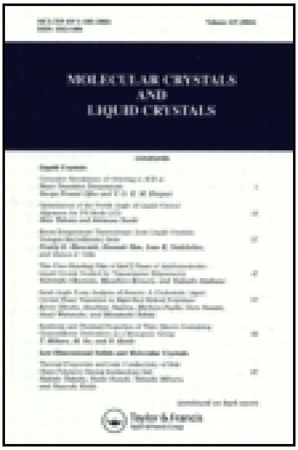

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Synthesis of Two-Photon LC Materials

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Synthesis of Two-Photon LC Materials

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A number of derivatives of distyrlbenzene, having a high cross section for two-photon absorption, are synthesized. Gradual variations in design are carried out to understand the structure-activity correlation and to bring in liquid crystalline nature. The goal is to synthesize liquid crystals with high nonlinear absorption, specifically two-photon absorption, so they can be used as optical shutters and laser hardening materials.

Keywords: Two-Photon Absorption; Liquid crystals; Laser hardening; Distyrlbenzene; Structure-activity correlation

INTRODUCTION

Advent of laser opened up the whole field of Nonlinear Optics widely with its potential for applications in information processing and data storage. Hitherto, most widely sought after are second and third order materials. Multi-photon, specifically two-photon materials seem to have a greater potential in biomedical application and optical data storage. Another of its important application would be in addressing the major concerns of the Air Force to protect human eyes from harmful short laser pulses. One of the best possible solutions would be a good optical switch, shutters or limiters that can provide protection over a wide spectrum of frequencies and duration [1-3]. The materials needed are liquid crystals with inherent strong optical nonlinearity. Currently available, commercial liquid crystals have very weak nonlinear optical responses and the reported two-photon absorption cross section is not large enough to be used with high-energy short pulses. The available lc shutters are also too slow to respond to short laser pulses.

Possible approaches to overcome these limitations are either to incorporate nonlinearity into lc materials or to design good nonlinear absorbers with mesogenic structural features. The field is still in its infancy. Synthesis of a series molecules are tried to optimize the structural features that will confer a high Two-Photon Absorption Cross Section, TPACS, along with liquid crystalline nature. Systematic structural variations are tried to understand the structure-activity correlation to enable effective tuning of the molecules.

WHAT IS TWO-PHOTON ABSORPTION?

Generally molecules absorb a single photon at a time and emit another photon of lower frequency. This is an optically linear behavior. However, certain molecules, when irradiated with light of high intensity (laser) absorb two photons simultaneously and emit a photon of higher energy. Usually it occurs when the sum of the energies of the two photons is close to transition energy[4]. Such molecules are optically nonlinear and Two-Photon Absorption (TPA) is an example of such nonlinear optical behavior.

Typically, a molecule absorbs two photons of lower frequency and goes from the ground state S_0 to an excited level S_{2P}, relaxes back to the first excited level, S_{1P}; from S_{1P}, it has many choices to decay as outlined in Jablonski diagram (Figure 1).

The TPASC, δ is defined as[5-6]

$$\delta_{S_0 \to S_2} \propto \frac{M_{01}^2 M_{12}^2}{(E_1 - E_0 - \hbar\omega)\Gamma}$$

Where M is the transition dipole moment between states, E is the energy of states and Γ is a damping factor.

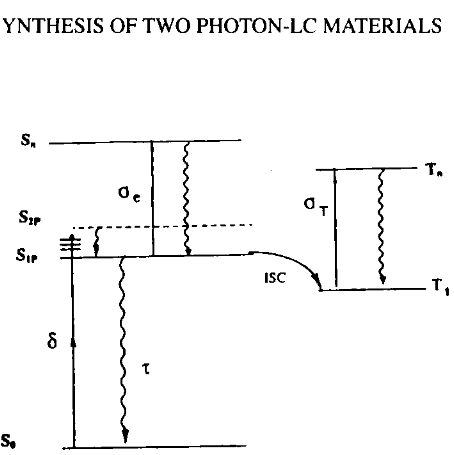


FIGURE 1. Jablonski Diagram for Two-Photon Absorption

WHY IS THE NEED FOR TWO-PHOTON LC MATERIALS?

Two photon absorption allows a precise excitation of molecules very near the focus of the beam for its transition probability depends on I^2, which in turn has an inverse dependenceof d^2; this finds application in 3-d optical data storage[7-8], optical limiting[9-10] and biological fluorescence imaging[2,11-13]. Further, there is minimal or no scattering and photobleaching with TPA. The phototoxicity is minimal for it involves the use of two low energy photons in the place of a single high-energy photon. They seem to exhibit the requisites of an ideal optical limiting material.

Liquid crystals have good switching capabilities. If one can design a molecule to have a good optical limiting capacity with switching capabilities, an ideal laser hardening material will be born. Hence is our interest in TP-LC materials.

