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Semiempirical Calculations of Molecular Polarizabilities and Hyperpolarizabilities of Polycyclic Aromatic Compounds

YUH-JY LU

Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China

SHYI-LONG LEE*

Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China, and Department of Chemistry, National Chung-Cheng University, Ming-Hsiung, Chia-Yi, Taiwan 62117, Republic of China

Abstract

The correlation of 2D conjugation and the nonlinear properties of a series of polycyclic aromatic compounds were studied by performing semiempirical calculations using the MOPAC package. For linear polyacenes, both linear and nonlinear properties are found to be increased as the number of six-membered rings increases. In general, the polarizabilities, $\langle\alpha\rangle$, and second hyperpolarizabilities, $\langle\gamma\rangle$, are found to correlate very well with total resonance energies. In the case of first hyperpolarizabilities, $\langle\beta\rangle$, symmetry is the dominating factor. © 1992 John Wiley & Sons, Inc.

I. Introduction

Recently, there has been a growing interest in understanding the structure–optical–property relationships in nonlinear optical materials [1–4]. Materials with dramatic optical properties, i.e., high polarizabilities and hyperpolarizabilities of its constituent molecules, are essential to laser technology and photonics [5,6]. Because of the desire for higher-order nonlinearity, say third harmonic generation [7], recent efforts have been focused on organic materials or polymers, in particular, on those equipped with appropriately constituted or substituted conjugation. These systems may be the suitable candidates for developing highly enhanced electronic nonlinear optical polarization responses [8,9]. It is believed that the large electron delocalization is responsible for large values of the nonlinear optical coefficients and this can be met with the π electrons in conjugated molecules and polymers where charge asymmetry can also be adequately introduced to obtain noncentrosymmetric structures. In this paper, we report some results from our recent effort in searching for structure–optical–property relationships in polycyclic aromatic hydrocarbons (PAHs) using semiempirical calculations.

*To whom correspondence should be addressed after August 1, 1992, at the Department of Chemistry, National Chung-Cheng University, Ming-Hsiung, Chia-Yi, Taiwan 62117, Republic of China.

The quantum mechanical calculations of polarizabilities and hyperpolarizabilities have been performed at varying levels of sophistication, including *ab initio* methods [10] and semiempirical methods [11]. In most calculations, the finite-field method is generally used for computing the derivatives in which only a lower order of numerical differentiation is required and the demand of the computer code is lowered. For our purpose, we also adopted the finite-field technique in our calculations. In a recent review, Urban et al. [35] pointed out that accurate *ab initio* calculation of hyperpolarizability is still difficult even for atoms [12] and small molecules [13]. For example, the nonlinear optical properties of the water molecule were recently reported by Bloor [14] using finite-field *ab initio* calculation and it is asserted that the addition of a multiple set of polarization functions on all atoms is important to obtain satisfactory results for the first and second hyperpolarizabilities. Hurst et al. [15] calculated the nonlinear optical properties of linear polyene systems with 1D conjugation in an *ab initio* coupled-perturbed Hartree–Fock scheme in which they ignored the electron–electron correlation effects. Although they concluded that the chain-length dependence of $\langle\alpha\rangle$ and $\langle\gamma\rangle$ in linear polyenes and that the linear polarizability for C_4H_6 is in good agreement with experimental values, they found that the second hyperpolarizabilities are far less than the experimental values even for C_4H_6 and C_6H_8 using the 6-31G plus PD basis set [15]. This situation might be changed rapidly as computational chemistry expands; *ab initio* calculations are, for the time being, a long shot for the practical design of nonlinear optical compounds. On the contrary, semiempirical methods are valuable and have been widely applied in the calculations of optical nonlinearities [16]. In earlier theoretical calculations, semiempirical INDO approximation was used to study linear and nonlinear optical properties of substituted benzenes [17] in order to understand the respective contribution of σ and π electrons to nonlinear susceptibilities. Recently, Ulman et al. also performed semiempirical calculations in their studies of the nonlinear optics in new sulfonyl-containing materials [18] and substituted stilbenes [19]. For linear polyenes, de Melo and Silbey [20] easily achieved the chain-length dependence of $\langle\alpha\rangle$ and $\langle\gamma\rangle$ using a variation-perturbation treatment of a Pariser–Parr–Pople Hamiltonian. We present here our recent effort in the study of correlation of 2D conjugation and the nonlinear properties of a series of polycyclic aromatic compounds by the MOPAC package [21].

