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Odd-even oscillations of SHG efficiencies in twin NLO chromophores

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ABSTRACT

Twin NLO chromophores having two azobenzene units linked by a flexible polymethylene spacer of varying lengths are shown to exhibit odd-even oscillations in their second harmonic generation (SHG) efficiencies, when measured in the powder form. These twin systems were designed to also exhibit liquid cystallinity, and indeed most of them do exhibit a nematic mesophase. The anticipated odd-even oscillations, in both their isotropization transition temperatures (Ti) and isotropization entropies (ΔSi), were also observed. The odd-even oscillation of the SHG efficiencies has been ascribed to a more effective cancellation of mesogenic dipoles in the even twins as compared to their odd counterparts, due to a preferred centrosymmetric packing in the former case. Based on the behaviour of these twin chromophoric molecules, it may be anticipated that such odd-even oscillations will also be observed in the analogous main chain NLO polymers.

INTRODUCTION

The molecular structural criteria that would enable molecules to exhibit high nonlinear optical activity have now been reasonably well enunciated.[1] However, for second harmonic generation (SHG), the greater challenge is the construction of non-centrosymmetric molecular assemblies. Several approaches using the methods of crystal engineering, Langmuir-Blodgett techniques and electric field poling, specifically in polymer based systems, have been successfully explored during the last decade.[2] The polymer based approaches, both of the doped and covalently linked types, have the distinct advantage of ease of proccessability and device fabrication. In doped polymeric systems, one major constraint is the solubility of the chromophore in the polymer matrix which limits the number density and hence the finally achievable SHG efficiency. In an effort to overcome this limitation, polymers in which the NLO chromophores are covalently linked, both as a pendant group and as an integral part of the backbone, have been extensively investigated.[3]

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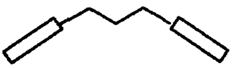
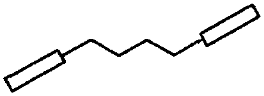
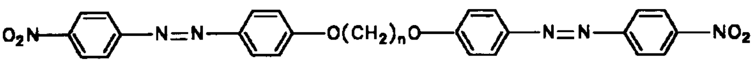
The simplest model for polymers with NLO chromophores in the backbone is a molecule in which the two chromophores are linked by a flexible spacer in the manner: chromophore-spacer-chromophore. Twin chromophoric molecules, in which two electronically isolated chromophores have been suitably linked to a rigid molecular framework, have been successfully employed as an approach to enhance the NLO activity by virtue of directional dipole additivity.[4-6] More recently, such twin systems have also been utilized to generate poled crosslinked polymeric systems.[7] While several polymers with the chromophores in the backbone have been studied, the role of the connecting spacer has not been addressed.[8] In the context of main chain liquid crystalline polymers, however, it has been noticed that the spacer segment plays an important role in governing the phase transition temperatures and also the entropies associated with these transitions.[9-11] Dimeric liquid crystals (DLC's), in which two mesogens are linked by a flexible polymethylene spacer in the sequence, mesogen-spacer-mesogen, have been extensively investigated as low molar mass models of polymeric liquid crystals in which the mesogens are linked together by flexible spacers to form the polymer backbone[12-14]. Just as in the case of polymers, a significant oscillation of the isotropization temperatures (Ti) and isotropization entropies (ΔSi) with varying spacer length (odd vs even) has been observed in the dimers, although to a slightly lesser extent. These dimers have, therefore, been considered as ideal models in the conceptual progression: monomer→dimer→polymer. The odd-even oscillations in these systems are believed to arise due to the preference of the polymethylene spacer to adopt a conformation that leads to a co-linear arrangement of the two mesogens in the even cases, while it leads to a biaxial one in the odd cases.[15-17] X-ray diffraction studies have indeed shown that, in the crystalline phase of one such dimer, the polymethylene spacers does adopt an all-trans conformation[18]. Such a conformational preference would lead to two different preferred orientations of the mesogens relative to one-another in the odd and even series, which may be schematically represented as shown below.





