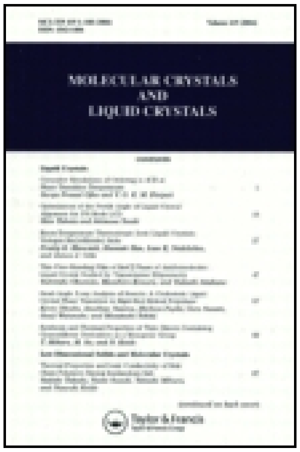

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N-State Interpretations of the First and Second Hyperpolarizabilities of Cyanobiphenyl-Based Liquid Crystal Molecules

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N-State Interpretations of the First and Second Hyperpolarizabilities of Cyanobiphenyl-Based Liquid Crystal Molecules

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Electronic structure calculations on the frequency-dependent hyperpolarizabilities of 5-alkyl cyanobiphenyl have been performed using the AM1 Hamiltonian and time dependent Hartree-Fock theory. Both the average first and second hyperpolarizabilities decrease with increasing twist angle, ϕ, between the two phenyl groups, and increase with increasing incident frequency. While the nonlinear optical properties of materials are frequently interpreted within the framework of two and three state models for the electronic spectrum, systems with a more complex electronic structure require an approach which can denote state importance. The linear optical properties of 5CB are dominated by two low-lying charge transfer transitions from the ground state, which would seem suitable to a three state model. However, large state dipole moments offset of low oscillator strengths for other transitions allowing them to also become significant contributors to the nonlinear optical properties.

Keywords: Liquid crystals; hyperpolarizability; electronic structure; cyanobiphenyl molecules

INTRODUCTION

The optical properties of liquid crystals have generated much interest due to their ability to form optically anisotropic phases and their potential applications in nonlinear optical devices [1–3]. The molecular structure of many liquid crystals, such as MBBA (N-(*p*-methoxybenzylindene)-*p*-butylaniline) or 5CB (4-*n*-pentyl-4′-cyanobiphenyl) (Fig. 1), consists of a central aromatic moiety with various substituent groups, such as *n*-alkyl chains, appended to

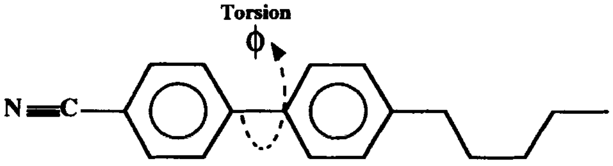

FIGURE 1 Molecular structure of 5CB. Molecular geometries were obtained by force relaxation techniques, constraining only the twist angle ϕ between the phenyl rings.

this basic structure. The linkage between the phenyl rings and the attached substituent groups determines the properties of the exhibited liquid crystal phases. The nature of the linkage and the electron donating/withdrawing properties of the substituent groups also modulate the nonlinear optical properties of the molecules, which are determined primarily by the delocalized π electrons of the aromatic core [4–10].

In this paper, we examine the relationship between the structural properties and nonlinear optical properties for a specific liquid crystal chromophore, 5CB (4-*n*-pentyl-4′-cyanobiphenyl). We use electronic structure methods to determine both the optimized molecular geometries, and the frequency-dependent hyperpolarizabilities. We show the dependence of the first and second hyperpolarizability on the twist angle between the phenyl rings, and also the dependence on the incident frequency. We show that the response is related to changes in excitation energies, oscillator strength of the low lying π-π^* transitions, and state dipole character.

METHODS

We have used the AM1 Hamiltonian [11]as implemented in MOPAC93 [12], to both calculate the optimized geometries and the hyperpolarizabilities. The AM1 Hamiltonian has been shown to provide accurate descriptions of the hyperpolarizabilities in aromatic molecules [13]. All bond lengths and angles were optimized by force relaxation methods [14]. The twist angle (ϕ) between the phenyl rings was the only constraint for mapping the conformational space of 5CB . The minimum energy conformation occurs for a twist angle between the phenyl groups of 40.14° in good agreement with the experimental values. Components of the frequency-dependent first and second hyperpolarizabilities were determined by the time dependent HF method implemented by Kurtz [15]. We report the orientationally averaged hyperpolarizabilities in esu units.

