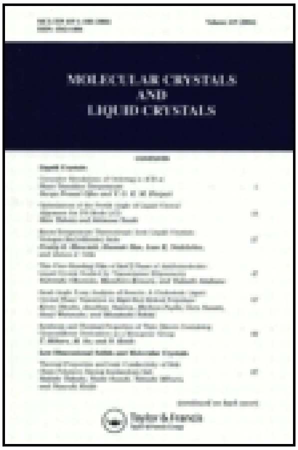

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

The Effect of Conjugation Length and Electron Donor Groups on the Second Order Nonlinear Polarizability of Cyano Substituted Aromatic Molecules

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Version of record first published: 13 Dec 2006.

To cite this article: G. Berkovic , Y. R. Shen & M. Shadt (1987): The Effect of Conjugation Length and Electron Donor Groups on the Second Order Nonlinear Polarizability of Cyano Substituted Aromatic Molecules, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 150:1, 607-616

To link to this article: http://dx.doi.org/10.1080/00268948708074818

Mol. Cryst. Liq. Cryst., 1987, Vol. 150b, pp. 607–616
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Printed in the United States of America

The Effect of Conjugation Length and Electron Donor Groups on the Second Order Nonlinear Polarizability of Cyano Substituted Aromatic Molecules

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(*Received July 7, 1987*)

Second order nonlinear polarizabilities, $\alpha^{(2)}$, were measured for various cyano-substituted aromatic (phenyl, biphenyl, terphenyl and phenylpyrimidine) molecules. The largest nonlinearity was found in cyano-biphenyl compounds, indicating that ring twisting may be causing a decrease in terphenyl nonlinear polarizability. Electron donating substituent effects were demonstrated by comparison of the nonlinearity of alkyl and alkoxy cyanobiphenyls. In all cases $\alpha^{(2)}$ was determined from analysis of the optical second harmonic generation from a monolayer of amphiphilic molecules spread at the air/water interface.

INTRODUCTION

There is considerable current interest in the nonlinear polarizability of organic materials due to the possibilities of utilizing this property for fabrication of optoelectronic devices,[1] as well as quantifying, both theoretically and experimentally, the relationship between molecular structure and the magnitude of molecular nonlinear polarizability. It has become clear[2] that the highest values of second order nonlinear polarizability, $\alpha^{(2)}$, are found in molecules where electron donating and electron accepting groups are connected through a delocalized π electron system. However, the best insight into the relationship between $\alpha^{(2)}$ and molecular structure is achieved when $\alpha^{(2)}$ values are determined for a series of molecules in which there is systematic variation in the relevant structural parameters—e.g. the electron donor group, the electron acceptor group, or the type and length of the delocalized π electron system between them. Several such studies, both theoretical and experimental, have been carried out.[3-6] The present work extends such studies to a new family of compounds, cyano substituted aromatic molecules, in which various aromatic systems (bridging the electron accepting cyano group to the electron donating alkyl chain) have been compared. The effect of an alkoxy chain as the electron donor species has also been examined.

Experimental determinations of $\alpha^{(2)}$ have mostly been made by the electric field induced second harmonic generation (EFISH) method. In this method,[2] the optical second harmonic generation (SHG) is measured when the molecule in solution is subjected to a DC electric field. Consequently the EFISH response results from a combination of second order and third order nonlinear effects arising from the solvent, solute and the cell. Thus, even after subtraction of the background signal, an accurate determination of the solute $\alpha^{(2)}$ requires a good knowledge of solvent–solute interactions and local field effects.

