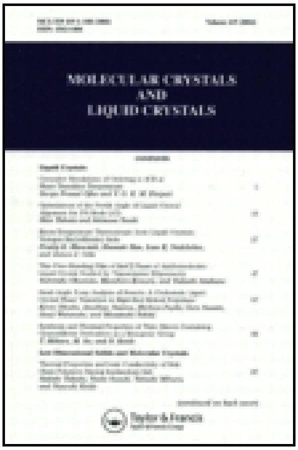

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THEORETICAL DETERMINATION OF NONLINEAR MOLECULAR POLARIZABILITIES

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Abstract We have initiated a theoretical evaluation of the nonlinear molecular polarizability of a group of molecules common to the core molecular structure of liquid crystals. The evaluation of three features of the molecular polarizability of these aromatic systems; the effect of bond alternation, the contribution of Coulomb interactions and the modification resulting from substituent groups are reported. We provide theoretical and experimental evidence that for general predictive theoretical calculations, a simple Hückel model Hamiltonian provides adequate information about the effects of molecular structure and chemical variation on the inherent nonlinearity in liquid crystal systems.

INTRODUCTION

The theoretical calculation of the response of an organic liquid of anisotropic molecules to intense optical electromagnetic fields is a complex and sometimes nonintuitive problem. The nonlinear macroscopic polarization density produced by the field is expressed as an expansion in the cartesian component of the electric field F,

$$P_i = \chi_{ij} F_j + \chi^{(2)}_{ijk} F_j F_k + \chi^{(3)}_{ijk\ell} F_j F_k F_\ell + \ldots.$$

where i,j,k,ℓ are indices for Cartesian components of tensors, repeated indices are summed over, and $\chi^{(n)}$ is the n-th order (hyper)polarizability tensor. Generally the nonlinearity of the macroscopic polarizability of a fluid arises from on two physical phenomena: 1) a dynamic reorientation of the anisotropic molecules (the Kerr effect), and 2) the higher order nonlinearity of the molecular electronic polarizability.

Recent experimental measurements[1] suggest that some liquid crystal molecules have sizeable fast optical nonlinearities. Since the molecular origin of these nonlinearities is likely to be dominated by the electronic structure of the aromatic core of the molecules, we have initiated a program of calculating the π-electron contribution to the molecular hyperpolarizability of such molecules. The separate determination of electronic properties associated with the delocalization of π-electrons is achieved by employing an "effective" π-electron Hamiltonian. In the following sections we will present two model Hamiltonians to describe the π-electrons of conjugated molecules, the Pariser-Parr-Pople (PPP) Hamiltonian[2] and the Hückel Hamiltonian.[3] The PPP model includes effective Coulomb interactions. A comparison of calculated molecular hyperpolarizability demonstrates that the Hückel model yields qualitatively similar results to the PPP model but with shorter computation time. The Hückel model is then used to calculate molecular hyperpolarizabilities for benzene molecules with halogen substitutions.

CALCULATION METHODS AND MODELS

The molecular polarizability may be calculated by considering a Hamiltonian of the form $H = H_o + H_1$ where H_o is the Hamiltonian in the absence of an optical field and

$$H_1 = e \sum_n \mathbf{F} \cdot \mathbf{r}_n .$$

H_I is the energy change of the molecule when an external electric field **F** is applied. The index n labels the π-electrons of the molecule. The molecular polarizabilities are defined by

$$E = E_o - P^o_i F_i - \alpha_{ij} F_i F_j /2! - \beta_{ijk} F_i F_j F_k /3! - \gamma_{ijk\ell} F_i F_j F_k F_\ell /4! + \ldots$$

where as before repeated Cartesian indices are summed over, E_o is the ground state energy in the absence of a field, $\mathbf{P}^o$ is the molecular dipole moment at zero field, α is the usual molecular polarizability tensor, and β and γ are the second and third order molecular hyperpolarizability tensors. Values for the various components of α, β, and γ can then be calculated from a perturbation theory expansion,[4] or by directly solving the full Hamiltonian for a variety of values of field strength and then fitting the function E(**F**) as a function of F_i.

The basic model Hamiltonians that we will compare differ in the form of H_o. First we will consider the Hückel, or tight-binding, model. The basis states that are used for the matrix formulation are the set of $|\phi_i>$ for all i, where $|\phi_i>$ is a p-orbital centered at atom i. The matrix elements of the Hückel Hamiltonian then are

$$H^H_{oij} = <\phi_i|H^H_o|\phi_j> = \alpha_i \delta_{ij} + \beta_{ij}$$

with β_{ij} non-zero if atoms i and j are σ-bonded to each other but zero if i and j do not form a σ-bond, and α_i being essentially an atomic energy level. An additional matrix element is technically relevant because the basis states are not orthogonal, $<\phi_i|\phi_j> = 1$ if $i=j$; S_{ij} if i and j are σ-bonded; 0 otherwise. However we will neglect this differential overlap and assume $<\phi_i|\phi_j> = \delta_{ij}$. We have tested the validity of neglecting S_{ij} by carrying out calculations with non-zero values for S_{ij}. The results differ quantitatively, but leave general trends unchanged. We have assumed standard values[5] of $\alpha_c = -9.4$ eV for carbon atoms and $\beta_{cc} = -2.4$ eV + 3.21 eV Å$^{-1}[a-a_o]$ for carbon-carbon bonds of various bond lengths, a, (a_o is 1.397 Å, as occurs in benzene). In second quantized notation the Hückel Hamiltonian may be written

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

where $c_{i\sigma}^+$ ($c_{i\sigma}$) is the elctron creation (annihilation) operator.