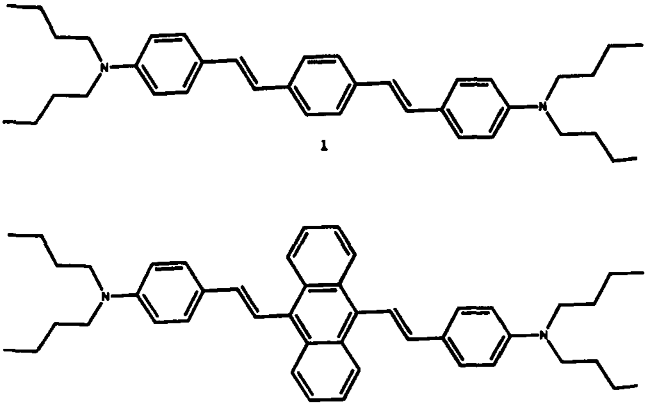
DESIGN STRATEGY

One of the requisites for high TPACS is, as stated earlier, that the sum of the energies of two photons is close to a one-photon transition energy; this is achievable by a large redistribution of charge density either from the center towards the end of the molecule or vice versa. The design needs to maximize the transition dipoles between states as shown in the definition of δ. This could be achieved easily by substitution of electron donors or acceptors on either end of the molecule. Our previous experience with polyphenyls[14], distyrylbenzenes[15], symmetric LCs[16] and structure-NLO activity [17,18] embarked us on synthesizing distyrylbenzenes with bis-donor groups.

SYNTHESIS

Phase I

Synthesis of compounds **1-2**, shown in Figure 2 formed the first phase of our investigation. The very first compound synthesized, Compound **1**, has a hitherto unreported high cross section for TPA[19] and had a bright greenish yellow fluorescence. However no phase transitions were detected in DSC. Microcopy reveals it to be incredibly birefringent with beautiful display of colors. The same behavior is observed for **2**.



2

FIGURE 2. Structures of Compounds **1** and **2**

Synthetic Strategy Tips from Phase I

The absence of mesogenic nature in **2** was not surprising given its shape. However, despite the ideal lathe shape needed for exhibiting liquid crystalline nature, absence of lc phases in 1 puzzled us. Molecular modeling calculation and AM1 optimization (Figure 3) reveal that the very likely culprit distorting this ideal geometry is the di-n-butyl groups on a sp^3-nitrogen; however, these longer alkyl chains are very much needed to make it soluble. One way of reducing the distortion would be to use shorter chains but with polar groups to give the desired solubility. This hypothesis led to the Phase II of our synthetic efforts.

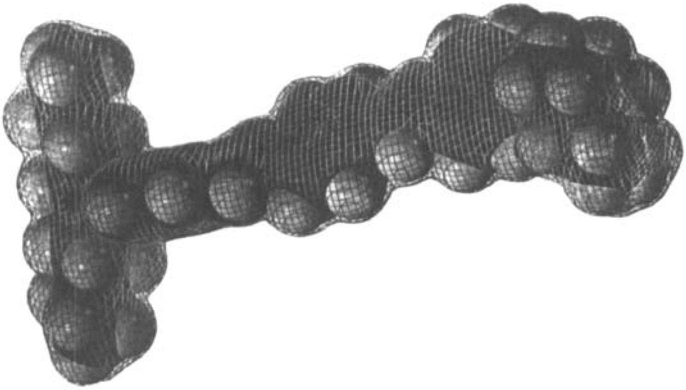


FIGURE 3. AM1 Optimized Geometry of **1**

Phase II

Variations in polarity are tried at the donor ends to induce mesogenic nature and compounds **3**, **4** and **5** were synthesized (Figure 4). Compound **4** and **5** area bright yellowish green in color, are highly fluorescent and have high solubility in common solvents whereas compound **3** has limited solubility and is not as fluorescent. Compound **4** show a short range, high temperature phase transition just before it reaches the clearing point. DSC and photomicrograph confirms a phase transition (Plate 1). The exact identity of the phase is yet to be determined. Other compounds did not show any detectable phase transitions in DSC. Microscopic examination is yet to be carried out.

Compound **6**, designed to see the influence of increased conjugation did show detectable transitions in DSC; its solubility is too little to pursue any further investigation.

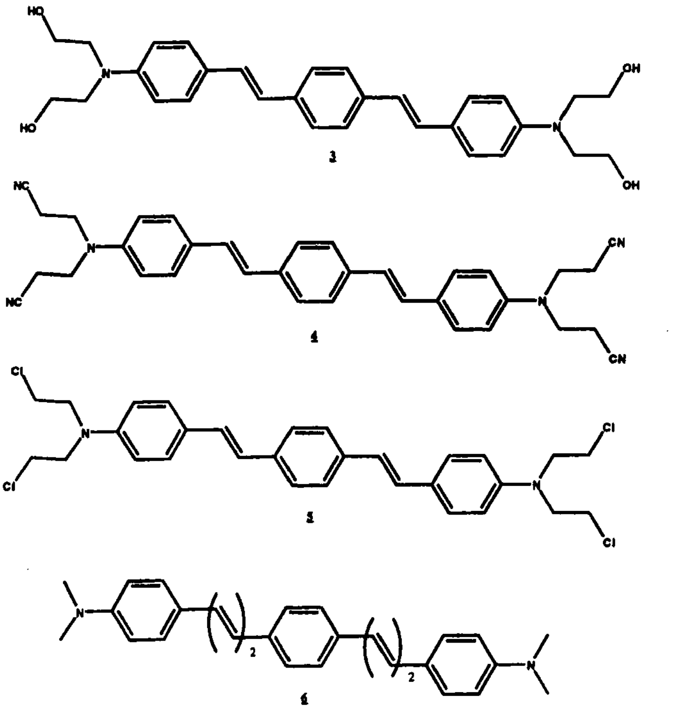


FIGURE 4. Structures of Compounds **3-6**.