Consequently, other workers[7-10] have preferred to determine $\alpha^{(2)}$ via SHG from an ordered molecular monolayer spread on an isotropic substrate such as water, glass or fused quartz. An isotropic substrate cannot have electric dipole allowed SHG due to symmetry considerations, although there still may be weak SHG from the bare substrate due to quadrupole effects.[11] Consequently, the SHG from an isotropic substrate covered by an aligned, noncentrosymmetric molecular adsorbate layer will typically be many times larger than the SHG from the bare substrate alone.[7-10]

In this communication we use the monolayer method to evaluate $\alpha^{(2)}$ for representative n-alkyl cyanophenyl, cyanobiphenyl, cyanoterphenyl and cyano-phenylpyrimidine molecules. This series enables us to study the effect on $\alpha^{(2)}$ caused by the various conjugated systems connecting an electron donor (the alkyl chain) and an electron acceptor (the CN group). In addition, the effect on $\alpha^{(2)}$ by using an alkoxy chain as the electron donor is also examined. All the above molecules are known to form liquid crystalline bulk phases,[12,13] and consequently several molecules in each class differing only in alkyl chain length are available and characterized in the literature. We have shown[9] (for the *n*-alkyl cyanobiphenyls) that the length of the alkyl chain does not influence $\alpha^{(2)}$; thus we have chosen as a representative molecule for each class a molecule whose alkyl chain length is such as to cause the molecule to spread and form a good monolayer on water.[10,14]

THEORY

The value of $\alpha^{(2)}$ for individual molecules may be deduced from the SHG arising from a molecular monolayer spread on a water surface. The second harmonic intensity, $I(2\omega)$, observed in reflection after laser radiation of intensity $I(\omega)$ impinges on the monolayer covered surface is given by[7,9]:

$$I(2\omega) \propto |\mathbf{e}_{2\omega}\overleftrightarrow{\chi}_s^{(2)}:\mathbf{e}_\omega\mathbf{e}_\omega|^2 I^2(\omega) \tag{1}$$

where $\mathbf{e}_\Omega = \mathrm{L}_\Omega\hat{\mathbf{a}}_\Omega$ with $\hat{\mathbf{a}}_\Omega$ denoting the unit polarization vector of the field at frequency Ω, and L_Ω is the Fresnel factor for the field. Here the Fresnel factors are calculated assuming that the linear dielectric constant of the monolayer is unity.[15] The magnitude of the components of $\overleftrightarrow{\chi}_s^{(2)}$, the second order surface susceptibility tensor, may be determined by comparison of the SHG from the adsorbate covered surface to that arising from a surface of known $\overleftrightarrow{\chi}_s^{(2)}$ (e.g. the bare water surface) under the same experimental conditions.

The contributions to $\overleftrightarrow{\chi}_s^{(2)}$ may be represented[10,11]

$$\overleftrightarrow{\chi}_s^{(2)} = \overleftrightarrow{\chi}_w^{(2)} + \overleftrightarrow{\chi}_m^{(2)} + \overleftrightarrow{\chi}_i^{(2)} \tag{2}$$

where $\overleftrightarrow{\chi}_w^{(2)}$ and $\overleftrightarrow{\chi}_m^{(2)}$ are the susceptibilities of the substrate (water) and the monolayer of adsorbate molecules respectively, and $\overleftrightarrow{\chi}_i^{(2)}$ includes any perturbational interaction between them. As stated above, $\overleftrightarrow{\chi}_w^{(2)}$ is weak, often leading to $\overleftrightarrow{\chi}_s^{(2)} >> \overleftrightarrow{\chi}_w^{(2)}$. Thus, assuming $\overleftrightarrow{\chi}_m^{(2)} >> \overleftrightarrow{\chi}_i^{(2)}$, we have $\overleftrightarrow{\chi}_s^{(2)} \cong \overleftrightarrow{\chi}_m^{(2)}$.

Evaluation of the molecular polarizability tensor $\overleftrightarrow{\alpha}^{(2)}$ of individual molecules from $\overleftrightarrow{\chi}_m^{(2)}$, the susceptibility of an adsorbate monolayer, is simplest for molecules in which $\overleftrightarrow{\alpha}^{(2)}$ is dominated by a single component $\alpha^{(2)}_{\xi\xi\xi}$ along a molecular axis ξ. In such cases the only nonvanishing components of $\overleftrightarrow{\chi}^{(2)}_{m}$ are related to $\alpha^{(2)}_{\xi\xi\xi}$ by[7,9]

