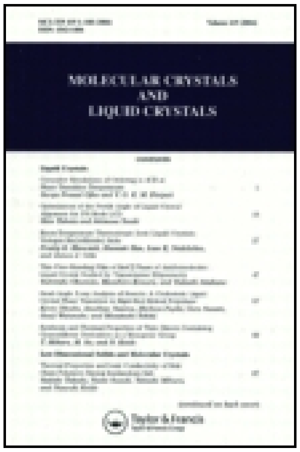

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The Effects of Substituent Groups and Structure on the Electronic Hyperpolarizability of Aromatic Liquid Crystal Cores

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THE EFFECTS OF SUBSTITUENT GROUPS AND STRUCTURE ON THE ELECTRONIC HYPERPOLARIZABILITY OF AROMATIC LIQUID CRYSTAL CORES

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Abstract Calculations have been performed to determine the third order static hyperpolarizability of various aromatic organic molecules typical of those which form liquid crystals. Two effective pi-electron model Hamiltonians have been solved to investigate the role of Coulomb interactions. The Pariser-Parr-Pople model, including electron-electron interactions, is solved exactly for a sequence of halogen-substituted benzene molecules to provide comparison with non-interacting (Hückel model) calculations for these molecules.

Additional Hückel model calculations have been performed on a group of molecules containing two aromatic rings connected by various linkages. The simplicity of the Hückel model allows the determination of the hyperpolarizability of such large molecules. We have investigated trends resulting from geometric and substituent effects in these more complicated molecules, such as cyano-biphenyls, which have liquid crystalline mesophases.

INTRODUCTION

Large optical nonlinearities have been observed in liquid crystals for some time[1], and there is wide interest in using liquid crystals for a variety of applications such as optical switches.[2] There are nominally two mechanisms for this nonlinearity. The reorientational response (optical Kerr effect) common to anisotropic molecular liquids is very large in liquid crystals[1,3] and has been the subject of extensive research.[4] More recently, the magnitude of the electronic nonlinearity has been investigated[5] and been found to be large. The nonlinear index of refraction of some liquid crystals has been found to be comparable to that of the well known Kerr liquid, carbon disulphide. Although both second and third order electronic hyperpolarizabilities in liquid crystals have been of interest,[6,7] we will report only the determination of the third order tensor in this work.

THEORY

Both experimental[8] and theoretical[9,10] investigations have suggested that the significant contribution to the electronic hyperpolarizability of liquid crystals and similar organic molecules is attributable to the extended conjugation of the pi-electrons in the aromatic framework. There is experimental support[8] for the view that the sigma bonds in many of these systems contribute to the total molecular hyperpolarizability in a "bond additive" fashion. Thus large changes in hyperpolarizability from one molecular formula to another are identifiable as due to the pi-electrons.

Accordingly, we have performed calculations using effective pi-electron Hamiltonians to determine the third order hyperpolarizability of various aromatic framework structures. The new results that are obtained are twofold:

(1) third order hyperpolarizabilities are calculated within the free-electron (Hückel) model for a series of liquid crystalline molecular structures and

(2) the PPP model with Coulomb interactions is solved exactly for halogen-substituted benzene molecules.

Both model Hamiltonians deal only with the delocalized pi-electrons which are assumed to occupy P_z orbitals that are normal to the plane of the molecule in the cases we have considered. Each model also assumes that the pi-electrons move in an effective one-particle potential formed by the atomic core electrons and nuclei and the sigma-bonded electrons. The two Hamiltonians differ in that the Hückel model neglects Coulomb interactions between the pi-electrons while the PPP model explicitly includes them.

In second quantized form, the Hückel Hamiltonian may be written as

$$H_O^H = \sum_{i\sigma} \alpha_i c^+_{i\sigma} c_{i\sigma} + \sum_{(bonds)ij,\sigma} \beta_{ij} (c^+_{i\sigma} c_{j\sigma} + c^+_{j\sigma} c_{i\sigma})$$

where $c^+_{i\sigma}$ ($c_{i\sigma}$) is the creation (destruction) operator for an electron of spin σ in the P_z orbital located on the i^{th} atomic site. The two constants needed in the Hamiltonian can be considered adjustable or to be obtained by separate theoretical determination. In such theoretical determinations[11] two types of integrals must be evaluated. The constant alpha is given by the so called Coulomb integral and the value is set approximately equal to the ionization energy of a P orbital for an isolated atom of the species. The second type of matrix element that needs to be evaluated is the transfer matrix β which has subscripts for the relevant atomic sites. The integral is set equal to zero for i not bonded to j and is otherwise determined from the bond lengths and atomic species. A third type of matrix element, the differential overlap between P_z orbitals is often approximated as

$$<\phi_i|\phi_j>=\delta_{ij}$$

even though the value of the matrix element is approximately 0.25 for atoms that are bonded together.

