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Hückel Model Calculations of Polarizability and Hyperpolarizability for Conjugated Molecules

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We have conducted a theoretical evaluation of the linear and nonlinear polarizabilities of various hydrocarbon compounds using perturbation theory of the Hückel Hamiltonian. We have found that for polyene chains the alternation of carbon–carbon bond lengths is a crucial feature. Secondly, we have found that for halogen substituted benzene molecules, the inclusion of differential overlap is essential to reproduce the trend in the hyper-polarizability that is observed in experiment. This contrasts with the standard result that differential overlap produces no qualitative change for pure hydrocarbon molecules.

INTRODUCTION

The recognition in recent years of the presence of large optical nonlinearities in organic materials has led to a surge of interest in thermotropic liquid crystals.[1] Two particular points of interest have developed regarding liquid crystals. Firstly, what roles do the unusual structural properties of liquid crystals play in determining the nonlinear response of these materials, and secondly, how may the nonlinear properties be understood and controlled by relating them to the chemical structure of the molecules which form liquid crystals.

In describing the chemical structural features of organic molecules which form liquid crystalline phases, it is often stated that an important requirement is the presence of a polarizable aromatic core. This polarizable core often consists of more than one benzene ring connected by a variety of linkages. Further analysis of liquid crystal chemical structures show that the type of linkage and the presence

of various constituent groups strongly influence the type of liquid crystalline phases that the material exhibits.

The chemical features of molecules, which are crucial in determining the type or existence of liquid crystalline phases, seem to be nearly identical to the chemical considerations to be studied in investigating methods of enhancing optical nonlinearities. Although there seems to be a large base of experimental information on the effects of chemical structure on liquid crystallinity, the empirical information on the correlations between chemical structure and nonlinear optical properties is more tenuous.

In a theoretical approach one would like to begin with the chemical formula of a liquid crystal molecule and eventually predict the bulk linear and nonlinear electric susceptibility tensors. This rather ambitious task can be divided into a molecular problem of calculating the electronic linear and nonlinear properties of a single molecule, and the problem of then relating properties of the bulk to those of the constituent molecules. In addition to this separation, there are considerations of static *vs.* dynamic properties which involve reorientation and relaxation processes in the bulk and frequency dependence of electronic properties.

The study being presented here is concerned with the theoretical determination of the static electronic linear and nonlinear polarizability of conjugated molecules. The "polarizable core" of a liquid crystal molecule is such a system.

There is substantial experimental evidence[2] that the large optical nonlinear response in thermotropic liquid crystals and similar organic materials is directly linked with the delocalized character of the π-electron wavefunctions. The experimental evidence supports the theoretical model that separates the contributions of various molecular segments into additive and non-additive classes. The delocalized conjugated portions of the molecule, such as a benzene ring, are non-additive in that two connected rings do not simply produce twice the polarizability of a single ring. In contrast, an alkyl chain with twice as many CH_2 segments is essentially twice as polarizable, once simple geometrical considerations are made. In a similar vein, the σ bonds and core electronic contributions may also be treated as additive, leaving only π-electrons and the complications of the heteroatoms and substituent groups as the principal theoretical problem.

In the following sections we will outline the theoretical methods employed to determine this non-additive part of the molecular polarizability. In particular, we will present results for selected chain and ring geometries which particularly provide information on the

effects of molecular geometry on nonlinear polarizability as well as the effect of certain specific chemical substituent groups.

METHODS

The energy of a molecule in an applied field can be written as an expansion in powers of the field strength

$$E = E_o - p_i F_i - \frac{1}{2} a_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l$$

where E_o is the ground state energy in the absence of an applied field, p_i is the dipole moment in the ith direction, α is the linear polarizability, β and γ are the second and third order hyperpolarizabilities, F_i is the applied field along the i axis and repeated indices are summed over the cartesian components, x,y,z. The quantities α, β, and γ are determined by the electronic structure of the molecule, including all electrons, but in general the π-electrons are the major contributors. We note that β is zero by symmetry for the pure hydrocarbons we have studied, but non-zero for the substituted benzenes. However, the spatial average of β, taking into account the different molecular orientations in the condensed phase, is zero for all the molecular systems considered in this work. In principle, one must solve the Schroedinger equation to obtain all the necessary information, but from the practical point of view this is impossible. Instead, we employ a model Hamiltonian to describe the π-electrons with the contention that this will provide the polarizability and hyperpolarizability with sufficient accuracy.[3]

The Hamiltonian which we employed for these calculations was the Hückel Hamiltonian which has been extensively described elsewhere.[4] The assumptions in the Hückel Hamiltonian are that each electron in the π-system moves in an effective one-particle potential formed by the atomic core electrons and nuclei and by the σ-bonded electrons. Its principal simplifying assumption is that the Coulomb repulsion among the π-electrons is ignored. The basis states which were used were the set of atomic P_z orbitals. The state vectors were formed by the linear combination of atomic orbitals (LCAO) method. In the atomic orbital basis set, we must concern ourselves with the two following types of matrix elements,

$$\langle \phi_a | H | \phi_b \rangle = \beta_{ab},$$

and

$$\langle \phi_a | \phi_b \rangle = S_{ab}$$

where ϕ_a and ϕ_b refer to P_z orbitals centered on sites a and b.