The excitation energies have been determined using configuration interaction (CI) methods. The use of CI for semi-empirical Hamiltonians entails some care as inclusion of more configurations can often increase the excitation energy. Excitation energies were obtained by performing configuration interaction (CI) calculations using the 4 highest occupied and lowest 4 unoccupied orbitals. The interaction space consisted of the 100 lowest energy configurations that could be created by excitations from the 4 highest filled molecular orbital to the lowest 4 vacant molecular orbitals. Diagonalization of the resulting matrix yielded the excitation energies and the oscillator strength (transition moments) of the transition. State dipole moments were determined using the ROOT option guided by the CI determination of the more significant electronic states (oscillator strength >0.1).

RESULTS AND DISCUSSION

The molecular structure of 5CB (4-*n*-pentyl-4′-cyanobiphenyl), consists of a central biphenyl core with attached cyano and alkyl groups. The optical properties of 5CB are sensitive to the twist angle between the phenyl rings, as this controls the delocalization of the π electrons. In our determination, the optimized twist angle between the phenyl rings was 40.1° with the change in the heats of formation for the coplanar and perpendicular twist cases relative to the energetic minimum as 2.05 kcal/mol and 1.09 kcal/mol, respectively. Previous experimental and theoretical work has determined the twist angle between the phenyl rings in biphenyl to be in the range of 40–45° [16–20]. The energy barriers relative to the coplanar and perpendicular cases have been determined by Raman spectroscopy to be 1.00 kcal/mol and 2.03 kcal/mol. Electron diffraction measurements have estimated these energy differences to be 1.54 kcal/mol and 1.64 kcal/mol, and electronic structure calculations have noted similar low barriers depending upon both basis set extent and electron correlation. The nonlinear optical properties have been shown previously [10, 21] to be independent of the length and conformation of the alkyl ligand.

In view of the low rotational barriers for phenyl rings, we have examined the frequency dependence of both the first and second hyperpolarizabilities as a function of the twist angle between the two phenyl rings. In Figure 2 we show the magnitude of the first hyperpolarizability, β, as a function of twist angle for incident frequencies of 0.0 eV and 0.60 eV. β shows a minimum at a twist angle of 90°, with a value of approximately 1/3 that of the value at 0°. In simple terms, this result can be attributed to the decrease in delocalization of the electrons, as the two phenyl rings are now mutually orthogonal. β is also approximately 15% larger at 0.60 eV than for the static value.

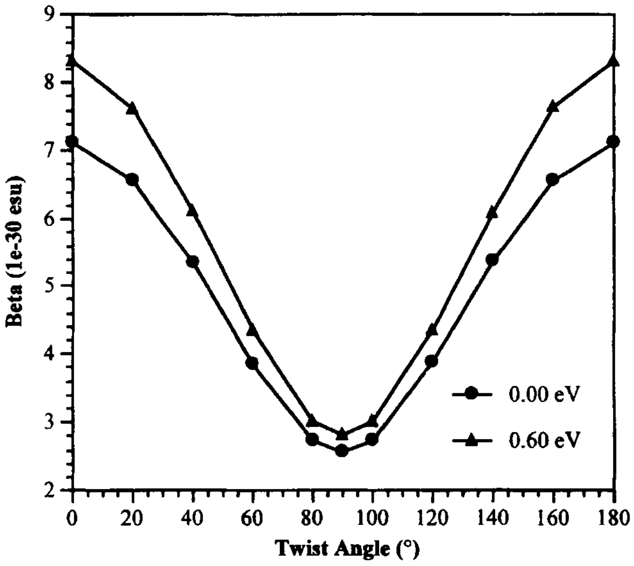

FIGURE 2 Variation of the average first hyperpolarizabilities with twist angle ϕ between the phenyl rings for 5CB.

Figure 3 shows the average second hyperpolarizability as a function of twist angle for frequencies of 0.0 and 0.60 eV. Again, γ has a minimum at 90°, due to decreased delocalization across the rings. γ is approximately 30% larger at 0.60 eV than at the static value.