For the Hückel model, the eigenstates are formed by a linear combination of atomic orbitals (LCAO). We determine the eigenstates and eigenenergies by diagonalizing an NxN matrix (where N is the number of conjugated sites in the molecule) and obtain the single particle eigenstates and eigenenergies. The correct eigenstates of the Hückel Hamiltonian are then obtained by simply populating the single particle states and forming a Slater determinant.

The molecular hyperpolarizability tensors are defined from the expansion of the induced molecular dipole moment in powers of the field F.

$$P_i = p_i^o + \alpha_{ij} F_j + \frac{1}{2} \beta_{ijk} F_j F_k + \frac{1}{6} \gamma_{ijkl} F_j F_k F_l + \ldots$$

In the above expression, p^0 is the intrinsic dipole moment, and α, β, and γ are the linear polarizability, second order hyperpolarizability and third order hyperpolarizability tensors respectively. In general, the tensors and fields are frequency dependent and the tensors may have both real and imaginary parts. The polarizability tensors are given by perturbation theory[12] in terms of matrix elements of the dipole operator between the eigenstates of the Hamiltonian. The expression for the static third order hyperpolarizability tensor is

$$\gamma_{\alpha\beta\lambda\delta} = \mathrm{P} \left\{ \sum_{ijk\neq 0} \frac{<0|\mu_\alpha|i><i|\mu_\beta|j><j|\mu_\lambda|k><k|\mu_\delta|0>}{(E_i - E_0)(E_j - E_0)(E_k - E_0)} \right.$$

$$- \sum_{ij \neq 0} \frac{<0|\mu_\alpha|i><i|\mu_\beta|0><0|\mu_\lambda|j><j|\mu_\delta|0>}{(E_i - E_0)(E_j - E_0)}$$

$$-2 \sum_{ij \neq 0} \frac{<0|\mu_\alpha|0><0|\mu_\beta|i><i|\mu_\lambda|j><j|\mu_\delta|0>}{(E_i - E_0)^2 (E_j - E_0)}$$

$$+ \sum_{i \neq 0} \frac{<0|\mu_\alpha|0><0|\mu_\beta|0><0|\mu_\lambda|i><i|\mu_\delta|0>}{(E_i - E_0)^3} \Bigg\}$$

The sums over i,j,k include all excited states of the Hamiltonian. This expression was evaluated to obtain the molecular hyperpolarizability from the Hückel model.

The PPP model Hamiltonian can be written[13]

$$H_O^P = \sum_{i\sigma} \alpha_i c^\dagger_{i\sigma} c_{i\sigma} + \sum_{(bonds)\, ij,\sigma} \beta_{ij} (c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma}) +$$

$$\sum_{i<j,\sigma,\sigma'} V(i,j) c^\dagger_{i\sigma} c_{i\sigma} (c^\dagger_{j\sigma'} c_{j\sigma'} - 1)$$

where α_i is equal to the energy of a P_z electron at site i, β_{ij} is the resonance integral (or hopping term or transfer integral) as defined above and V(i,j) is the screened Coulomb interaction. The Coulomb interaction is often taken to be of the Ohno[14] form or as in the current calculation, the Mataga-Nishimoto[15] form.

$$V(i,j) = \frac{e^2}{r_{ij} + 2e^2/(\alpha_i + \alpha_j)}$$

For the PPP model the basis states are the set of all possible combinations of occupied atomic P_z orbitals of the contributing atoms. A true eigenstate is no longer a Slater determinant of single-particle eigenstates but rather is made up of *a linear combination of all configurations*. A configuration is considered to be a specific arrangement of the electrons on the N atomic sites, subject to the constraint that only one electron of each spin may occupy any given atomic site. The number of pi-electrons is denoted by N_e and is even for all the systems we have considered here.