In the Hückel approximation the first matrix element is treated as follows. If a is equal to b, then it is referred to as the Coulomb integral, α_a, and is approximately equal to the ionization energy of an electron in a P_z orbital on an isolated atom of that species. If a and b are neighboring atomic site labels (i.e. atoms connected by a chemical bond), the matrix element is termed the resonance integral, β, which depends on the two atom types and on the bond length. If a and b are not equal or bonded neighbors, the integral is set equal to zero. Similarly, S_{ab} is unity if $a = b$, a number S_{ab} determined by atom types and bond length if a and b are bonded neighbors, and zero otherwise. The quantity S_{ab} for $a \neq b$ is called the differential overlap.

To perform actual calculations, numerical values must be assumed for the above matrix elements. In the zero differential overlap approximation (i.e. $S_{ab} = \delta_{ab}$), the value of β for the C—C bond in benzene (which has a length of 1.397 Å) is -2.40 eV.[5] This value results in the first excited state of benzene lying 4.80 eV above the ground state. As the C—C bond length varies from molecule to molecule, we have varied β according to the standard formula[6] $\beta = \beta_o + (3.21 \text{ eV/Å})(r - r_o)$ where r is the bond length and β_o and r_o are the corresponding values given above for benzene. The value of α for a carbon atom was taken to -11.26 eV although this in practice serves only to set the zero of energy. For heteroatoms the relevant α's, β's, and bond lengths are given in Table I, along with the sources from which we obtained our values.

The value of S has been calculated to be 0.268 for C—C in benzene and 0.296 for C—C in ethylene.[8] These data lead to the empirical form $S = S_o - (0.46/\text{Å})(r - r_o)$ where S_o and r_o are the values for a C—C bond in benzene. When the effect of overlap is included, the values for the β's change. By assuming the same respective energies for the first excited states of benzene and ethylene as obtained without overlap, we get the relationship $\beta = \beta_o + (7.83 \text{ eV/Å})(r - r_o)$, where β_o, the value for a C—C bond in benzene, is -5.24 eV. The α for carbon doesn't change, and the expressions in Table I are still valid for heteratom parameters when overlap is not neglected. Due to a lack of more detailed information, S was assumed to be 0.25 for all bonds other than C—C (e.g. C—N, etc.).

TABLE I

Values of parameters used for substituted aromatic rings.

X	Y	α_y (Ref. 5)	β_{xy} (Ref. 5)	r_{xy} (Ref. 7)
C	C	α_o	β_o	1.397 Å
C	N	$\alpha_o + 1.5\,\beta_o$	β_o	1.38 Å
C	O	$\alpha_o + \beta_o$	$0.8\,\beta_o$	1.36 Å
C	F	$\alpha_o + 3\,\beta_o$	$0.7\,\beta_o$	1.30 Å
C	Cl	$\alpha_o + 2\,\beta_o$	$0.4\,\beta_o$	1.70 Å
C	Br	$\alpha_o + 1.5\,\beta_o$	$0.3\,\beta_o$	1.85 Å

To calculate the polarizability and hyper-polarizability, the single particle eigenstates and eigenenergies of the Hamiltonian of the molecule must be determined. To accomplish this, we solved the eigenvalue equation $HC_n = \epsilon_n SC_n$, where H and S are N by N matrices, N is the number of atom sites that are part of the conjugated system, ϵ_n is the nth eigenenergy and C_n is the nth eigenvector which is normalized to one, $\langle C_a|S|C_b\rangle = \delta_{ab}$. In practice, it was found easier to solve the equation as $S^{-1}HC_n = \epsilon_n C_n$, where $S^{-1}H$ now has the role of the usual Hamiltonian.

Once the Hamiltonian matrix was formed, it was diagonalized to give the eigenvalues and eigenvectors. This gave a set of N single particle eigenenergies. The π-electron ground state was then formed by doubly filling the $N_e/2$ lowest energy levels, where N_e is the number of electrons in the π system (an even number in all cases considered here). The wave function is a Slater determinant using these occupied single particle levels. The value of the polarizability is then given by first-order perturbation theory as[9]

$$\alpha_{\beta\gamma} = P \sum_{i \neq 0} \frac{\langle o|\mu_\beta|i\rangle\langle i|\mu_\gamma|o\rangle}{E_i - E_o}$$

where μ_a is the dipole operator along the $\hat{e}_a$ axis,

$$\mu_a = e \sum_n^{N_e} (\mathbf{R}_n \cdot \hat{e}_a)$$

P is the permutation operator which counts all permutations of the indices β and γ, $|i\rangle$ is an electronic state different from the ground

state, $|o\rangle$ is the ground state, and E_n is the energy of the state $|n\rangle$ which is equal to the sum of the energies of the occupied single particle eigenstates. Since the dipole operator is a single particle operator, the relevant states $|i\rangle$ have only one electron in a single particle eigenstate different from the eigenstate it occupied in the ground state.

For the case of benzene, with six carbon atoms and six π-electrons, the ground state would be formed by putting two electrons, one of spin up and one of spin down, in the lowest three single particle energy levels. An example of an excited state would then be three spin up electrons in the lowest three energy levels, two spin down electrons in the lowest two energy levels, and the third spin down electron in the highest energy level.

