinsic polarity, P_{ind} is the induced polarization and $\chi^{(1)}$ the electrical susceptibility or linear polarizability tensor. If the applied electromagnetic field strength E is very high as in laser light, the perturbation is not anymore linear with respect to the electric field and the induced polarization is better expressed by a power series expansion in the electric field:

$$P \;=\; P_0 + \chi^{(1)}E + \chi^{(2)}E^2 + \cdots + \chi^{(n)}E^n \qquad\qquad (1.2)$$

$\chi^{(2)}$, $\chi^{(3)}$ and $\chi^{(n)}$ are tensors which are the second-, third-, and n-order electrical susceptibilities respectively, which correspond to non-linear responses of the bulk material. If instead of a bulk material with molecule, the polarization induced in a molecule by an applied electric field is expressed by Eq. (1.3):

$$P = \mu_0 + \alpha E + \beta E^2 + \gamma E^3 + \cdots \qquad\qquad (1.3)$$

μ_0 is the molecular ground state electric dipole moment, α the linear polarizability, β and γ the quadratic and cubic hyperpolarizabilities, respectively. The terms βE^2 and γE^3 correspond to the generation, by a non-linear polarization process of a second-order and third-order emission of light, with wavelength corresponding to 1/2 or 1/3 times that of incident light.

1.1.2 Second-Order Nonlinear Optical Properties

Second Harmonic Generation (SHG), the second-order nonlinear optical (NLO) effect is generated from the mixing of three waves. Two incident waves with ω frequency interact with the molecule or the bulk material, characterize by a given value of quadratic hyperpolarizability value β or of the second-order electrical susceptibility $\chi^{(2)}$, to produce a new wave with frequency 2ω as shown in Fig. 1a.
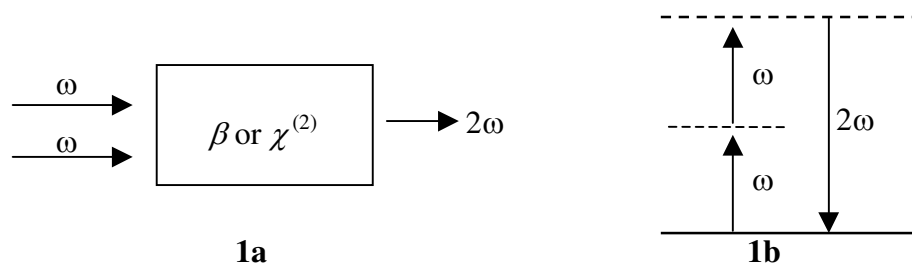

Figure 1a Second Harmonic Generation (SHG).
    1b Energy-level diagram describing second-harmonic generation.

The SHG can also represent by considering the interaction of an electron in molecule and a photon from incoming light. This process visualized in Fig. 1b, an electron absorbs a photon from the incident light and makes a transition to the next higher unoccupied allowed state, then the excited electron absorbs another photon of the same frequency and makes a transition to yet another allowed state at higher energy. This electron when falling back to its original state emits a photon of a frequency

which is two times that of the incident light. This results in the frequency doubling in the output.

The SHG of crystalline materials depends both on the magnitude of the molecular hyperpolarizability β (microscopic non-linearity) and on the orientation of the molecules in the crystal lattice. In 1977, Oudar and Chemla produced a theoretical interpretation of the electronic origin of β and providing a simple model for the design of second-order NLO molecular materials. NLO properties are concerned to the polarizability of the electrons with electric field E of the light, second-order NLO properties are dependent on electronic transition with high charge-transfer character. Oudar and Chemla assumed that in asymmetric 1D organic NLO chromophores the second-order NLO response is dominated mainly by one major charge-transfer process, so that it is possible to assume that:

$$\beta_{zzz} = \frac{3}{2h^2 c^2} \frac{v_{eg}^2 \, r_{eg}^2 \, \Delta\mu_{eg}}{(v_{eg}^2 - v_L^2)(v_{eg}^2 - 4v_L^2)} \tag{1.4}$$

This equation represents the so-called "two level" models, z is the direction of the charge-transfer, $v_{eg}(\text{cm}^{-1})$ the frequency of the charge-transfer transition, r_{eg} its transition dipole moment, $\Delta\mu_{eg}$ its difference between the excited state and ground state molecular dipole moment (μ_e-μ_g) and v_L is the frequency of the incident radiation.