One must calculate the matrix elements of the Hamiltonian in the complete basis set of all configurations. This yields an N_c by N_c matrix where N_c refers to the possible number of configurations. The number of possible configurations is given by

$$N_c = \left[\frac{N!}{(N_e/2)!(N-N_e/2)!} \right]^2$$

For the halogen substituted benzenes with eight pi-electrons on seven sites, the number of configurations in the complete basis is 1225. The Hamiltonian matrix was then diagonalized and the energy of the ground state obtained. To calculate the hyperpolarizability, an electric field was added to the Hamiltonian and matrix elements were taken between the configurations. This new Hamiltonian was then diagonalized at a series of field strengths and the ground state energy was fit to a power series in the field. The coefficient of the fourth order term is then the hyperpolarizability. By applying the electric field in the direction of the x axis, the y axis and their bisectors, it is possible to determine all three components of the hyperpolarizability that are needed for the spatial average.

$$\gamma_{ave} = (\gamma_{xxxx} + 2\gamma_{xxyy} + \gamma_{yyyy})/5$$

Any tensor element referring to the z coordinate direction, perpendicular to the plane of the molecule, is zero within the present model.

RESULTS

This work has been motivated by the desire to be able to qualitatively reproduce the nonlinear optical properties of conjugated systems that have been observed experimentally[5] as well as to predict similar properties for systems that have not yet been measured. To determine the applicability of our models, the results must therefore be compared to known experimental values[16] and the various models contrasted.

Table I contains the hyperpolarizabilities for a series of halogen-substituted benzenes. Calculations are presented for the PPP Hamiltonian, along with experimental results. Also included in Table I are the results of our calculations for the Hückel Hamiltonian, with and without differential overlap. Without overlap, the hyperpolarizability grows monotonically with the increasing size of the appended atom, while the inclusion of differential overlap produces a minimum in the hyperpolarizability for fluorobenzene. As seen in the table, the calculated values track well with the experimental results.

As previously noted, the large hyperpolarizabilities observed in liquid crystals have been attributed to the central conjugated framework of the molecules. In Table II we present both the XXXX component and the average value of the hyperpolarizability for a group of similar molecules containing two benzene rings with various connecting linkages and

X	Hückel S=0	Hückel S≠0	PPP	Expt[a]
H	0.48	0.28	0.40	0.39
F	0.58	0.27	0.41	0.32
Cl	0.67	0.33	0.52	0.43
Br	0.78	0.45	0.84	0.54
I	0.86	0.82	0.51	0.82
$\bar{I}$			2.56	

[a] Reference 16

TABLE 1. Average hyperpolarizability of halogen-substituted benzenes. Values are given in units of $10^{-35}cm^7esu^{-2}$.

substituents. For all these molecules, the x axis is defined to lie along the axis connecting the phenyl group to the first atom of the linkage (i.e. horizontal as pictured in the table).

From the table it can be seen that the largest hyperpolarizabilities are obtained for a linkage of four carbon atoms, and for cyanobiphenyl. This is consistent with the empirical expectation that the linear size of the conjugated system is a determining factor for the magnitude of the hyperpolarizability, while the addition of electron donor or acceptor groups further enhances the hyperpolarizability.[1]

CONCLUSION

The results shown in Table I provide us with several qualitative insights. Except for the hyperpolarizability of iodobenzene, the theoretical results generally predict the same trend in the progression of hyperpolarizabilities as observed experimently. First we note that the theoretical model does

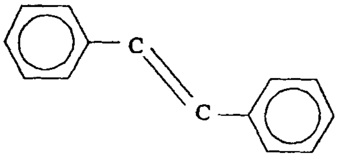
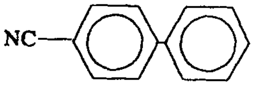
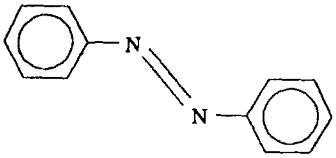
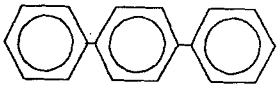
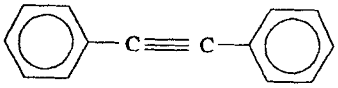
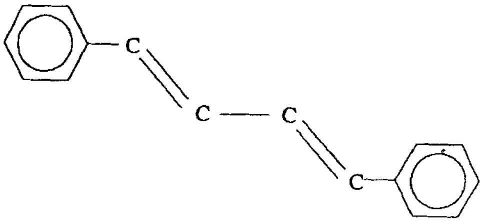
	γ_{xxxx}	γ_{AVE}
	0.72	0.14
	2.39	0.47
	6.91	1.32
	2.51	0.50
	4.33	0.83
	3.12	0.62
	6.90	1.45