The introduction of strong electron donors and acceptors in the 4 and 4' positions of many of the typical mesogens, like azobenzene, stilbene, biphenyl etc., make them potential candidates for observation of nonlinear optical (NLO) activity.[2] As seen from the above schematic representation, the packing constraints experienced by the odd and even series are likely to be very different, giving rise to the possibility of observing odd-even oscillations in the measured SHG efficiencies in such twin systems. In this paper, a series of twin chromophoric molecules A(n), having two azobenzene based mesogens linked with a flexible polymethylene spacer of varying lengths, n, have been synthesized and both their mesogenic properties and SHG efficiencies have been investigated.



A(n)

EXPERIMENTAL SECTION

^{1}H-NMR spectra were recorded on a Bruker ACF-200 MHz spectrometer, using TMS as the internal reference and $CDCl_3$ as the solvent. The UV-visible spectra were recorded using a Hitachi U3400 instrument. DSC studies were done using a Rheometric Scientific DSC Plus instrument. The thermograms were recorded, both during the heating and cooling runs, using a heating/cooling rate of 10 deg/min. A slow purge of dry nitrogen gas (5ml/min) was maintained to prevent any possible oxidative degradation. The reproducibility of the thermograms was confirmed by recording the second and third heating runs. Polarized light microscopic studies were carried out using a Leitz Ortholux II Pol-BK microscope equipped with a Mettler FP82HT hot stage. All solvents were purified before use using standard methods. 4-Hydroxy-4'-nitro azobenzene was prepared using a previously reported procedure.[19] The α-ω dibromoalkanes were either purchased from Aldrich Chemical Company or prepared from the corresponding diols using red phosphorous and bromine.

A typical procedure for the synthesis of A(n): 1.8 g (7.4 mmols) of 4-hydroxy-4'-nitro azobenzene and 0.4 g (1.97 mmol) of 1,3-dibromopropane were dissolved in 40 ml of dry acetone and taken in a round bottom flask. 1.97 g (14.3 mmol) K_2CO_3 and 0.618 g (1.9 mmol) of tetrabutylammonium bromide were then added to it and the contents of the flask were allowed to reflux with stirring under a nitrogen blanket. After about 96 h, the acetone was removed using a rotary evaporator and distilled water was added to the residue. The insoluble organic residue was washed several times with water, filtered and dried. The solid residue was further extracted in refluxing methanol for a few hours and then hot filtered to ensure complete removal of any residual dye. The product was further recrystallized from 1,1,2,2-tetrachloroethane, washed with chloroform and then dried. Yield = 64%. All other dimers of this series were prepared similarly and their yields varied between 50-67%, except A(1) and A(2) which were obtained in yields of 6 and 12%, respectively.

H-NMR ($CDCl_3$) (δ in ppm) : 1.5-2.0 (m, 2H, CH_2,); 4.1 (t, 4H, $ArOCH_2$); 7.0 (d, 4H, Ar); 7.9-8.0 (two doublets, 8H, Ar); 8.3 (d, 4H, Ar)

NLO Measurements: The powdered samples were first sieved (<100μm) and taken in a glass capillary. The fundamental of a Q-switched Nd:YAG laser was used as the incident source. The scattered second harmonic light ($I_{2\omega}$) was collected (at 90° to the incident beam) by an efficient condenser system, consisting of a concave mirror and an aspherical lens (in order to ensure high sensitivity), and was directed towards a photocathode of a UV-Vis photomultiplier tube. Any scattered light other than the second harmonic were eliminated by using a 4nm bandwidth 532nm interference filter. A similar measurement was carried out for a standard sieved sample of urea, and the SHG efficiencies are taken as the ratio $I_{2\omega(sample)}/ I_{2\omega(urea)}$.