For obtaining the materials with large macroscopic second-order NLO susceptibilities (χ^2), optimization of both the molecular first hyperpolarizabilities (β) and their orientation in the bulk are required. It must be non-centrosymmetric, according to the useful guideline of two-level model. It should have a large difference in dipole moment of molecule between the ground state and excited state, large $\Delta\mu_{eg}$ and v_{eg}, and a small band-gap energy (charge-transfer transitions). In synthesis, these can be achieved in a linear organic chromophore by attaching strong donor and acceptor group through a π-conjugated polarizable spacer and/or elongation of the π-conjugated electron system, as it occur in classical 1D organic dipolar so called push-pull system (Fig.2).
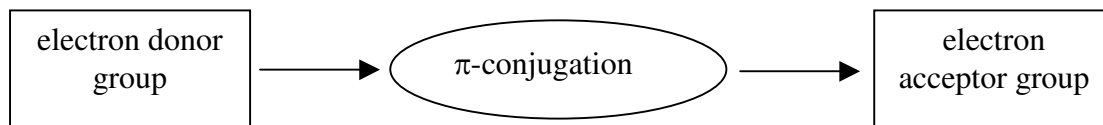
Figure 2 Scheme of a push-pull chromophore.

Nevertheless in such system, molecules with large ground-state dipoles tend to pack in an antiparallel (centric) manner due to intermolecular head-to-tail interactions. For this reason, much effort has been employed to overcome this problem such as the use of supramolecular strategies (Desirajn, 1995), co-crystallization or salt formation strategies (Duan, 1999), inclusion formation with inorganic zeolites strategies (Cox, 1988), etc.

1.1.3 Structural requirements

The basic structure of organic NLO materials is based on the π bond system. Due to the overlap of π orbital, delocalization of electronic charge distribution leads to a high mobility of the electron density. Functionalization of both ends of the π bond system with appropriate electron donor (D) and acceptor (A) groups can enhance the asymmetric electronic distribution in either or both ground and excited states. This asymmetry results in a high degree of intramolecular charge-transfer (ICT) interaction from the donor to acceptor, which seems to be a prerequisite for large second-order nonlinearity (Oudar and Chemla, 1977). The nonlinear part of the induced molecular polarization is the result of the polarizability of the π-electron system. Extensively studied classes of NLO-chromophores of this type are 1,4-disubstituted benzenes and stilbenes, from which *p*-nitroaniline (*p*NA) and 4-(*N,N*-dimethylamino)-4′-nitrostilbene (DANS) are prototypical examples (**Fig. 3**) (Levine, 1975).
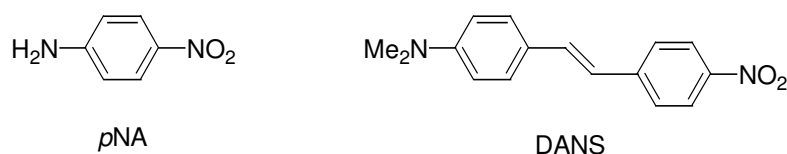
H_2N—◯—NO_2

Me_2N—◯—◯—NO_2

*p*NA

DANS

Figure 3 Prototypical examples of nonlinear optical molecules

The second-order nonlinearity can be enhanced by using stronger donor and acceptor substituents to increase the electronic asymmetry or by increasing the conjugation length between the substituents. Dulcic and Sauteret (Dulcic and Sauteret, 1978) were the first to study the substituent effect in *p*-disubstituted benzene derivatives and Oudar and Le Person reported about the effect of the conjugation length by using a stilbene instead of a benzene π-system (Oudar and Le Person, 1975).

The *p,p*-disubstituted molecules possessed largest β values are obtained when the molecule contains substituents that lead to low-lying charge-transfer resonance states (**Fig. 4**) (Williams, 1984).