$$\chi^{(2)}_{m;zzz} = N_s\langle\cos^3\theta\rangle\alpha^{(2)}_{\xi\xi\xi}$$

$$\chi^{(2)}_{mii} = \chi^{(2)}_{m;izi} = N_s\langle\sin^2\theta\ \cos\theta\rangle\alpha^{(2)}_{\xi\xi\xi}/2 \qquad (i = x, y) \qquad (3)$$

where θ is the polar angle between $\hat{\xi}$ and the surface normal $\hat{\mathbf{z}}$, and N_s is the surface density of adsorbate molecules. In addition to neglecting components other than $\alpha^{(2)}_{\xi\xi\xi}$, this model also assumes an isotropic distribution in the surface (xy) plane, and neglects local field effects caused by intermolecular interactions. Earlier work[10] on similar molecules has shown these assumptions to be justified for less than half full monolayers.

It thus follows that determination of $\chi^{(2)}_{m;zzz}$ and $\chi^{(2)}_{m;zii}$ from SHG with appropriate polarizations of fundamental and second harmonic fields will yield a weighted average for θ. A sharply peaked distribution for θ is expected for an aligned monolayer of amphiphilic molecules in which that part of the molecule dominating the nonlinearity includes the polar head group which determines the molecular alignment at the air/water interface. A narrow distribution of θ values about its average value θ_0 means that the experimentally measured ratio of $\chi^{(2)}_{m}$ components given by $\langle\sin^2\theta\ \cos\theta\rangle/\langle\cos^3\theta\rangle$ can be equated, to a good approximation, to $\tan^2\theta_0$. As a numerical example, it is easily calculated that if θ is given by a rectangular distribution function centered at $\theta = 60°$, the function $\langle\sin^2\theta\ \cos\theta\rangle/\langle\cos^3\theta\rangle$ equals 3.00, 2.91 or 2.70 if the half width of the θ distribution is taken to be 0°, 5° or 10° respectively. Equating these values to $\tan^2\theta_0$ gives $\theta_0 = 60°$, 59.6° and 58.7° respectively. It is noted, however, that when θ distributions are very broad, the measured ratio of $\chi^{(2)}_{m}$ components may be consistent with a range of average values and distributions of θ.[16] Due to the expected narrow distribution of θ values in our experiments employing a monolayer of an amphiphilic molecule on water, we have evaluated $\alpha^{(2)}_{\xi\xi\xi}$ assuming that the orientationally averaged θ functions may be replaced by the functions evaluated using θ_0.

EXPERIMENTAL

The spreading and monolayer forming characteristics of cyano-aromatic molecules were surveyed by monitoring the surface pressure when appropriate volumes of such materials in hexane solution were pipetted onto the water surface in a standard Langmuir-trough arrangement. When possible, several molecules with the same aromatic ring system but different alkyl chain lengths were tested to find the best spreading one to represent that class. A good spreading molecule will exert a stable surface pressure, usually in the region 20–40 Å^2/molecule. Molecules chosen for SHG study are shown in Figure 1. This set includes two cyano-phenylpyrimidines, (IV and V). The former has a small solubility in water, and was used in an earlier study[10] in which its monolayer was spread on a pre-saturated water substrate. Compound V, however, could be spread to form a good, stable monolayer on pure water subphase.

SHG measurements were performed on monolayers spread at 40 Å^2/molecule, after they had been allowed sufficient time to stabilize and equilibrate. (In earlier work[10] it has been found that SHG signals from monolayers on water may only become stable ~2 hr after spreading, although the surface pressure equilibrates much faster). Pulsed laser radiation of frequency ω, incident at 60° to the normal, was focused down to a spot of ca. 0.5 mm diameter on the water surface. After appropriate spectral filtering, photons of frequency 2ω were detected in the reflected output via gated photon counting, and averaged over at least 6000 pulses. (The input laser power was adjusted to ensure that average signals were no more than 0.2 photon counts per laser pulse). The laser employed was either a Nd-YAG laser or a dye laser; the former was a 500 Hz Q-switched mode locked Nd-YAG laser where each Q-switch envelope contained approx. 10 mode locked pulses of 70 ps width. The energy per Q-switch envelope was 0.7 mJ (at 1.06 μm) or 0.3 mJ (at 532 nm). Frequency-tunable laser excitation was provided by the dye laser which gave 7 ns pulses at 10 Hz with pulse energies typically 5 mJ.