Similarly, 4th-order perturbation theory gives as the expression for the hyper-polarizability[9]

$$\gamma_{\alpha\beta\gamma\theta} = P\left\{ \sum_{ijk\neq 0} \frac{\langle o|\mu_a|i\rangle\langle i|\mu_\beta|j\rangle\langle j|\mu_\gamma|k\rangle\langle k|\mu_\theta|o\rangle}{(E_i - E_o)(E_j - E_o)(E_k - E_o)} \right.$$

$$- \sum_{ij\neq 0} \frac{\langle o|\mu_a|i\rangle\langle i|\mu_\beta|o\rangle\langle l|\mu_\gamma|j\rangle\langle j|\mu_\theta|o\rangle}{(E_i - E_o)^2(E_j - E_o)}$$

$$- 2\sum_{ij\neq 0} \frac{\langle o|\mu_a|o\rangle\langle o|\mu_\beta|i\rangle\langle i|\mu_\gamma||j\rangle\langle j|\mu_\theta|o\rangle}{(E_i - E_o)^2(E_j - E_o)}$$

$$\left. + \sum_{i\neq 0} \frac{\langle o|\mu_a|o\rangle\langle o|\mu_\beta|o\rangle\langle o|\mu_\gamma|i\rangle\langle i|\mu_\theta|o\rangle}{(E_i - E_o)^3} \right\}$$

where i, j, k are all labels for electronic states different from the ground state. Here again, since the dipole operator is a one particle operator, any matrix element between two states must have those states differ by only one of the single particle states in their Slater determinants in order to be non-zero.

In addition to the various spatial components of the molecular polarizability and the hyper-polarizability, we will also present results for the spatial average values of the polarizability and hyper-polarizability. This is of special interest because much of the experimental evidence is obtained from isotropic fluids.[10]

For convenience in calculating molecular quantities, since all the molecules we study are assumed to be planar, we chose the x direction

to be along the long axis of the molecule, the y axis to be perpendicular to x and in the plane of the molecule, and the z axis to be perpendicular to the plane of the molecule. For the spatial averaging process, the molecules were assumed to be part of an isotropic fluid with no orientational order. By averaging over all solid angles, for the average value of α we get $\alpha_{ave} = 1/3(\alpha_{xx} + \alpha_{yy})$. We assume that all components with a z coordinate are zero for planar molecules. For the hyperpolarizability, the spatial averaging gives a value of $\gamma_{ave} = 1/5(\gamma_{xxxx} + 2\gamma_{xxyy} + \gamma_{yyyy})$.

RESULTS

In this section we will report the results of our calculations on various conjugated structures. These calculations have been made with and without the inclusion of differential overlap, and in the case of linear polyene chains, with and without bond alternation. The results will be divided into three sub-sections: polyene chains, aromatic rings, and substituted aromatic rings. The polarizabilities are in units of $\alpha_o \equiv 10^{-23}$ cm^3 and the hyperpolarizabilities are in units of $\gamma_o \equiv 10^{-33}$ cm^7/esu^2.

Polyene Chains

The simplest conjugated structures that we consider in this paper are linear polyene chains of formula C_nH_{n+2}. As the odd-n chains occur rarely in nature, we only will consider chains with an even number of carbon atoms.

First, we will present the results for chains with all C—C bonds the same length, all C—C resonance integrals the same value, and all on-site Coulomb energies the same. In Table II are presented polarizability results for linear chains with non-alternating bond lengths and the differential overlap set equal to zero. The components in the xx and yy directions are presented, along with the spatial average value.

Table II also presents the results from our calculations of the hyperpolarizability of uniform linear chains with the differential overlap set equal to zero. In the table are given the $xxxx$, $xxyy$, and $yyyy$ components, and the spatial average value. From the table we see that the $xxxx$ and $xxyy$ components are of the same order of magnitude, but of opposite sign, with the $xxyy$ component being negative and larger for most of the chains, while the $yyyy$ component is much

TABLE II

Polarizabilities and hyper-polarizabilities of non-alternating polyene chains without overlap.

N	α_{xx}/α_o	α_{yy}/α_o	α_{ave}/α_o	γ_{xxxx}/γ_o	γ_{xxyy}/γ_o	γ_{yyyy}/γ_o	γ_{ave}/γ_o
4	2.564	0.3287	0.9642	-0.023	-0.036	-0.004	-0.020
6	7.498	0.5297	2.678	0.0693	-0.201	-0.010	-0.069
8	16.36	0.7443	5.703	0.5835	-0.718	-0.021	-0.175
10	30.28	0.9695	10.42	2.106	-1.97	-0.039	-0.377
12	50.38	1.203	17.20	5.571	-4.57	-0.064	-0.728
14	77.78	1.444	26.11	12.34	-9.38	-0.098	-1.30
16	113.6	1.691	38.43	24.28	-17.6	-0.142	-2.20
18	159.0	1.944	53.63	43.85	-30.7	-0.198	-3.55
20	215.0	2.202	72.40	74.14	-50.7	-0.267	-5.49
22	282.8	2.464	95.09	111.90	-79.9	-0.351	-8.23
24	363.5	2.730	122.1	183.1	-121.0	-0.450	-12.0

TABLE III

Polarizabilities and hyper-polarizabilities of non-alternating polyene chains with overlap.