A—◯—D ⟷ A=◯=D

A   D ⟷ A   D

A—◯—D ⟷// A—◯—D
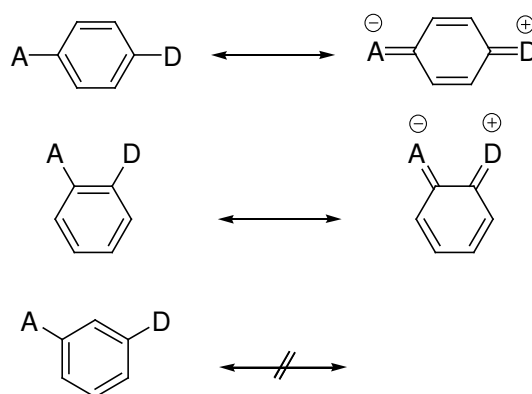
Figure 4 Ground-state and lowest energy polar resonance forms for *para*- and *ortho*-substitution. Resonance is forbidden in the case of *meta*-substitution.

The polarization occurred from contributions of the substituent-induced asymmetry of the π cloud and the σ skeleton of the molecule, as well as from field-induced mixing of the excited state (polar character) into the ground electronic configuration.

Organic crystals were the first bulk organic materials to be investigated for their nonlinear optical properties (Marder and Perry, 1993). About 75% of all organic molecules tend to crystallize in a centrosymmetric space group, which is a serious disadvantage of this approach. Meredith (Williams, 1984) first reported ionic organic NLO (**Fig. 5**).
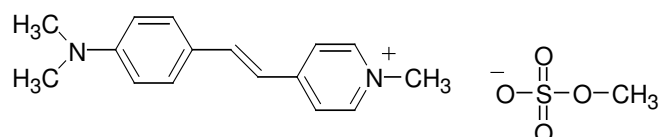

Figure 5 An ionic organic molecule with high SHG efficiency.

This salt had SHG efficiency about 220 times that of urea. Crystallization of organic ionic salts is interesting because they exhibit large β values at molecular level, e.g., the β values of 4-(dimethylamino)pyridinium cation are about 35 x 10^{-30} esu, which is twice larger than that of *p*NA (Anwar, 1997). Moreover, crystals of hydroxyl-substituted stilbazoliums with *p*-toluenesulfonate, MC-PTS, (Okada, 1990) exhibit extremely large $\chi^{(2)}$ more than ten times of inorganic materials such as $LiNbO_3$. In addition, ionic organic NLO crystals possess high values for hardness and have high melting points. Their crystal structures can also be controlled by changing the counter-ions (Nogi, 2000). Benzenesulfonate is most frequently used to co-crystallize with cations to form compounds which are expected to have second-order nonlinear optical properties.

1.2 Nonlinear optic materials

In order to exhibit second-order nonlinearity, a bulk organic material has to possess a non-centrosymmetric alignment of the (di)polar molecules which it consists of. There are several ways to achieve a parallel orientation of NLO-chromophores; those most frequently used are:

(1) Non-centrosymmetric crystals;

(2) Langmuir-Blodgett films;

(3) Poled polymers.

In this study, only the non-centrosymmetric crystals used will be discussed.
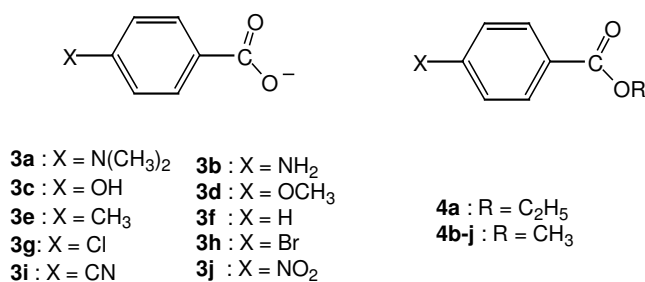
Non-centrosymmetric crystals