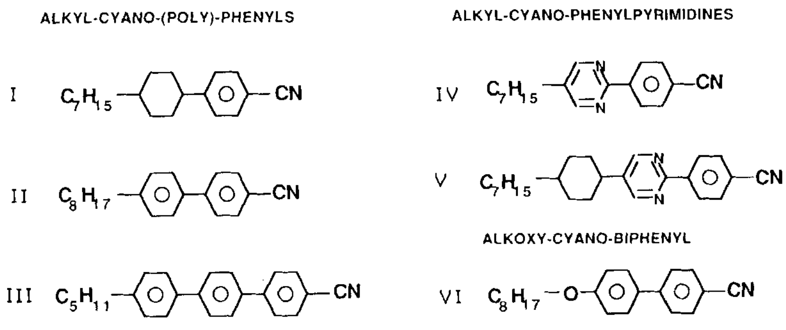

FIGURE 1 Materials used in this study.

RESULTS AND DISCUSSION

The linear optical properties of the molecules studied were first compared by examination of their UV absorption spectra in hexane (see Figure 2). These spectra are in agreement with data reported earlier.[17] All molecules have their lowest lying excited state between 260–295 nm (33,900–38,500 cm^{-1}). The cyanophenyl lowest energy absorption band is much weaker than that of the other molecules, analogous to the situation of their parent compounds (benzene, biphenyl etc).[18]

These absorption spectra indicate that SHG of 532 nm laser light should exhibit some 2ω resonance enhancement, and thus more

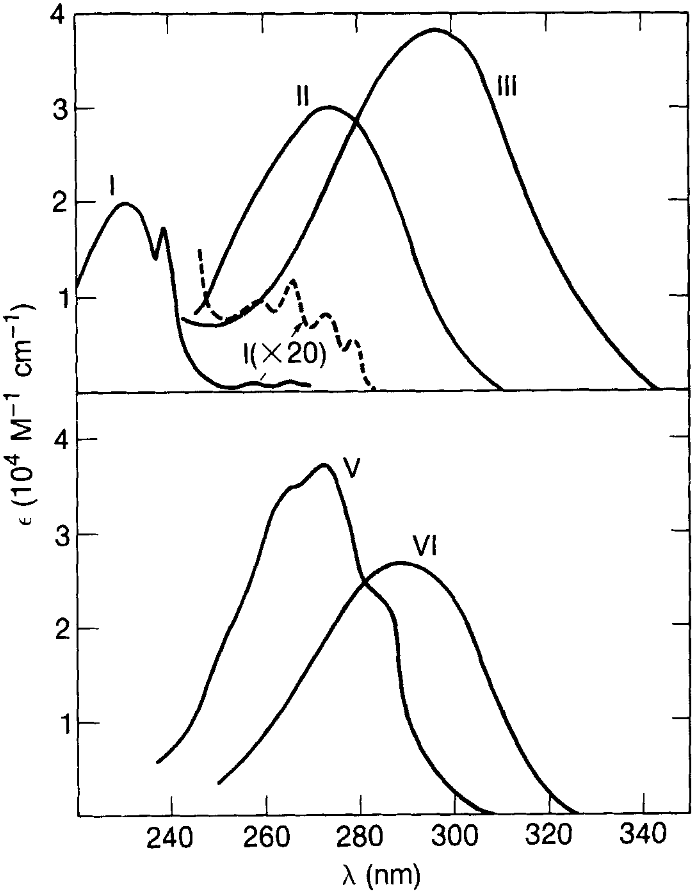

FIGURE 2 Absorption spectra for I–VI in hexane solution. The absorption spectrum of IV (omitted for clarity) is essentially identical to that of V.