N	α_{xx}/α_o	α_{yy}/α_o	α_{ave}/α_o	γ_{xxxx}/γ_o	γ_{xxyy}/γ_o	γ_{yyyy}/γ_o	γ_{ave}/γ_o
4	2.769	0.3551	1.041	-0.053	-0.044	-0.005	-0.029
6	8.101	0.5723	2.891	-0.051	-0.250	-0.013	-0.112
8	17.68	0.8041	6.169	0.2857	-0.897	-0.027	-0.307
10	32.72	1.047	11.26	1.524	-2.47	-0.48	-0.725
12	54.43	1.300	18.58	4.586	-5.74	-0.080	-1.39
14	84.03	1.560	28.53	10.83	-11.8	-0.123	-2.57
16	122.7	1.827	41.52	22.13	-22.1	-0.178	-4.45
18	171.7	2.100	57.95	40.94	-38.6	-0.249	-7.30
20	232.3	2.379	78.22	70.38	-63.8	-0.336	-11.5
22	305.5	2.662	102.7	114.4	-101.0	-0.441	-17.4
24	392.8	2.949	131.9	177.5	-153.0	-0.567	-25.7

smaller than either of the other two. The negative value of the *xxyy* component thus drives the average hyper-polarizability negative.

Table III presents the results for the polarizability of linear chains when the differential overlap is set equal to 0.27 for all the C—C bonds. Here again are given the two spatial components and the spatial average. As in the case where the differential overlap was set equal to zero, the average polarizability for the longer chains is dominated by the *xx* component. Comparison of the results from Table II and Table III shows that the only apparent effect of adding a non-zero value for the differential overlap was to increase the average polarizability by a factor of 1.08.

Table III also gives the hyper-polarizability results when the differential overlap was set equal to 0.27. The addition of the overlap had very little effect on the *xxxx* component of the hyperpolarizability, causing a decrease of approximately 3%. The value of the *xxyy* component increased in magnitude by about 25%, and the value of the *yyyy* component increased in magnitude by 20%, but remained small in comparison to the other two components. The net effect of these changes was to increase the magnitude of the average hyper-polarizability by a factor of 2, while keeping the sign of the average negative.

These results for the hyper-polarizability both with and without overlap are inconsistent with experimental results and with the results of other theoretical calculations. For the longer polyene chains, it is found expeirmentally that the average hyper-polarizability is positive.[11-14] Other calculations have also concluded that the *xxxx* component of the hyperpolarizability is much greater than the other components.[15,16]

Furthermore, experimentally it has been found that for the even-numbered polyene chains, all the bonds are not of the same length, but instead the bonds alternate in length, varying between 1.35 Å and 1.45 Å.[17] This causes the resonance integral to vary, as has been discussed previously, and also causes the differential overlap to vary.

The results in Table IV represent calculations of the polarizability done with the differential overlap equal to zero when the C—C bond lengths were alternated between 1.45 Å and 1.35 Å, with the shorter bond existing between the first two carbon atoms and then alternating. The values used for the resonance integrals were 2.23 eV and 2.57 eV, as discussed previously. The first thing that should be noted from the data is the fact that alternating the bond length drastically reduced the value of the *xx* component and of the average polarizability.

TABLE IV

Polarizabilities and hyper-polarizabilities of alternating polyene chains without overlap.

N	α_{xx}/α_o	α_{yy}/α_o	α_{ave}/α_o	γ_{xxxx}/γ_o	γ_{xxyy}/γ_o	γ_{yyyy}/γ_o	γ_{ave}/γ_o
4	1.925	0.2996	0.7416	0.0467	-0.021	-0.003	0.0005
6	5.042	0.4725	1.838	0.7668	-0.092	-0.006	0.1152
8	9.882	0.6513	3.511	4.523	-0.264	-0.011	0.7965
10	16.47	0.8337	5.761	17.31	-0.588	-0.018	3.224
12	24.72	1.018	8.581	50.70	-1.11	-0.025	9.692
14	34.53	1.205	11.91	123.2	-1.86	-0.034	23.89
16	45.73	1.392	15.71	260.6	-2.86	-0.044	50.97
18	58.17	1.579	19.92	495.3	-4.12	-0.055	97.41
20	71.69	1.768	24.49	864.8	-5.65	-0.066	170.7
22	86.14	1.956	29.37	1409.0	-7.44	-0.078	278.8
24	101.4	2.145	34.51	2169.0	-9.47	-0.090	430.0

Table IV also presents the components and average hyperpolarizability for polyene chains when bond alternation is included, but the differential overlap is set equal to zero. It can be seen immediately that the addition of bond alternation had a profound effect on both the *xxxx* and the *xxyy* components. The magnitude of the *xxxx* component was increased by a factor of ten to twelve, while the magnitude of the *xxyy* component decreased by a factor of up to twelve. This has the net result of pushing the average value of the hyper-polarizability positive, in agreement with experimental evidence.

Table V gives the polarizability results for chains that alternate bond length when the differential overlap is not set to zero. The values used for the overlap were 0.25 and 0.29, as discussed previously. Here again the *xx* component and the average are drastically reduced from the non-alternating case. When the bond lengths are alternating, the addition of non-zero overlap reduces the polarizability, where in the non-alternating case addition of overlap increased the polarizability.

In Table V are also the hyper-polarizabilities for polyene chains when bond alternation and differential overlap are included. The addition of the overlap decreases the rate at which γ_{xxxx} and γ_{ave} increase with chain length, and also decreases the average value by 25%, although the average hyper-polarizability still remains positive, in agreement with experimental values.