In this work we calculate the polarizabilities, hyperpolarizabilities, and second hyperpolarizabilities of a series of polycyclic aromatic compounds using the MNDO semiempirical method [22]. Note that we are not attempting to compute the absolute values for $\langle\alpha\rangle$, $\langle\beta\rangle$, and $\langle\gamma\rangle$. Instead, our goal is focused on the semi-quantitative trend of these optical properties in different PAHs, namely, we are interested in the correlation between optical responses and electron delocalization for a series of polycyclic aromatic compounds. Understanding of the structure–optical–property relationships is a key step to further predict and to search the possible candidate for nonlinear optical materials.

This paper is structured as follows: A brief review of the quantum chemistry approach for nonlinear optics and the essence of our method are given in Sec-

tion II. Computational detail and results are discussed in Section III. Conclusions are drawn in Section IV.

II. Quantum Chemical Approaches

Reliable theoretical predictions of the magnitude of microscopic nonlinearities are believed to be useful in providing guidelines for the synthetic chemists and may orient their work toward previously unexplored species of potential interest. It is recognized that the polarization induced in an atom or molecule by an external field E can be written as

$$P = \alpha \cdot E + \beta \cdots EE + \gamma \cdots EEE + \dots,$$

where the vector quantities P and E are related by the tensor quantities α , β , and γ , which are often referred to as the polarizability, hyperpolarizability, and second hyperpolarizability, respectively.

For quantum mechanical calculations of molecular optical nonlinearities, two conceptually different methods, namely, the sum-over-states (sos) method [23] and the derivative method [24], are generally used. In the sos method, or the excited-state perturbation expansion, the perturbational expansion over molecular states is applied to account for the effects of an externally applied electromagnetic field on the motions of electrons associated with the molecule of interest. The limitation of sos comes from the arbitrary truncation of the summation for the sake of computational efficiency where only contributions from a limited number of excited states are included. In practice, one often utilizes the sum over only low-lying excited states [25]. The derivative method, such as the finite-field method [26] and the analytical method [27], is less restricted compared to the sos method. This method is based on expansion of energy or dipole moment as a function of the applied field in the power series form [28]

$$U(E) = U^0 - \sum \mu^0 E_i - 1/2 \sum \alpha_{ij} E_i E_j - 1/3 \sum \beta_{ijk} E_i E_j E_k - 1/4 \sum \gamma_{ijkl} E_i E_j E_k E_l \quad (1)$$

$$\mu_i(E) = \mu_i^0 + \sum \alpha_{ij} E_j + \sum \beta_{ijk} E_j E_k + \sum \gamma_{ijkl} E_j E_k E_l, \quad (2)$$

where U^0 is the energy in the absence of field and μ^0 is the permanent dipole moment. The coefficient α corresponds to the polarizability of the molecule and is estimated by computing the second derivative of the energy or the first derivative of the dipole moment with respect to the optical field. The first hyperpolarizability, β , and second hyperpolarizability, γ , are also given by the third derivative of the energy (or the second derivative of the dipole moment) and the fourth derivative of the energy (or the third derivative of the dipole moment) with respect to the applied field. The various derivatives are then calculated either numerically as in the finite-field method or analytically as in the analytical method. In the

numerical method, fitting of the computed energies and dipole moments into a polynomial of the applied field E is involved, whereas in the analytical approach one has to solve the generalized coupled-perturbed Hartree–Fock (CPHF) [24, 29] equations. Although the analytical approach was developed for up to the third hyperpolarizabilities, δ , of AH_n and A_2H_n molecules, extension of this method to larger molecules is not feasible [30].