Organic molecules containing conjugate systems are highly polar in their ground state and tend to set up antiparallel arrangements leading to centrosymmetric structure in the solid state which vanish all components of $\chi^{(2)}$, or although they achieve noncentrosymmetric structure, the orientation of their molecular dipole moments in the crystalline solid with respect to the polar crystal axes are not optimum for maximizing second-order NLO response (Anwar, 2000). Furthermore, it it difficult to direct the crystallization of an organic compound towards a crystal of the required size, processability, environmental stability and transparency for a typical application. Strategies to favour non-centrosymmetric crystallization are incorporation of chiral substituents in the molecular structure (Zyss *et al*., 1984), organic salts (Marder *et al*., 1989) or designing molecules with specific intermolecular interaction such as hydrogen bonding (Etter and Frankenbach, 1989).

1.3 Review of Literatures

Usman *et al.*, (1997) studied second-order hyperpolarizability of pyridinium cations (**1, 2**).

1

2

X = H, CH$_3$, C$_2$H$_5$, NH$_2$, N(CH$_3$)$_2$
CONH$_2$, COOCH$_3$, CN

X = CONH$_2$, COOCH$_3$, Cl
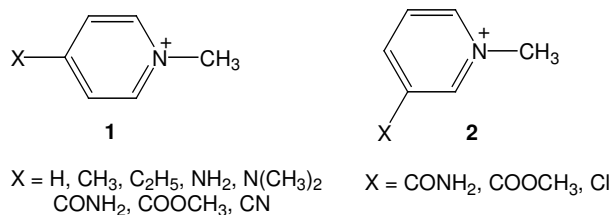
Usman *et al.*, (1998) studied hyperpolarizability of benzoate anions (**3a-j**) and ester (**4a-j**).

3a : X = N(CH$_3$)$_2$ **3b** : X = NH$_2$
3c : X = OH   **3d** : X = OCH$_3$
3e : X = CH$_3$ **3f** : X = H
3g: X = Cl   **3h** : X = Br
3i : X = CN   **3j** : X = NO$_2$

4a : R = C$_2$H$_5$
4b-j : R = CH$_3$

Usman *et al.*, (1999) synthesized substituted pyridiniumbenzene-sulfonate (**5a-h**, **6f**, **6g**, **6i**) crystals for nonlinear optical properties.

5a : X = H
5b : X = CH$_3$
5c : X = C$_2$H$_5$
5d : X = NH$_2$
5e : X = N(CH$_3$)$_2$
5f : X = CONH$_2$
5g : X = COOCH$_3$
5h : X = CN

6f : X = CONH$_2$
6g : X = COOCH$_3$
6i : X = Cl

Z = H, CH$_3$, OH, OCH$_3$,
NH$_2$, NHCOCH$_3$, Cl, Br
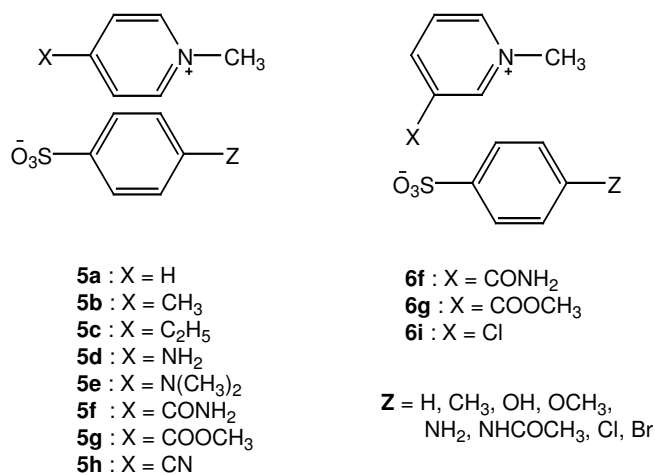
Usman *et al*., (1999) synthesized 4-carbamoylpyridinium benzene-sulfonate (**7**) salts for nonlinear optical properties.

Z = OH, OCH$_3$, Br

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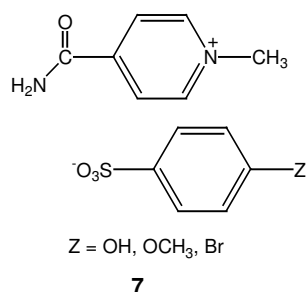
Zelichenok *et al.,* (1999) reported the synthesis and characterization using X-ray diffraction (XRD), NMR and FT-IR and optical spectroscopy measurements of derivatives of donor-acceptor substituted quinolinium iodide (**8**).