Figure 4 shows the energy dependence of the first hyperpolarizability for three distinct twist angles of 0°, 40.1°, and 90°, across the energy range of 0.0–1.20 eV. β is largest for the 0° twist, and shows uniform increase with increasing energy. The other two twist angles show similar results, with the relative magnitude of the increase in β with increasing energy almost the same for all twist angles. In Figure 5 the energy dependence of the second hyperpolarizability, (γ) shows similar behavior with the 0° twist angle exhibiting the largest value. The γ results exhibit much greater divergence at larger energies, as the energy approaches the three photon resonance energy.

Within the context of two and three-state models for nonlinear properties, it is tempting to relate the variation in the first and second hyperpolarizability caused by the twist angle with the changes in excitation energies and transition moments. However, we must first examine the nature of the electronic structure in these molecules. In Figure 6, we show the excitation energy of the lowest charge transfer state as a function of twist angle and number of orbitals in the active space. The minima in the transition energy are located at 0° and 180° biphenyl twist angles and is largest at 90°. Since β

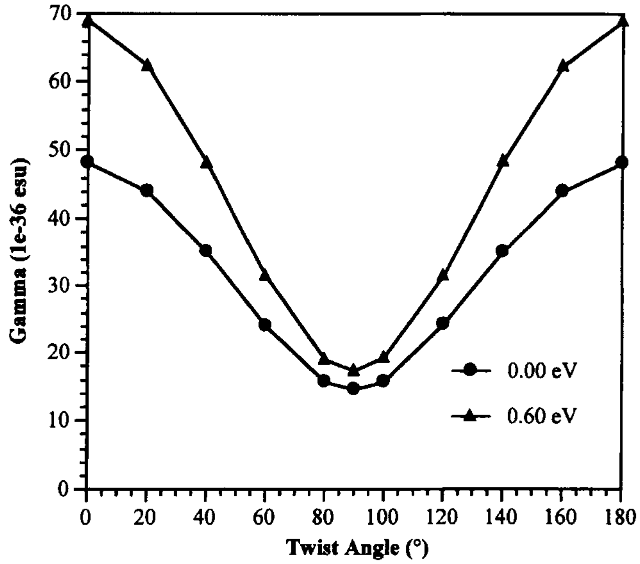

FIGURE 3 Variation of the average second hyperpolarizabilities with twist angle ϕ between the phenyl rings for 5CB.

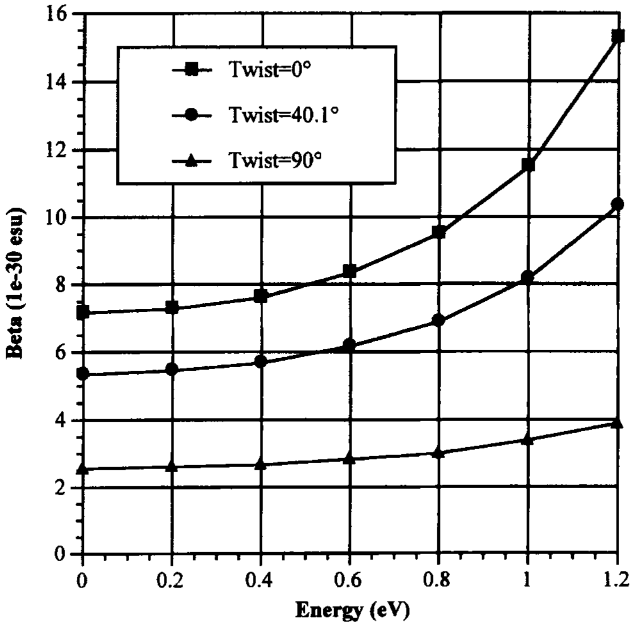

FIGURE 4 Energy dependence of the average first hyperpolarizability for three distinct twist angles (ϕ) between the phenyl rings of 5CB.