The underlying quantum chemical problem may then be treated via either semiempirical or ab initio schemes. Ab initio sos calculations, which offer a certain advantage for frequency-dependent polarizabilities and provide more direct relationships between polarizability and spectroscopic properties such as HOMO–LUMO band gaps, are subject to systematic errors due to the use of finite orbital basis sets and finite many-body basis sets, i.e., truncation of the configuration interaction expansion and the choice of basis sets [31]. To the best of our knowledge, few of the ab initio sos methods can presently be applied to the larger organic molecules of interest. Ab initio finite-field calculations were reported to calculate the linear and nonlinear optical properties for simple molecules, such as F_2 , N_2 , and H_2O [14, 32, 33]. Although high accuracy of dipole polarizabilities can be achieved [34], there is not, however, a clear-cut rule in choosing the basis set for the first and second hyperpolarizabilities, which are known to be very sensitive to the size and nature of the basis sets [35]. In fact, only very few ab initio calculations that were reported to take into account electron–electron correlation have been reported for the dipole polarizability [36], or even for larger correlation effects for the hyperpolarizability [37]. In contrast to time-consuming ab initio calculations, semiempirical calculations, even the simple CNDO version, for the linear and nonlinear polarizabilities, were reported to give estimates that are in satisfactory agreement with available experimental results [38–41]. For example, the CNDO–sos calculations have been successfully performed by Morley et al. [42] to calculate the second-order hyperpolarizability of benzene, aniline, nitrobenzene, and *p*-nitroaniline. Dewar and Stewart carried out MNDO–FF calculations to test a new additivity procedure in computing the polarizabilities for a number of molecules [43]. However, semiempirical sos calculations require information about many states of the system, such as the spectra and transition dipole derived from the configuration interaction (CI) [18] and the number of excited states needed in the summations [44]. Therefore, to avoid the difficulties connected with perturbation expansion, the finite-field method within the semiempirical framework implemented in the MOPAC package is adopted in our calculations.

The finite-field approach implemented in the MOPAC semiempirical program is applied to calculate the polarizabilities and hyperpolarizabilities in our present work. The current version has been tested by Stewart [21]. The main principle of the methods is to diagonalize a molecular Hamiltonian that takes into account the static-field dipolar perturbation. The Hartree–Fock equation is given as

$$H = H_0 + r \cdot E,$$

where H_0 is the unperturbed one-electron Hartree–Fock Hamiltonian; r , the one-electron dipolar operator; and E , the static perturbing field. By the iterative diag-

onalization procedure [45], the polarizabilities, α , first hyperpolarizabilities, β , and second hyperpolarizabilities, γ , may be, in principle, obtained by computing the gradient of $\mu(E)$ with respect to E in the limit of zero field, as allowed by the Hellman–Feynman theorem [46]:

$$\begin{aligned}\alpha_{ij} &= \partial\mu_i/\partial E_j|_{E=0}, \\ \beta_{ijk} &= (1/2) \partial^2\mu_i/\partial E_j \partial E_k|_{E=0}, \\ \gamma_{ijkl} &= (1/3!) \partial^3\mu_i/\partial E_j \partial E_k \partial E_l|_{E=0}\end{aligned}$$

In practice, this is done numerically by computing

$$\begin{aligned}\alpha_{ii} &= [\mu_i(E, 0, 0) - \mu_i(-E, 0, 0)]/2E, \\ \beta_{iii} &= [\mu_i(2E, 0, 0) + \mu_i(-2E, 0, 0) - 2\mu_i(0, 0, 0)]/8E^2, \\ \gamma_{iii} &= \{\mu_i(3E, 0, 0) - \mu_i(-3E, 0, 0) - 3[\mu_i(E, 0, 0) - \mu_i(-E, 0, 0)]\}/48E^3,\end{aligned}$$

in particular, the following five terms:

$$\begin{aligned}\beta_{zxx} &= [\mu_x(2E, 0, 0) + \mu_x(-2E, 0, 0) - 2\mu_x(0, 0, 0)]/8E^2 \\ \beta_{zyy} &= [\mu_y(0, 2E, 0) + \mu_y(0, -2E, 0) - 2\mu_y(0, 0, 0)]/8E^2 \\ \gamma_{xxy} &= \{\mu_y(E, E, 0) - \mu_y(E, -E, 0) + \mu_y(-E, E, 0) - \mu_y(-E, -E, 0) \\ &\quad - 2[\mu_y(0, E, 0) - \mu_y(0, -E, 0)]\}/12E^3 \\ \gamma_{zzy} &= \{\mu_y(0, E, E) - \mu_y(0, E, -E) + \mu_y(0, E, -E) - \mu_y(0, -E, -E) \\ &\quad - 2[\mu_y(0, E, 0) - \mu_y(0, -E, 0)]\}/12E^3 \\ \gamma_{zzx} &= \{\mu_x(E, 0, E) - \mu_x(-E, 0, E) + \mu_x(E, 0, -E) - \mu_x(-E, 0, -E) \\ &\quad - 2[\mu_x(E, 0, 0) - \mu_x(-E, 0, 0)]\}/12E^3.\end{aligned}$$

The finite-field method provides a straightforward computational technique that is applicable to almost any quantum chemical formalism. However, the method does require care to avoid numerical differentiating errors and is less efficient than are analytical methods where they are available [31]. For our purpose, the finite-field approximation seems to be a viable method for all PAHs of interest.

III. Computational Details and Results

The calculations reported here are carried out using the semiempirical MNDO Hamiltonian in the MOPAC package [21]. The geometries of polycyclic aromatic compounds are optimized by the ALCHEMY II program (Tripos Associates, Inc., St. Louis, MO) [47], which performs a conjugated gradient minimization on a force-field equation that is dependent on positions of atoms in a selected molecule. Because the finite-field method implemented in MOPAC is a numerical one, care must be exercised in selecting the range of field of strengths to avoid numerical instability. We adopt here the field strength of 0.001 au for an error in the energy that will result in a similar error as small as possible in the calculation of

optical properties [48]. For the comparison among a series of polycyclic aromatic compounds, we record here the mean values of polarizabilities, $\langle\alpha\rangle$, first hyperpolarizabilities, $\langle\beta\rangle$, and second hyperpolarizabilities, $\langle\gamma\rangle$, of polycyclic aromatic compounds that resulted from the MNDO calculations, and the equations for computing the respective expectation values are given by

$$\langle\alpha\rangle = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\langle\beta\rangle = 3/5\{\beta \cdot \mu\}/\|\mu\|$$

$$\langle\gamma\rangle = 1/5\{\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2[\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}]\},$$

where $\beta \cdot \mu = \beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z$ and $\beta_i = \{\beta_{iii} + \beta_{ijj} + \beta_{ikk}\}$.

In Table I we present the polarizabilities, $\langle\alpha\rangle$, first hyperpolarizabilities, $\langle\beta\rangle$, and second hyperpolarizabilities, $\langle\gamma\rangle$, of benzene calculated using semiempirical schemes including PM3 [49], AM1 [50], and MNDO, which are implemented as alternatives in the MOPAC package. Our computed results for benzene, which should have zero dipole moment (μ) and first hyperpolarizabilities (β) due to the possession of a center of symmetry, are nearly but not exactly zero, which is caused by numerical inaccuracies. It should be noted that the results obtained from the MNDO calculation are much better than the results from the other two schemes. To further understand the structure-optical-property relationships, a series of polycyclic aromatic compounds were studied by computing their optical responses using the MNDO semiempirical method. Results from these calculations are given in Table II (see also Fig. 1). It can be easily seen from Table II that only phenanthrene, 1,2-benzanthracene, and 3,4-benzanthracene have larger $\langle\beta\rangle$ values; the mean first hyperpolarizabilities of other polycyclic aromatic compounds are nearly zero. These results suggested that the large nonvanishing $\langle\beta\rangle$ values of some polycyclic aromatic molecules are caused mainly by the noncentrosym-