meaningful comparison of $\alpha^{(2)}$ values is expected if measurements are performed such that all molecules experience the same resonance enhancement. We have chosen to compare $\alpha^{(2)}$ values both without resonance enhancement and at maximum enhancement within the lowest energy absorption band. Therefore, monolayer SHG measurements were performed using the dye laser at a wavelength equal to twice the wavelength of the linear absorption maximum of the molecule under study. At these wavelengths, SHG signals from water surfaces covered with I–VI were 15–2000 times that of pure water, indicating the dominance of the $\overleftrightarrow{\chi}^{(2)}_m$ term in $\overleftrightarrow{\chi}^{(2)}_s$. Values of $\alpha^{(2)}$ far from resonance were compared using 1.06 μm laser excitation. SHG intensities from monolayer covered water surfaces were recorded for both *s*- and *p*-polarized output following 45° polarized laser input. The *s*-polarized output field is proportional to the $\chi^{(2)}_{yzy}$ component, while the *p*-polarized signal yields a linear combination of $\chi^{(2)}_{yzy}$ and $\chi^{(2)}_{zzz}$ according to eq. (1). The measured $\chi^{(2)}$ values were calibrated against that of pure water for which $\chi^{(2)}_{yzy} = 2 \times 10^{-17}$ esu.[9] From the experimental results, values of $|\alpha^{(2)}_{\xi\xi\xi}|$ and θ_0 for the molecules were calculated via equations (1)–(3), and are presented in Table I.

Comparison of $\alpha^{(2)}_{\xi\xi\xi}$ values at 2ω resonance shows that for the series of alkyl-cyano (poly) phenyls I–III, the largest nonlinearity occurs in the cyanobiphenyl II. The anomalous decrease in nonlinearity when going from the biphenyl II to the terphenyl III is contrary to the usually accepted picture of nonlinear polarizability increasing with electron delocalization length. However, a recent theoretical study[6] has shown that nonlinearity ceases to increase rapidly with conju-

TABLE I

Second order polarizabilities, $\alpha^{(2)}_{\xi\xi\xi}$, for molecules I–VI. θ_0 is the average orientation angle of the molecular long axis to the surface normal, as calculated from the SHG data.

	$\alpha^{(2)}_{\xi\xi\xi}$ (10^{-30} esu)		
	at 2ω resonance	at 1.06 μm	θ_0 (°)
I	4	[a]	80 ± 10
II	25	3	71 ± 2
III	13	[a]	60 ± 2
IV	8	[a]	79 ± 3
V	8	[a]	82 ± 4
VI	40	5	78 ± 2

[a] – $|\alpha^{(2)}_{\xi\xi\xi}| \leq 2 \times 10^{-30}$ esu (see text).

gation length for polyphenyls having ≥3 phenyl rings, as opposed to polyenes.[4,6] In addition, this calculation was performed assuming a planar arrangement of phenyl rings, although experimental evidence suggests that under certain conditions terphenyls are not planar.[19] It thus seems most reasonable to conclude that the smaller $\alpha^{(2)}$ value for III relative to II is mainly a result of terphenyl ring torsion.

The $\alpha^{(2)}$ data for the phenyl pyrimidines IV and V shows that the pyrimidine ring is less efficient than phenyl as a bridging group for delocalizing electron donor and acceptor groups. This result is in accord with theoretical predictions.[20] However, the pyrimidine group does enhance the nonlinearity relative to the case of a single phenyl ring as in I, although some of this effect may be due to the larger resonant enhancement at 2ω resulting from the stronger oscillator strength of the resonant transition (see also below). The agreement in the value of $\alpha^{(2)}$ for IV (from earlier work[10]) and V (this work) verifies the result of the earlier work despite the difficulties encountered in obtaining a good monolayer of IV.

When the $\alpha^{(2)}$ values of II and VI (alkyl- and alkoxy-cyanobiphenyls) are compared, a significantly larger value is obtained for VI, which is easily rationalized by the fact that alkoxy aromatics are much better electron donors than alkyl aromatics.[21]

The values of $\alpha^{(2)}$ for all molecules are expected to decrease significantly if 2ω is tuned away from resonance. When SHG measurements were made using 1.06 μm excitation, only for materials II and VI (which also showed the strongest SHG at 2ω resonance) was the signal from monolayer covered water at least several times larger than that from pure water. Only in these cases could $\overleftrightarrow{\chi}^{(2)}_{m}$ be extracted from $\overleftrightarrow{\chi}^{(2)}_{s}$ with confidence. For the other materials we consequently set as an upper limit $|\alpha^{(2)}_{\xi\xi\xi}| \leq 2 \times 10^{-30}$ esu. Since the 1.06 μm excitation energy is far from both one- and two-photon resonances, $\alpha^{(2)}$ data at this excitation may be considered as the nonresonant part of $\alpha^{(2)}$, which clearly is largest for II and VI.