In Figure 1 we have plotted the average polarizability of the chains as a function of the number of carbon atoms in the chain. From the figure it can be clearly seen that bond alternation has a much larger effect on the polarizability of the polyene chains than does the addition of differential overlap.

Figure 2 is a graph of average hyper-polarizability *vs.* chain number for the alternating carbon chains. As we have stated previously, the addition of bond alternation has made the value of the average hyper-polarizability positive. The addition of differential overlap here has decreased the average value but qualitatively has not altered the results.

Rings

The second group of conjugated structures that we studied were bonded aromatic rings. The rings that we studied were connected in two distinct ways. The first type were chains of fused aromatic rings where two neighboring rings share a common side (i.e. two carbon atoms), such as naphthalene, anthracene, etc. For molecules of three and more rings we consider only the arrangement where the two

TABLE V

Polarizabilities and hyper-polarizabilities of alternating polyene chains with overlap.

N	α_{xx}/α_o	α_{yy}/α_o	α_{ave}/α_o	γ_{xxxx}/γ_o	γ_{xxyy}/γ_o	γ_{yyyy}/γ_o	γ_{ave}/γ_o
4	1.966	0.3164	0.7607	0.0438	-0.022	-0.003	-0.001
6	4.992	0.4969	1.830	0.8372	-0.095	-0.007	0.1281
8	9.522	0.6825	3.402	4.927	-0.260	-0.012	0.8790
10	15.48	0.8710	5.449	18.24	-0.553	-0.018	3.423
12	22.71	1.061	7.923	51.10	-0.998	-0.026	9.816
14	31.05	1.252	10.77	118.3	-1.61	-0.034	23.01
16	40.32	1.444	13.92	238.0	-2.38	-0.043	46.64
18	50.37	1.637	17.33	430.4	-3.32	-0.052	84.74
20	61.04	1.829	20.96	715.5	-4.40	-0.062	141.3
22	72.21	2.022	24.75	1111.0	-5.62	-0.073	220.0
24	83.79	2.215	28.67	1633.0	-6.95	-0.083	323.8

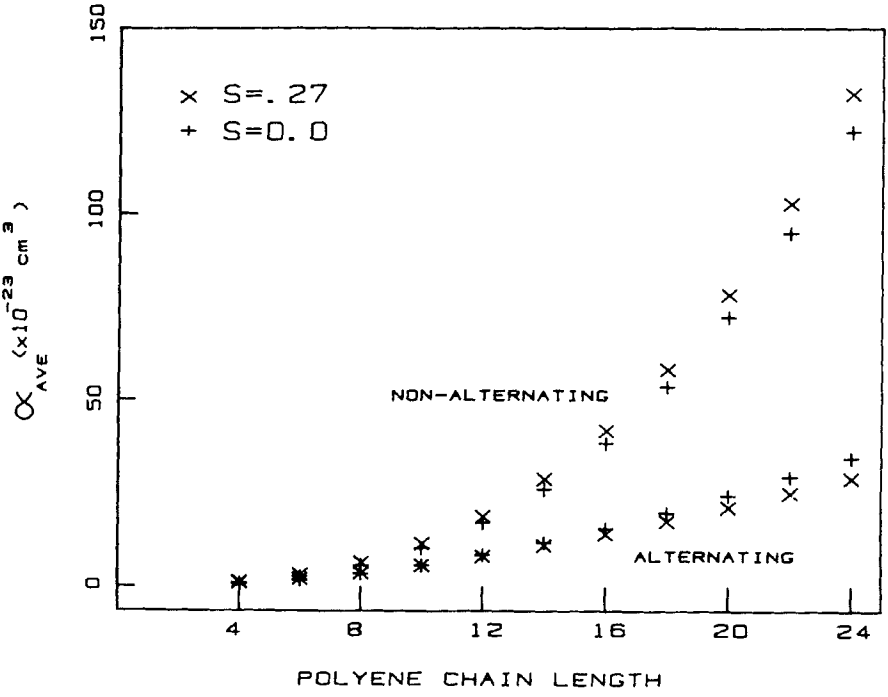

FIGURE 1 Average polarizability of polyene chains.

neighboring rings are on opposite sides of a ring in the interior of the chain. The second type of structures were linear chains of rings with neighboring rings linked by a C—C bond, such as biphenyl, terphenyl, etc. For both these types, the conjugation is assumed to extend across all the carbon atoms in the molecule, and the π-electrons are distributed across the whole planar molecule. The parameters used for these molecules were those commonly used for benzene: the bond length used was 1.397 Å and the value of the resonance integral was −2.40 eV for the case of no overlap. For the biphenyl-like structures, the assumption that the molecule is planar may not be valid for the physical molecule due to twist about the C—C bonds connecting successive rings. This effect can probably be treated reasonably by reducing the resonance integral for the twisted bond appropriately. We have not performed this calculation.