RESULTS AND DISCUSSION

The twin chromophores were readily synthesized from 4-hydroxy-4'-nitro azobenzene and the appropriate α,ω-dibromoalkanes using standard coupling conditions. The structures of the products were confirmed by their ^{1}H-NMR spectra. The UV-Vis spectra of all the dimers in solution were essentially identical and all of them exhibited a peak at 379nm (ε = 3.8 to 5.2 x10^4 l mol^{-1} cm^{-1}) with a tail extending to around 530nm. An exception was that of A(1), which had a λmax value that was slightly shifted to 365 nm. A model monomeric molecule, 4-nitro-4'-hexyloxy azobenzene (B) was also prepared for comparison. This monomer also had an essentially identical absorption spectrum suggesting that the two chromophores in most of the dimers are non-interacting in the ground state, and furthermore that they are also electronically identical to their monomeric analogue.

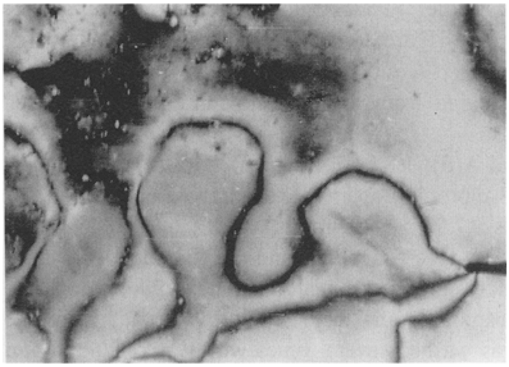


Figure 1. Typical schlieren texture of A(6) at 222°C

DSC and polarizing light microscopic studies confirmed that the monomer (B) exhibited a very narrow nematic phase (T_{K-N} =97°C, T_{N-I}=99°C), which is in agreement with the values previously reported[20]. Similarly, all the dimers also exhibited a nematic phase, except A(1) and A(3) which were not liquid crystalline. Furthermore, A(2), A(4) and A(5) were seen to be monotropic, and exhibited a nematic phase only while cooling. The formation of a nematic phase was confirmed by polarized light microscopic studies; typical schlieren textures characteristic of nematic phases were observed in all cases. A typical schlieren texture, that of A(6), is shown in figure 1. Additionally, several of these dimers also exhibited other transitions, which were confirmed to be crystal-crystal transitions by direct observation under the polarized light microscope. A plot of the transition temperatures as a function of the spacer length (Figure 2) shows that both the melting (T_{K-N}) and the isotropization temperatures (T_{N-I}) showed odd-even oscillations, which is characteristic of such dimeric liquid crystals. The temperatures plotted correspond to the values obtained during the cooling scans. As previously observed, in the cases of dimeric liquid crystals,[12-14] these oscillations were more pronounced in the case of short spacers, and they fall off with increasing spacer lengths. A plot of isotropization entropies (ΔS_{N-I}) versus n (Figure 3) also show similar oscillations, although the magnitude of these oscillations does not weaken with increase in spacer length, as observed previously.

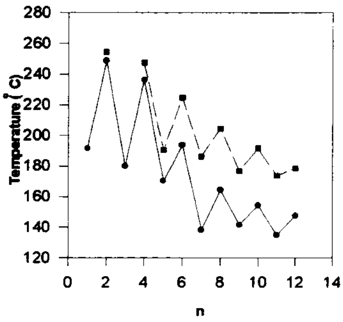


Figure 2. Variation of the transition temperatures of A(n) with n. ● - T_{K-N} (or T_{K-I}) and ■ - T_{N-I}.