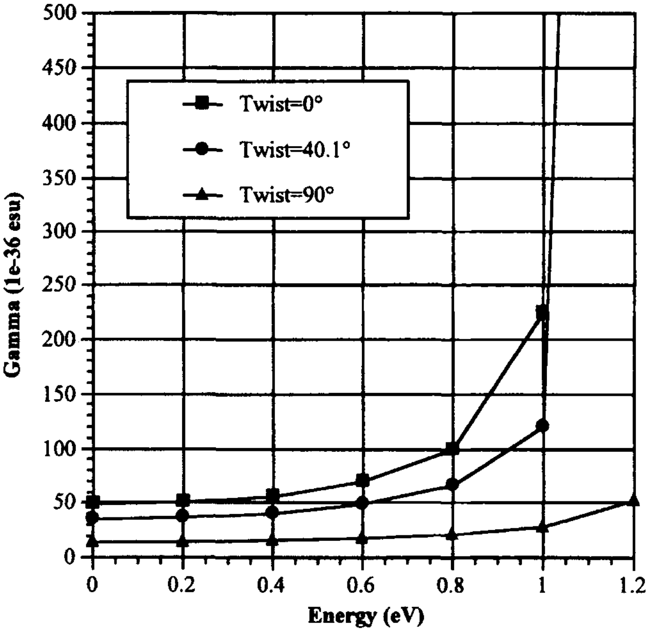

FIGURE 5 Energy dependence of the average second hyperpolarizability for three distinct twist angles (ϕ) between the phenyl rings for 5CB.

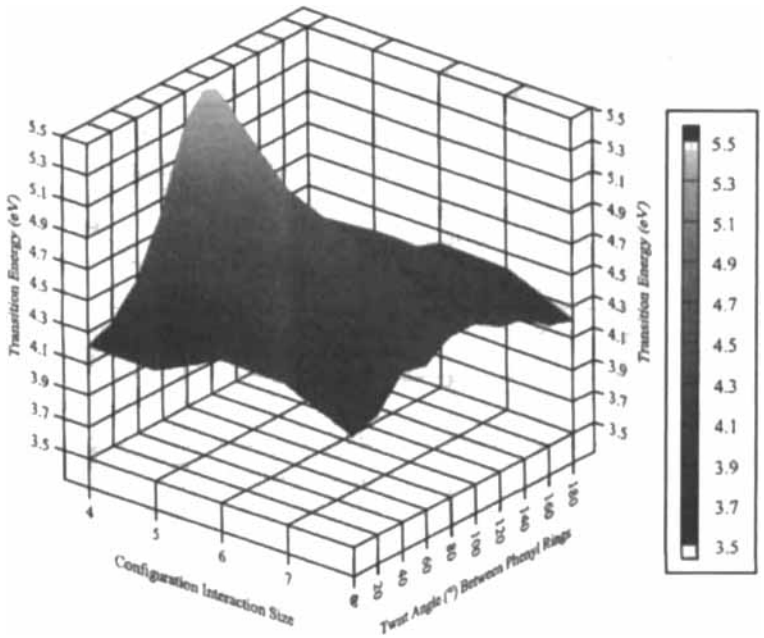

FIGURE 6 Energy of the lowest lying transition as a function of number of orbitals in the configuration space, and twist angle between phenyl rings.

is approximately inversely proportional to the square of these energies, this would result in β being largest at 0° and 180°, and smallest at 90°, as is seen in Figure 2. The location of the maximum and minimum in the excitation energy also explains the differences seen in the frequency dependence of γ. As the incident energy approaches 1/3 of the excitation energy, small differences in the excitation energy can produce drastically different amounts of resonance enhancement. Because semi-empirical methods implicitly contain some electron correlation in their parameterization, inclusion of more orbitals in the CI space does not necessarily lead to more accurate excitation energies. In the following discussion an 8 orbital active space was chosen as it minimizes the transition energy to the first charge transfer state.