Table VI presents the calculated polarizabilities for the naphthalene type structures, both with and without the inclusion of differential overlap. Here again we present the *xx* and *yy* components of the polarizability, along with the spatial average. As in the polarizability

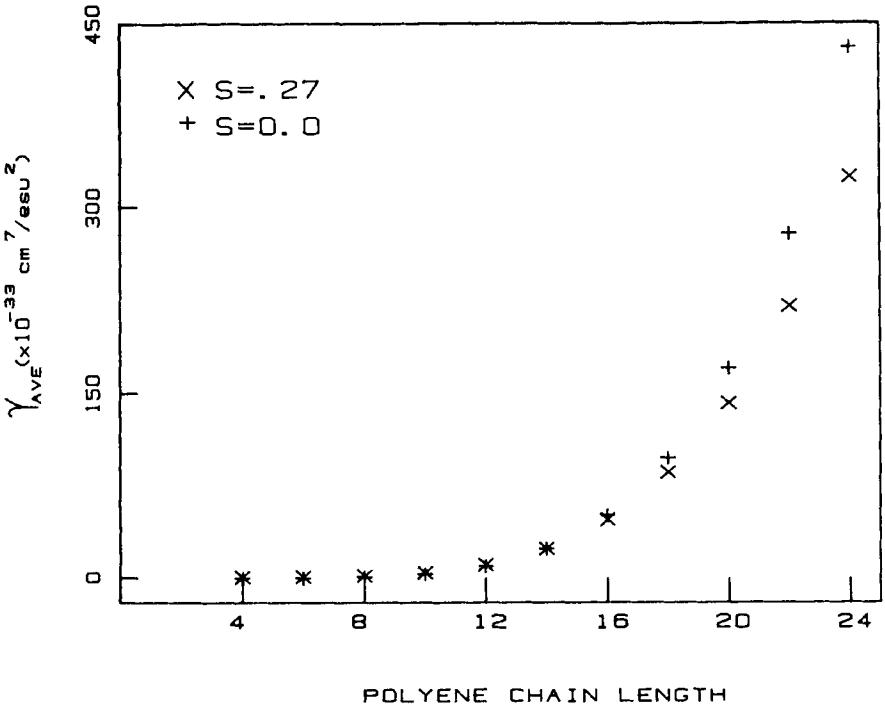

FIGURE 2 Average hyperpolarizability of alternating polyene chains.

calculations for the polyene chains, the inclusion of differential overlap has little effect on the polarizability of the naphthalene-like ring structures. The inclusion of overlap caused only about an 8 or 9% increase in the average polarizability. By way of comparison, the average polarizability of the fused six ring molecule is approximately equal to that of a fourteen carbon alternating chain from the previous section.

Table VI also includes the hyper-polarizability results for the fused ring naphthalene-like structures. As in the polyene chain section, we present the *xxxx*, *xxyy*, and *yyyy* components, along with the spatial average value of the hyper-polarizability. The results when the differential overlap was included, which are also in Table VI, show that the addition of the differential overlap does not qualitatively change the results, but does change the quantitative values of the various components and the average hyper-polarizability. Overlap increases the rate of growth of the average hyperpolarizability as the number of rings increases. Also interesting to notice is the fact that the *yyyy* component is negative for 3 or more rings and that the *xxyy* com-

TABLE VI

Polarizabilities and hyper-polarizabilities of napthalene-like molecules.

Number of rings	α_{xx}/α_o	α_{yy}/α_o	α_{ave}/α_o	γ_{xxxx}/γ_o	γ_{xxyy}/γ_o	γ_{yyyy}/γ_o	γ_{ave}/γ_o
1 S = 0	1.176	1.176	0.7839	0.0090	0.0030	0.0090	0.0048
1 S ≠ 0	1.270	1.270	0.8469	0.0053	0.0018	0.0053	0.0028
2 S = 0	3.285	2.283	1.856	0.3294	-0.045	0.0626	0.0605
2 S ≠ 0	3.559	2.466	2.009	0.3736	-0.064	0.0603	0.0611
3 S = 0	5.953	4.027	3.327	1.617	-0.200	-0.018	0.2399
3 S ≠ 0	6.470	4.350	3.607	2.034	-0.280	-0.055	0.2841
4 S = 0	8.863	6.480	5.114	4.491	-0.166	-0.971	0.6377
4 S ≠ 0	9.659	7.000	5.553	6.003	-0.297	-1.26	0.8297
5 S = 0	11.85	9.682	7.177	9.088	1.448	-4.69	1.458
5 S ≠ 0	12.94	10.46	7.799	12.63	1.614	-5.95	1.982
6 S = 0	14.84	13.65	9.497	15.08	8.443	-15.0	3.393
6 S ≠ 0	16.22	14.75	10.32	21.51	10.23	-18.9	4.611

ponent is negative for 2, 3, or 4 rings but becomes positive for 5 or more rings. The average hyper-polarizability of the six fused ring molecule is approximately the same as that for a ten carbon alternating chain.

In Table VII are presented the polarizability calculations for aromatic rings coupled in a biphenyl type structure, both with and without the inclusion of differential overlap. Here again, we see that the effect on the polarizability of adding differential overlap to the calculation is to increase the value of the components and average by 8–10%. If a comparison is made to the data presented in Table VI, it can be readily seen that the average polarizability is almost identical for both types of molecules with the same number of carbon rings in the molecule. This result holds true both with and without the inclusion of differential overlap. The biphenyl type molecules have a larger *xx* polarizability component than the naphthalene types, but the naphthalene type molecules have a larger *yy* component. In comparison, the average polarizability of the five ring molecule is almost the same as that for a twelve carbon alternating chain.