TABLE II. Average hyperpolarizability of aromatic framework. Values are given in units of $10^{-33}cm^7esu^{-2}$.

not contain the sigma electron contributions and thus it cannot be expected that the magnitude of the calculated results will match with experiment. Since the changes in the sigma bonds in the progression down the periodic table should be less dramatic than the changes in the pi-electron cloud, we believe that the Hückel and the PPP Hamiltonians are yielding the correct predictions for the direction which we expect the change to occur as well as a qualitative indication of the size of the change. Because the Coulomb interactions in the PPP Hamiltonian will tend to prevent charge buildup more effectively than in the Hückel case, one would naturally expect that the PPP values of linear and probably nonlinear polarizabilities would be smaller. This is consistent with our experience previously[9] and with other unpublished results.

The iodobenzene results in Table I are provided for two different sets of parameters. Tables III and IV contain all parameter values used in these calculations. The PPP parameters taken from the literature for iodobenzene not only gave unexpectedly low hyperpolarizabilities, but also do not fit with our intuitive expectation for the progression of the values of β from other halogens. In order to show the sensitivity of our calculations to the value of β, and thus the need for more accurate parameters, we have reported an additional value of the hyperpolarizability of iodobenzene, which we have labeled as $\bar{\mathrm{I}}$ for this molecule, using a value of β which better matches our expectations of the progression in β. We could have adjusted β to fit the experimental trend more closely; we did not since we are not suggesting that hyperpolarizabilities are a good experimental number with which to determine parameters for effective Hamiltonians.

X	Y	α_y	β_{x-y}	r_{x-y}(A)
C	C	α_0	β_0	1.397
C	N	$\alpha_0+1.5\beta_0$	β_0	1.38
C	O	$\alpha_0+\beta_0$	$0.8\beta_0$	1.36
C	F	$\alpha_0+3\beta_0$	$0.7\beta_0$	1.30
C	Cl	$\alpha_0+2\beta_0$	$0.4\beta_0$	1.70
C	Br	$\alpha_0+1.5\beta_0$	$0.3\beta_0$	1.85
C	I	$\alpha_0+1.1\beta_0$	$0.2\beta_0$	2.02
N	N	$\alpha_0+1.5\beta_0$	β_0	1.35

a) Reference 17
b) Reference 18

TABLE III. Hückel Parameters[a,b], $\beta_0=2.39$eV, $\alpha_0=11.2$eV.

Finally, the values of the hyperpolarizabilities for larger aromatic molecules are given in Table II. With the encouraging results of the halogen series plus other previous work[9] we find that the predictions given here should be considered as quite reasonable. There is of course the same

X	α_x(eV)	β_{c-x}(eV)	r_{c-x}(A)
C	11.13	-2.318	1.397
F	21.49	-2.20	1.30
Cl	13.58	-1.62	1.69
Br	10.88	-1.51	1.86
I	8.39	-0.23	2.02
$\bar{I}$	8.39	-1.39	2.02

a) Reference 19
b) Reference 20

TABLE IV. PPP Parameters[a,b]

proviso about the absence of the sigma bonds as was discussed above. For bulk materials, the number of sigma bonds per unit volume is going to be material independent for the class of liquid crystals. Bigger molecules may have more sigma bonds, but they occupy a correspondingly larger volume. Although the addition of the sigma bond polarizabilities using a scheme such as suggested by Bethea and Levine[8] will provide some improvement, the uncertainties in the pi-electron hyperpolarizability are probably comparable to the contributions from the sigma bonds and thus we have not as yet included this in our work.

Finally, we remark that the hyperpolarizability along the long axis of the molecule is consistently much larger in Table II than the isotropic average. This is consistent with one's intuition and particularly important in orientationally ordered liquid crystalline phases. Such considerations are important in connecting molecular properties to the experimentally measured properties of bulk materials. In addition, there are local field effects which must be considered. Perhaps the most important consideration omitted from the current predictions is the frequency dependence of the molecular polarizabilities. This is a difficult matter even in the context of an effective pi-electron Hamiltonian. Rather than dwell upon such difficulties or the legitimacy of previous theoretical attempts, we will end by saying that we hope to progress further towards both accurate predictions of molecular properties as well as bulk properties.

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