R = OCH$_3$, CH$_3$, H, Cl, NO$_2$

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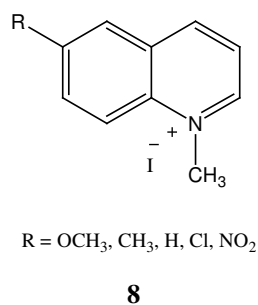
These quinolinium derivatives are transparency in the blue and this property is practically important for NLO usage.

Usman *et al*., (2000) synthesized 4-amino-1-methylpyridinium benzenesulfonate salts (**9**) for second-order nonlinear optical properties.

X = OH, OCH$_3$, CH$_3$, Cl, Br

9
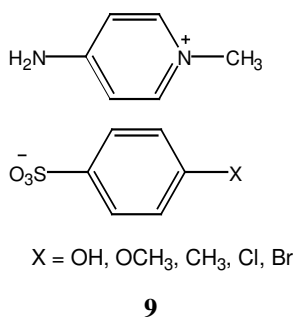
Nogi *et al.*, (2000) synthesized 1-methyl-4-(2-(4-(dimethylamino) phenyl)ethenyl)pyridinium *p*-toluenesulfonate (DAST) analogues (**10**) with increasing number of double bond number between pyridinium and (dimethylamino)phenyl ring.

n = 1, 2, 3, 4, 5

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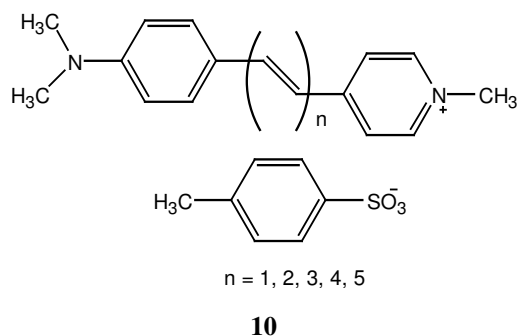
Umezawa *et al.,* (2000) synthesized compounds based on stilbazolium structure with extended π-conjugation by increasing the number of conjugated double-bond between two aromatic rings and/or using a fused ring system like naphthalene instead of phenylene for nonlinear optical materials.

a : X = CH₃, Y = H
b : X = Cl, Y = H
c : X = NO₂, Y = H
d : X = NH₂, Y = H
e : X = Y = H
f : X = Y = NO₂

11a-f : n = 1
12a-f : n = 2
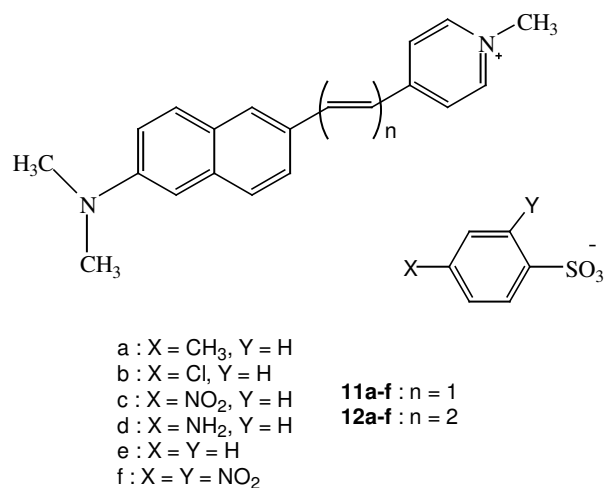
Usman *et al.*, (2001) synthesized 4-(dimethylamino)-1-ethylpyridinium iodide (DMAEPI) (**13**) for use in second-order nonlinear optics.
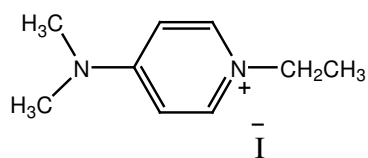
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Bourgogne *et al*., (2001) reported the synthesis, modeling of μ and β, and hyper-Rayleigh scattering (HRS) hyperpolarizability measurements of 4′-nitro-4-stilbazole-*N*-oxide (**14**) and its azo analogue (**15**). These molecules present an intramolecular donor/acceptor charge transfer (ICT) leading to high β hyperpolarizability, but it exhibits a vanishing dipole moment μ which was confirmed by Hartree-Fock calculations.
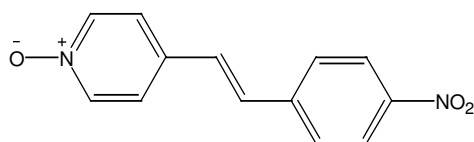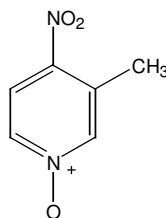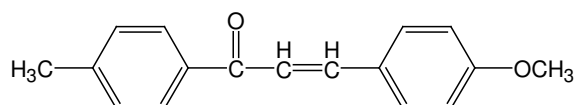