TABLE I. Polarizabilities ($\times 10^{-24}$ cm³), α , first hyperpolarizabilities ($\times 10^{-33}$ ESU), β , and second hyperpolarizabilities ($\times 10^{-36}$ ESU), γ , of benzene.^a

	Method			Obsd ^b
	PM3	AM1	MNDO	
$\langle\alpha\rangle$	6.756	7.22	10.18	10.33
α_{zz}	1.42	1.33	4.173	6.65
α_{yy}	9.42	10.16	13.19	12.27
α_{xx}	9.42	10.16	13.19	12.27
$\langle\beta\rangle$	-0.004	-0.007	-0.001	
$\langle\gamma\rangle$	0.773	0.747	0.711	12.4 \pm 0.3 ^c 9.36 \pm 1.40 ^d

^a The z-axis direction is along the principal axis. The quantities reported here are mean values of α , β , and γ .

^b Calculated from refractive indices [51].

^c [54].

^d [55].

TABLE II. The molecular polarizabilities, first hyperpolarizabilities, and second hyperpolarizabilities of polycyclic aromatic compounds calculated by the MNDO method (the unit of the values are same as in Table I).

Compound ^a	Polarizability		First hyperpolarizability	Second hyperpolarizability
	$\langle\alpha\rangle$ (ANG ³) _{component}		$\langle\beta\rangle$ ($\times 10^{-33}$ ESU)	$\langle\gamma\rangle$ ($\times 10^{-36}$ ESU)
Naphthalene	17.65	6.443	0.001	6.073
		20.153		
		26.699		
Anthracene	26.84	8.720	0.040	20.433
		27.690		
		44.130		
Phenanthrene	25.65	8.688	-202.688	17.807
		28.534		
		39.739		
Naphthacene	37.21	11.001	0.347	53.689
		35.775		
		64.856		
1,2-Benzanthracene	35.08	10.956	-268.866	44.359
		36.209		
		58.065		
Chrysene	34.27	10.938	-0.353	39.511
		35.691		
		56.186		
Triphenylene	33.26	10.913	0.627	31.117
		44.436		
		44.438		
3,4-Benzanthracene	33.51	13.048	-219.060	31.711
		39.471		
		48.039		
Pyrene	29.83	9.561	-0.435	19.062
		33.165		
		46.763		
Pentacene	48.64	13.283	0.905	116.834
		44.317		
		88.343		
Hexacene	60.92	15.565	0.049	219.812
		53.194		
		114.025		
Heptacene	73.85	17.848	-1.288	372.350
		62.306		
		141.405		
Octacene	87.24	20.131	-2.027	576.064
		71.574		
		170.036		

^aThe structures of polycyclic aromatic hydrocarbons are given in Figure 1.