The calculation is carried out by diagonalizing an $n \times n$ matrix (where n is the number of conjugated atoms in the molecule) and obtain the independent electron energies and eigenvectors. The explicit perturbation theory expressions for the components of the hyperpolarizabilities are then evaluated.

The PPP model Hamiltonian has the form

$$H_o^P = \sum_{i\sigma} \alpha_i c^+_{i\sigma} c_{i\sigma} + \sum_{\substack{(ij)\sigma \\ (bonds)}} \beta_{ij}(c^+_{i\sigma} c_{j\sigma} + c^+_{j\sigma} c_{i\sigma}) + \sum_{\substack{i<j \\ \sigma,\sigma'}} V(i,j) c^+_{i\sigma} c_{i\sigma} (c^+_{j\sigma'} c_{j\sigma'} - 1)$$

with $V(i,j) = (11.24 \text{ eV})/\{1+0.667 \text{ Å}^{-2} r_{ij}^{\,2}\}^{\frac{1}{2}}$. The last sum accounts for Coulomb interactions.[6]

This Hamiltonian includes electron-ion attraction and electron-electron repulsion, and therefore is more realistic but no longer can be solved by simple independent particle techniques. The Green's function Monte Carlo (GFMC) method was used to calculate the ground state energy in the presence of a field F, and the hyperpolarizability components obtained by fitting. Details of the solution method have been presented elsewhere.[7]

RESULTS FOR SELECTED POLYENES AND BENZENES

Using the two model π-electron Hamiltonians just described, the polarizabilities of the polyenes having an even number of carbon atoms have been calculated. The carbon atoms form a zig-zag chain which defines the x-y plane with the x-axis taken to be parallel to the chain, and the z-axis normal to the plane of the chain. The carbon-carbon bond lengths alternate short and long, starting with a short bond at the end of the molecule. Values chosen were 1.45 Å and 1.35 Å for the long and short bonds respectively. Assuming the liquid to consist of a random orientation of molecules, the orientationally averaged quantities are $\alpha_{ave} = 1/3(\alpha_{xx} + \alpha_{yy})$ and $\gamma_{ave} = 1/5(\gamma_{xxxx} + 2\gamma_{xxyy} + \gamma_{yyyy})$ contribute macroscopically. For these models there is no polarization perpendicular to the plane of the molecule.

Table I presents the values of the linear polarizability α and the nonlinear hyperpolarizability γ for the polyene containing six carbon atoms. Note that the Coulomb effects included in the PPP model reduce both the linear and nonlinear polarizabilities as calculated for the Hückel model by a factor of three or four. The Hückel model was further found to be very sensitive to the alternation of carbon-carbon bond lengths. Including bond length alternation, removed the pathology of negative γ_{ave} previously observed in Hückel chains.[8]

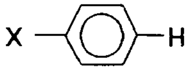
Our comparison calculations for polyene chains show that Coulomb effects always reduce both the linear and nonlinear polarizabilities. For both model Hamiltonians the same trend was observed that the polarizabilities increase more rapidly than linearly with increasing chain length. Thus it appears that the Hückel Hamiltonian is an adequate predictive model for indicating trends and qualitative features.

TABLE I. Polarizability tensors for alternating six carbon chain.

	Hückel	PPP
α_{xx}	4.29	1.05
α_{xy}	1.06	0.341
α_{yy}	0.402	0.184
α_{ave}	1.56	0.412
γ_{xxxx}	21.2	4.11
γ_{xxyy}	-2.56	0.194
γ_{yyyy}	-0.169	0.032
γ_{ave}	3.19	0.906

Table II presents the results for benzene and three halogen substituted benzenes with and without neglect of overlap. Also

TABLE II. Hyperpolarizability of substituted benzene.



X	γ_A (S = 0)	γ_A (S ≠ 0)	γ_A (exp)
H	0.1338	0.0778	0.106
F	0.1625	0.0751	0.0876
Cl	0.1693	0.0860	0.119
Br	0.1802	0.1038	0.148

given are experimental values.[9] It appears that the Hückel model, modified by the presence of the halogens,[10] adequately predicts the trends that are experimentally measured, although neglecting differential overlap appears to be more important in the systems.

All of the theoretical values presented here are static (zero frequency) calculations. One may expect that optical measurements, above vibrational frequencies and below electronic absorption thresholds, can be legitimately compared to such calculations. Modifications will be required if compared to measurement which induce molecular reorientation or are carried out near resonances.

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