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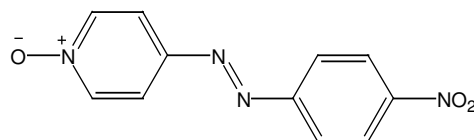
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Lakshmanaperumal *et al.,* (2002) synthesized a new organic nonlinear optical material of 4-methoxybenzaldehyde-*N*-methyl-4-stilbazolium tosylate (MBST) (**16**). Single crystals of MBST were grown by slow cooling solution growth technique. The growth crystals were characterized by IR, NMR and powder XRD techniques. The second harmonic generation studies were done with Kurtz powder technique.
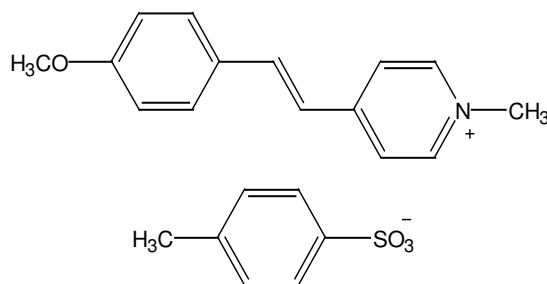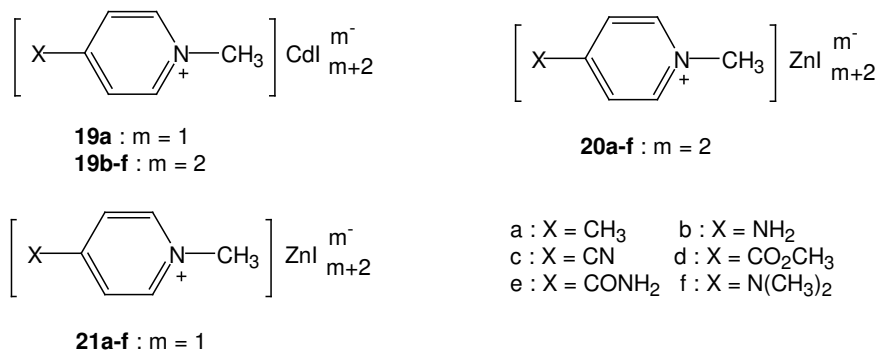
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Boomadevi *et al.,* (2004) grew organic nonlinear optical crystals of 3-methyl 4-nitropyridine 1-oxide (POM) (**17**). Growth technique used was the slow evaporation technique. Second harmonic generation was observed by using Q-switched Nd:YAG laser. Laser damage threshold value has been determined using Q-switched Nd:YAG laser. It was found to be 10.5 GW/cm^2 for single shot and 9.3 GW/cm^2 for multiple shots, indicating that POM had potential for high power laser application.

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Crasta *et al.*, (2004) synthesized new chalcone derivative, 1-(4-methyl-phenyl)-3-(4-methoxyphenyl)-2-propen-1-one (**18**). The crystals of chalcone derivative were grown by low temperature solution growth technique. These crystals were characterized using powder X-ray diffraction, FT-IR, UV-Vis and powder SHG studies.