The magnitude of the observed resonance enhancement effect is also in agreement with accepted theoretical models. The contributions to $\alpha^{(2)}$ come from a sum over all electronic states,[22] although a small number of states may still provide the dominant contribution. This model also suggests that the contribution from an individual electronic state is proportional to the product of matrix elements representing the cross-sections for one- and two-photon absorption to that state. In addition, when the incident laser field is either one- or two-photon resonant with an electronic state, the contribution of that state to $\alpha^{(2)}$ increases resonantly. For example, when the excitation frequency

(ω_{ex}) is tuned through a two photon resonance with the kth electronic state, the contribution, $\alpha_k^{(2)}$, of that state to the total $\alpha^{(2)}$ should vary as a function of ω_{ex} according to[16,22,23]

$$\alpha_k^{(2)} \propto (\omega_k - 2\omega_{ex} - i\Gamma_k)^{-1} \tag{4}$$

where $\hbar\omega_k$ is the excited state energy, and Γ_k the transition linewidth, of the kth electronic state. This formula predicts a slightly larger than order of magnitude increase in the contribution of the lowest excited state to $\alpha^{(2)}$ of II–VI when the excitation is changed from 1.06 μm to the 2ω resonance. This prediction can be easily rationalized with the experimental data for II and VI (see Table I) if it is assumed that the lowest excited state is responsible for a significant portion (but not all) of the nonlinearity at 1.06 μm. Although exact $\alpha^{(2)}$ values at 1.06 μm for III–V are not available, a similar conclusion can be made regarding the contribution of their lowest excited states to the total nonlinearity. Assuming again that at 2ω resonance the contribution of this state to the total $\alpha^{(2)}$ is a factor of 10–20 times larger than its contribution at 1.06 μm, this contribution at 1.06 μm must also represent a significant portion of the total nonlinearity, which is not more than 2×10^{-30} esu.

It should be noted, however, that although the lowest excited states of molecules II–VI all have fairly similar oscillator strengths and transition linewidths for one-photon absorption, the magnitude of $\alpha^{(2)}$ arising from this state is clearly not the same in all these molecules, demonstrating again that electron delocalization, as well as oscillator strength, is important in $\alpha^{(2)}$.

The case of molecule I is a little more complicated. The lowest excited state has a weak oscillator strength, and thus its contribution to $\alpha^{(2)}$ far from resonance may not be as significant as the contribution to $\alpha^{(2)}$ from the lowest excited states of the other molecules. However, the resonant enhancement factor for molecule I should be somewhat larger than that for the other molecules, because of both a narrower transition and the presence of a close lying state with a much larger oscillator strength.

The monolayer method for determining $\alpha^{(2)}$ also yields an average value for θ, the orientation of the major nonlinear optical axis to the water surface normal (see Table I). For I–VI this axis is the long molecular axis, passing through all the phenyl (or pyrimidine) rings and including the CN group. Thus it is seen that in all molecules these groups lie rather flat on the water surface, although the more flexible hydrocarbon chains may not.

CONCLUSION

This study has demonstrated the relationship between molecular structure and optical nonlinearity for a series of cyano substituted aromatic molecules. Measured $\alpha^{(2)}$ values have been correlated well with the accepted concepts of the role of electron delocalization lengths, electron donor and acceptor groups, and resonant enhancement in second order nonlinear polarizability.

Acknowledgements

The authors thank Dr. John Morley for a preprint of reference (6) and helpful correspondence. GB acknowledges a Chaim Weizmann postdoctoral fellowship. This work was supported by Minnesota Mining and Manufacturing Co. through the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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