A more detailed analysis of the effects of phenyl ring twist on the excitation energies and oscillator strengths of the transitions are given in Table I. Table I gives the significant excitation energies below 6.9 eV, the corresponding oscillator strength and state dipole, and the nature of the electronic transition for 5CB with the two phenyl rings coplanar, orthogonal, or at the minimum energy twist angle of 40.14°. All the transitions are π-π^* in character. As the twist angle increases, the lowest energy excitation increases in energy, and loses oscillator strength and excited state dipole moment. This state also begins to localize on phenyl groups drawing electron density towards the second phenyl ring (adjacent to the alkyl group) as the twist angle increases. The second excitation increases slightly in energy

TABLE I Excitation energies, oscillator strengths, and nature of low-lying excitations for three distinct twist angles of 5CB. E stands for an extended state, C stands for a state localized on the cyano and adjacent phenyl

Twist Angle (°)	*Transition Number*	*Excitation Energy (eV)*	*Oscillator Strength*	*State Dipole* (μ)	*Transition Nature*
0°	ground state			4.230	
	1	4.21	1.153	6.604	E->C
	2	5.69	0.251	7.998	E->C
	3	5.99	1.563	2.775	E->E
	4	6.38	1.206	6.869	E->C
	5	6.91	0.231	2.645	E->E
40°	ground state			4.143	
	1	4.38	1.045	5.184	E->C
	2	5.82	0.697	10.514	E->C
	3	6.04	1.464	1.743	E->E
	4	6.16	0.489	11.546	E->C
	5	6.47	1.185	6.570	E->C
90°	ground state			4.024	
	1	4.81	0.628	4.744	E->C
	2	6.19	1.873	4.103	E->E
	3	6.73	1.184	4.981	E->E

and also in oscillator strength as the twist angle increases. This state remains delocalized over both phenyl rings, with a only slight increase in the electron denstiy on the second phenyl ring. The state dipole moment increases as the twist angle increases to 40°, but then there is a large decrease as the twist angle approaches 90°. The third excitation also increases in energy but loses oscillator strength as the twist angle increases, with the transition tending to localize on the cyano and adjacent phenyl ring.

Because 5CB has a number of strong, low-lying excitations and no single dominant charge transfer state, it would be difficult to ascribe a two or three-state model for β [22–25]. Ordinarily, the three state model for β could be described as follows:

$$\beta_{\text{three-state}} = \sum_{i,k=1,2} \frac{\langle 0|\mu|i\rangle\langle i|\mu|k\rangle\langle k|\mu|0\rangle}{(E_i - E_0)(E_k - E_0)} - \sum_{i=1,2} \frac{\langle 0|\mu|0\rangle\langle 0|\mu|i\rangle\langle i\mu|0\rangle}{(E_i - E_0)^2} \tag{1}$$

where $\langle i|\mu|k\rangle$ is the transition moment between states i and k, and E_i is the energy of state i. However, as can be seen from Eq. 1 and the Table I results, the larger state dipole moments in the higher electronic transitions will offset the lower oscillator strengths, despite the increased transition energies. While the transition energy for the lowest three processes all increase with increasing twist angle, these three have distinctly different behavior in oscillator strength and state dipole moment. Thus, β is determined by the combination of low-lying π-π^* transitions, which have large transition moments, and higher state dipole moments generated by charge transfer processes. The utility of the two and three state models derived from their ability to model the electronic structure of these processes. In the case of the two state model, the HOMO-LUMO electronic transition would be only a portion of the relevant electronic manifold. The utility of the n-state models is dependent upon inclusion of all the relevant electronic processes. For 5-CB, adding another state to the model would not be sufficient. The variations in β and γ with phenyl ring rotation further complicate this interpretation of the relevant electronic excitation energies and transition moments.

CONCLUSIONS

We have calculated the frequency-dependent hyperpolarizabilities of 5-alkyl cyanobiphenyl using the AM1 Hamiltonian and time dependent perturbation theory. Both the average first and second hyperpolarizabilities decrease with increasing twist angle (ϕ) between the two phenyl groups and increase with increasing incident frequency. The linear optical properties of 5CB are dominated by two low-lying charge transfer transitions from the ground state, as noted by their larger oscillator strengths. However, large state dipole moments offset the low oscillator strengths for other transitions allowing them to also become significant contributors to the nonlinear properties. While it is tempting to interpret the nonlinear optical properties of these materials in terms of two and three state models of the electronic structure, an approach which includes state importance is needed.

Acknowledgements

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