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Glavcheva *et al.*, (2004) synthesized pyridinium-metal iodide complexes (**19a-f**, **20a-f** and **21a-f**) for second harmonic generation (SHG) materials.


19a : m = 1
19b-f : m = 2

20a-f : m = 2

21a-f : m = 1

a : X = CH$_3$ b : X = NH$_2$
c : X = CN   d : X = CO$_2$CH$_3$
e : X = CONH$_2$ f : X = N(CH$_3$)$_2$

Lakshmanaperumal *et al.,* (2004) synthesized a new nonlinear optical (NLO) material of 4-hydroxy benzaldehyde-*N*-methyl-4-stilbazolium tosylate (HBST) (**22**). Single crystals of HBST were grown using solution growth technique. The growth crystals were characterized by UV-Vis, FT-IR, NMR and powder XRD techniques. The second harmonic generations (SHG) studies were done with Kurtz powder technique.


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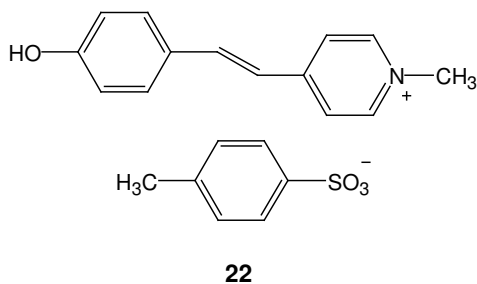
Ray *et al*., (2004) investigated the effect of π-conjugation on first hyperpolarizabilities of series of ionic hemicyanine dyes (**23-28**) using ab initio calculations. Their experimental values showed that the first hyperpolarizability was maximum for n = 2 in ionic organometallic complexes with Rutenium(II) amine donor and *N*-methyl pyridinium as acceptor and n = 3 for ionic *N*-aryl substituted stilbazolium chromophores.
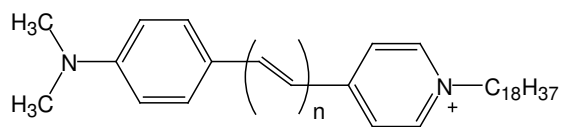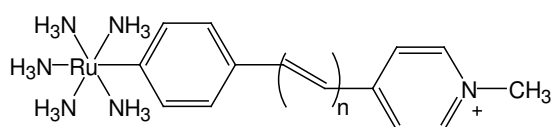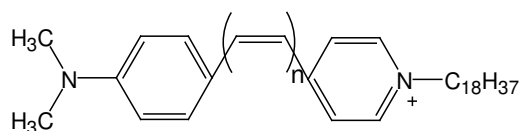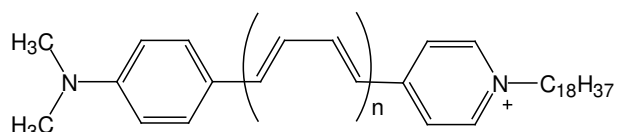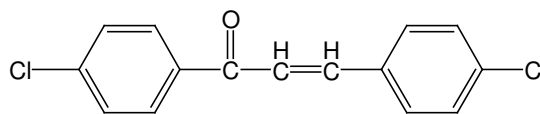
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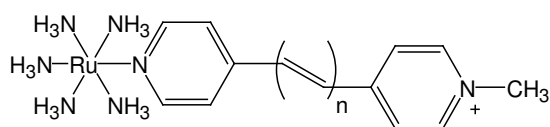
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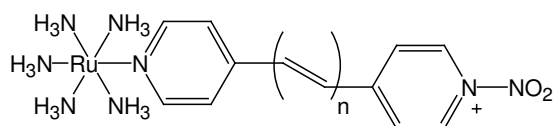
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Crasta *et al*., (2005) synthesized a new chalcone derivative, 1-(4-chlorophenyl)-3-(4-chlorophenyl)-2-propen-1-one (**29**). The chalcone derivative crystals were grown with low temperature solution growth technique. These crystals were characterized using single crystal X-ray diffraction (XRD), FT-IR, UV-Vis and powder SHG studies.
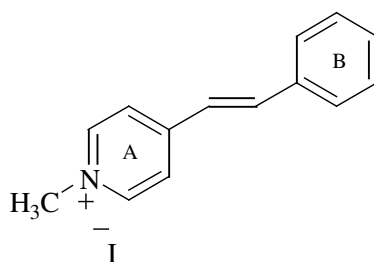
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1.4 Objective and outline of this study