In Table VII are also presented the various hyperpolarizability components and the spatial average for the biphenyl type ring structures. Here the addition of differential overlap has increased the value of the *xxxx* component by approximately 20%. The magnitude of the *xxyy* component also increased by about 20%, while the value of the *yyyy* component decreased by 8%. The net effect of these changes was to increase the value of the average hyper-polarizability by approximately 20%. If the comparison is made to Table VI, it can be seen that although the two types of molecules had almost identical average polarizabilities for molecules with the same number of aromatic rings, this is not the case for the average hyper-polarizability. The biphenyl type molecules have a much greater value for both the *xxxx* component and the average hyper-polarizability, compared to the naphthalene-like molecules with the same number of aromatic rings. The magnitude of the *xxyy* and the *yyyy* components is much smaller for the biphenyl-like molecules. For these molecules the *xxxx* component is much larger than either the *xxyy* or the *yyyy* components, in direct contrast to the results for the naphthalene-like molecules. The average hyper-polarizability of the five ring molecule lies midway between that for the ten and twelve carbon alternating carbon chains.

Substituted Rings

The third type of molecules for which we have calculated the polarizabilities is the substituted aromatic rings. We have examined the

TABLE VII

Polarizabilities and hyper-polarizabilities of biphenyl-like molecules.

Number of rings	α_{xx}/α_o	α_{yy}/α_o	α_{ave}/α_o	γ_{xxxx}/γ_o	γ_{xxyy}/γ_o	γ_{yyyy}/γ_o	γ_{ave}/γ_o
1 S=0	1.176	1.176	0.7839	0.0090	0.0030	0.0090	0.0048
1 S≠0	1.270	1.270	0.8469	0.0053	0.0018	0.0053	0.0028
2 S=0	3.770	2.376	2.049	0.7236	-0.018	0.0272	0.1429
2 S≠0	4.073	2.572	2.215	0.8162	-0.025	0.0233	0.1494
3 S=0	7.200	3.560	3.587	4.333	-0.119	-0.0479	0.8284
3 S≠0	7.779	3.857	3.879	5.105	-0.146	0.0435	0.9714
4 S=0	10.99	4.742	5.243	12.73	-0.286	0.0700	2.445
4 S≠0	11.87	5.139	5.670	15.24	-0.346	0.0649	2.923
5 S=0	14.91	5.922	6.943	25.90	-0.489	0.0925	5.002
5 S≠0	16.11	6.420	7.509	31.26	-0.590	0.0868	6.034

TABLE VIII

Polarizabilities and hyper-polarizabilities of hetero-atom molecules without overlap.

X	α_{xx}/α_o	α_{yy}/α_o	α_{ave}/α_o	γ_{xxxx}/γ_o	γ_{xxyy}/γ_o	γ_{yyyy}/γ_o	γ_{ave}/γ_o
Type a)							
F	1.584	1.217	0.9336	0.0691	-0.003	0.0104	0.0147
Cl	1.572	1.201	0.9243	0.0711	-0.003	0.0121	0.0154
Br	1.569	1.198	0.9223	0.0729	-0.003	0.0126	0.0158
Me	1.536	1.188	0.9077	0.0660	-0.003	0.0135	0.0146
Type b)							
F	2.962	1.481	1.481	0.5577	-0.028	0.0374	0.1076
Br	2.885	1.511	1.466	0.6215	-0.024	0.0316	0.1210
Me	2.724	1.529	1.418	0.4206	-0.013	0.0278	0.0845
Type c)							
F	1.236	1.178	0.8047	0.0148	0.0022	0.0097	0.0058
Cl	1.231	1.177	0.8028	0.0193	0.0024	0.0094	0.0067
Br	1.232	1.177	0.8028	0.0249	0.0025	0.0094	0.0078
H	1.176	1.176	0.7839	0.0090	0.0030	0.0090	0.0048

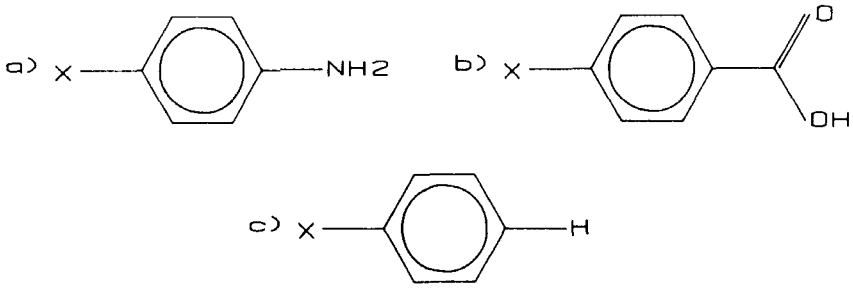

FIGURE 3 Schematic structures of substituted benzenes. Choices of X studied were H, F, Cl, Br.

effects of appending various halogens or a methyl group to three different aromatic ring structures (Figure 3), and have made comparisons between the polarizabilities with the different halogens attached. The values of the resonance integrals and the Coulomb integrals used for the heteroatoms were the values in Table I; for the overlap integrals a value of 0.25 was used for all the integrals.

In Tables VIII and IX are presented the polarizabilities and hyperpolarizabilities for the three types of molecules with and without the inclusion of overlap. A comparison of the two tables shows that including overlap has a much greater effect on these molecules than on the pure hydrocarbons. For the molecules presented in parts A) and B), the inclusion of overlap had no qualitative effect on the results. For the substituted aromatic rings, the inclusion of overlap alters the trends shown in the polarizability and hyperpolarizability for the substitution of the various halogens.