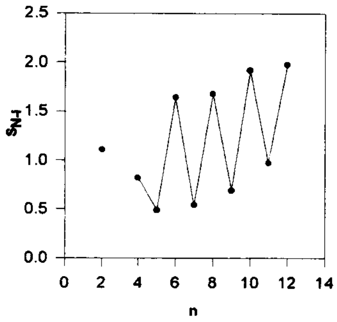
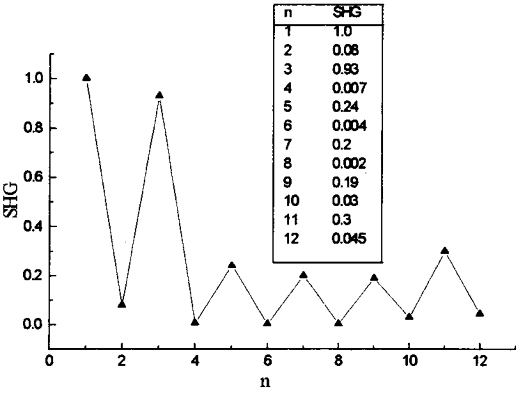


Figure 3. Variation of ΔS_{N-I} versus n for A(n). (Values from the cooling scans).

The SHG efficiency of the dimers were measured in the powder form.[21] The experimental setup for the SHG measurements was exactly similar to the HRS experimental setup which we have used to measure the β values in solution.[22] The only difference is that we used glass capillary containing the solid instead of the solution cell as in the HRS experiment. The SHG efficiencies of the samples are taken as the ratio $I_{2\omega(\text{sample})}/ I_{2\omega(\text{urea})}$. A plot of this ratio as a function of spacer segment length 'n' is shown in figure 4.

Firstly, it is noticed that the SHG efficiencies of the dimers belonging to the odd series (which lie in the range 1.00 to 0.19) were found to be significantly larger than those of the even one (which lie in the range $8\text{x}10^{-2}$ to $2.1\text{x}10^{-3}$). The SHG efficiency of the analogous monomer B, was found to be 0.38, which lies in between that of A(1) and A(2). Furthermore, these values decreases with the increase in the spacer segment length, the decrease being pronounced at small spacer lengths. However, at longer spacer lengths (n>4) the variation within both the odd and even series is small. It is also interesting to note that the SHG efficiencies appear to go through a minimum value, in both the odd and even series, although it is more pronounced in the odd



n	SHG
1	1.0
2	0.08
3	0.93
4	0.007
5	0.24
6	0.004
7	0.2
8	0.002
9	0.19
10	0.03
11	0.3
12	0.045

Figure 4. Variation of SHG efficiencies of A(n) with n.

case.[23] A possible reason for this behaviour may be the interplay between the chromophore and the polymethylene spacer in governing the crystal packing.

The significantly higher SHG efficiencies for dimers of the odd series implies that there is a less effective cancellation of dipoles, associated with the chromophores, in the crystalline state of the odd dimers as compared to the even ones. In the even cases, the all-trans arrangement of the methylene spacer of the dimer will lead to conformers that possess a centre of symmetry, while in the odd cases it could lead ones which may possess a mirror plane (see earlier schematic depiction). Based on the simple close-packing principle,[24] it may therefore be expected that the even dimers will crystallize, in all probability, in a centrosymmetric arrangement leading to a more effective cancellation of the chromophoric dipoles. However, the odd dimers appear to crystallize in a noncentrosymmetric arrangement, and hence exhibit significantly higher SHG efficiencies. Unfortunately, it was very difficult to grow good single crystals of any of these twin chromophores that were suitable for x-ray diffraction studies. The study of these dimers dispersed in polymer matrices, specifically to understand the role of the connecting spacer in governing their relaxation in poled systems, is one of the future objectives. The rather low solubility of these azo-twins make them poor candidates for the relaxation studies, and hence, other more soluble twin chromophoric molecules are currently being synthesized to address the above issues.

In conclusion, we have demonstrated that significant odd-even oscillations of the SHG efficiencies are observed in twin chromophoric molecules, wherein the two chromophores are linked by a polymethylene spacer. This, in turn, suggests that such oscillations may also be observed in main chain NLO polymers, probably even to a greater extent, considering the analogous behaviour in main chain liquid crystalline polymers. *This implies that the spacers in main chain NLO polymers, hitherto mostly considered as linking groups, may have an active role in governing both the maximum achievable SHG efficiencies upon poling, as well as their temporal stability.* Work to test this hypothesis is currently underway.

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