The objectives of this study are:

1. To synthesize the compounds of aryl ethenyl-1-methylpyridinium benzenesulfonate and aryl ethenyl-1-methylquinolinium benzenesulfonate.

2. To determine the structures of aryl ethenyl-1-methylpyridinium benzenesulfonate and aryl ethenyl-1-methylquinolinium benzenesulfonate by spectroscopic techniques and single crystal X-ray structure determinations.

In this work, introduction of an oxochromes, such as OH, OCH_3 on ring **B** or modification of ring **A** with quinolinium unit in the stilbazolium cation was expected to increase π-conjugation. The structures of synthesized compounds were shown in **Figure 6**.
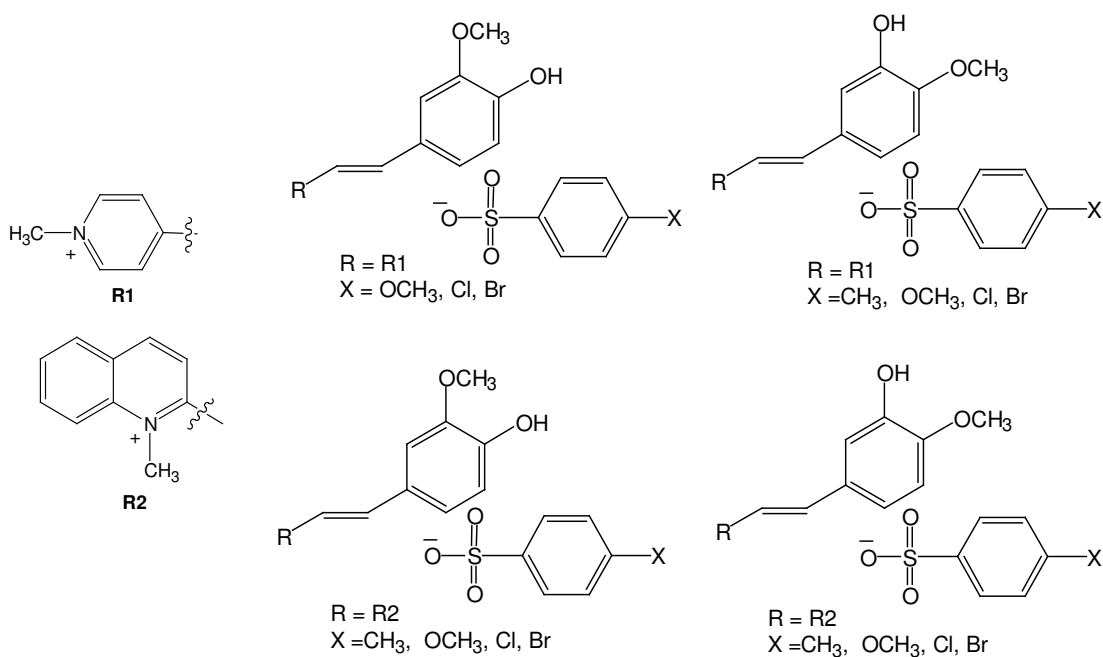
Figure 6 Derivatives of Aryl ethenyl-1-methylpyridinium benzenesulfonate and
Aryl ethenyl-1-methylquinolinium benzenesulfonate.

In this study, focus shall be on the adducts of derivatives of aryl ethenyl-1-methylpyridinium benzenesulfonate and aryl ethenyl-1-methylquinolinium benzenesulfonate (**Fig. 6**) which are expected to exhibit the NLO property. Crystals of a size and quality suitable for single crystal X-ray diffraction studies are grown with the objective to study their structures in solid state.