Synthetic Tips from Phase II

The results seem to confirm our hypothesis that having shorter, polar chains will take us towards the goal of making TP-LC materials. Having encouraged by the appearance of short-range mesogenic transitions in **4**, our efforts are directed in its structural variations and form the current Phase III of our efforts.

Phase III

Structural variations of **4** (Figure 5) that would help in getting a low temperature, long range liquid crystalline phases are being tried. In order to see the influence of heteroatom – nitrogen versus oxygen – compounds **10** and **11** are made along with **7**, **8** and **9**. Compound **9** showed some interesting microscopic textures indicative of some liquid crystalline phases (Plate 2); however these transitions are not observed in DSC. Other compounds are yet to be studied.

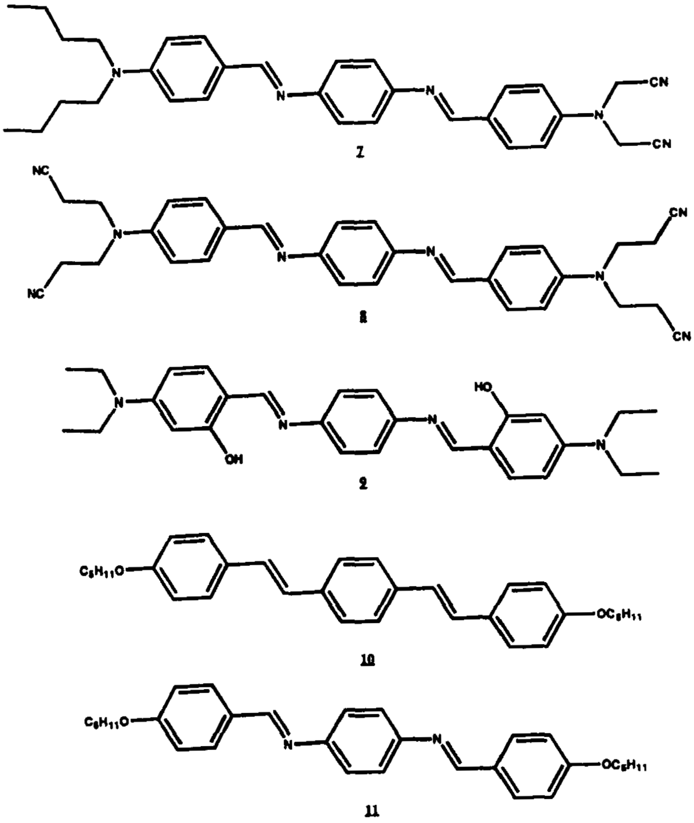


FIGURE 5. Structures of Compounds **7-11**

PLATE 1. LC Texture of Compound **4**
See Color Plate I at the back of this issue.

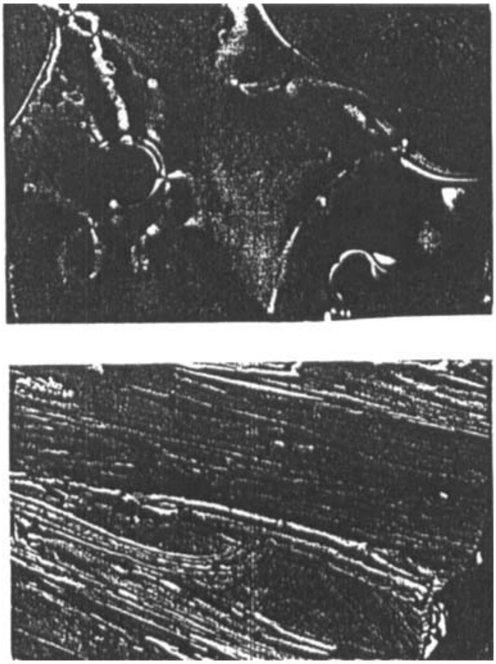


PLATE 2. LC Textures of Cpmpound **9**
See Color Plate II at the back of this issue.

EXPERIMENTAL

1,4-Bis-styrylbenzene with N, N-dialkylamino donors was used as the central core for most of the compounds synthesized. All the compounds are prepared by the Wittig reaction between phosphonium salts and aryl aldehydes following the reported procedure[20]. All the compounds synthesized are well characterized and isolated as E, E-isomers in >90% yield. DSC runs were made using a Perkin-Elmer DSC-7 at the heating rate of 10° C /min.

FUTURE DIRECTION

This work reveals that dialkyl amino end groups are not favoring mesogenic phase formation. Further work in carrying out more detailed investigation of the compounds synthesized. Our future direction will be devoted to non-symmetric design, but without losing the intrinsic high TPACS of this set of molecules.

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