One of the major goals of this work was to be able to predict qualitatively whether the inclusion of a different atom or atom group would increase or decrease the polarizability and hyperpolarizability of a molecule. In Table X and also in Figure 4 we present the average hyperpolarizability of halogen-substituted benzenes (C_6H_5X), type C in Figure 3, both with and without overlap. We also included in the table the experimentally determined value of the average hyperpolarizability for the molecules.[18]

As can be seen from the table, the experimental values lie between the values we determined with and without the inclusion of differential overlap. Although the calculated average hyperpolarizabilities when differential overlap is discounted are of the same size as the experimental values, their relative values are not in the same order as those determined experimentally. When the differential overlap is

TABLE IX

Polarizabilities and hyper-polarizabilities of hetero-atom molecules with overlap.

X	α_{xx}/α_o	α_{yy}/α_o	α_{ave}/α_o	γ_{xxxx}/γ_o	γ_{xxyy}/γ_o	γ_{yyyy}/γ_o	γ_{ave}/γ_o
Type a)							
F	1.252	1.235	0.8290	0.0025	0.0042	0.0023	0.0027
Cl	1.297	1.237	0.8445	0.0051	0.0035	0.0033	0.0031
Br	1.339	1.240	0.8597	0.0085	0.0032	0.0029	0.0036
Me	1.273	1.236	0.8363	0.0035	0.0037	0.0032	0.0028
Type b)							
F	3.455	1.449	1.635	0.9353	-0.123	0.0844	0.1546
Br	3.947	1.391	1.779	1.280	-0.176	0.0927	0.2043
Me	3.478	1.462	1.647	0.9398	-0.126	0.0841	0.1546
Type c)							
F	1.252	1.266	0.8393	0.0044	0.0022	0.0048	0.0027
Cl	1.304	1.270	0.8582	0.0085	0.0012	0.0055	0.0033
Br	1.371	1.2672	0.8793	0.0160	0.0003	0.0058	0.0045
H	1.270	1.270	0.8469	0.0053	0.0018	0.0053	0.0028

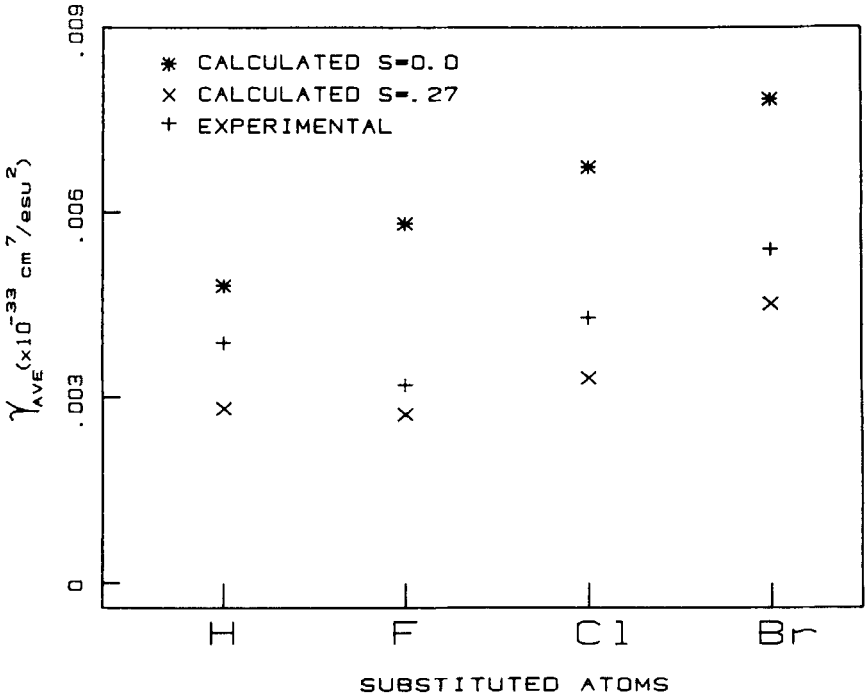

FIGURE 4 Comparison of experimental and calculated hyperpolarizabilities of substituted benzene molecules.

included, the average hyperpolarizability now falls below the experimental values, but more significantly, the calculated values now agree with the experimental as far as whether appending various halogens will increase or decrease the average hyperpolarizability.

TABLE X

Experimental and calculated average hyper-polarizabilities of substituted benzene.

X	$\gamma(S=0)/\gamma_o$	$\gamma(S\neq 0)/\gamma_o$	γ(Exp.)/γ_o (Ref. 16)
H	0.0048	0.0028	0.0039
F	0.0058	0.0027	0.0032
Cl	0.0067	0.0033	0.0043
Br	0.0078	0.0045	0.0054

CONCLUSIONS

In this paper we have presented calculations of the polarizabilities of assorted conjugated hydrocarbons and substituted benzene. We have shown that while the inclusion of the differential overlap does quantitatively alter the values of the polarizability and hyperpolarizability for the polyene chains, the results are qualitatively the same in either case. The inclusion of bond alternation on the other hand has a radical effect on the hyperpolarizability, causing the average value to change sign from negative to positive, which is consistent with the positive values measured experimentally. The results for the aromatic rings also show that while the inclusion of differential overlap changes the hyperpolarizability, the changes remain fairly consistent across the series of molecules. When the results of the calculations for the halogen containing compounds are compared to the experimental results, we have shown that to predict the relative values of the hyperpolarizability between molecules containing different halogens it is necessary to include the differential overlap.

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