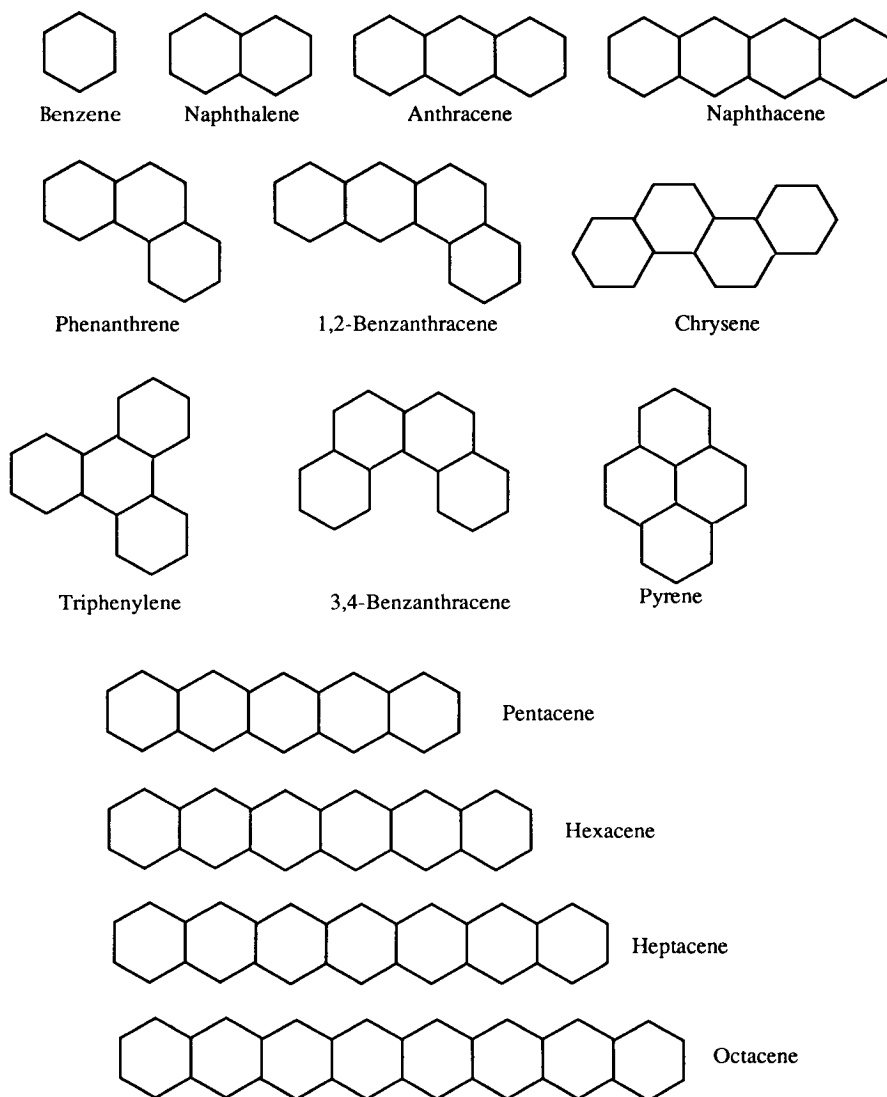


Figure 1. Structures of polycyclic aromatic hydrocarbons selected in our calculations.

metric structure and the delocalization of π electrons. Because heptacene and octacene are very unstable hydrocarbons that were never reported to be obtained either in the laboratory or in nature [52], the $\langle\beta\rangle$ values calculated here are only for reference.

From the view of chain topology, our computational results show some interesting features: For polyacenes with 3 six-cycles, $\langle\alpha\rangle$ and $\langle\gamma\rangle$ of anthracene are

larger than those of phenanthrene. For the 4 six-cycle PAH family, we also found that $\langle\alpha\rangle$ and $\langle\gamma\rangle$ of naphthacene are the largest among the family members. Besides, the *trans*-isomer, chrysene, has relatively larger $\langle\alpha\rangle$ and $\langle\gamma\rangle$ values than those of the *cis*-isomer, 3,4-benzanthracene. The values of $\langle\alpha\rangle$ and $\langle\gamma\rangle$ for the compact-shaped pyrene are the smallest in this PAH family and even smaller in $\langle\gamma\rangle$ than those of anthracenes. These observations are not easily rationalized according to our current understanding of stabilities of PAHs based on the Kekule structure count [52]. In addition, our computed results are found to be in better agreement with available experimental values than are the results using the MNDO scheme plus an corrected values with atomic terms [42]. Also, including the CI procedures in our calculations was found to yield poor results for benzene as compared to the reliable observed values, let alone larger molecules in the series of polycyclic aromatic compounds, which would be expensive in terms of computing time and core storage. It is argued that an arbitrary CI wave function does not satisfy the Hellmann-Feynman theorem [45].

For correlating 2D conjugation with $\langle\alpha\rangle$, $\langle\beta\rangle$, and $\langle\gamma\rangle$, the mean values of $\langle\alpha\rangle$, $\langle\beta\rangle$, and $\langle\gamma\rangle$ are plotted in Figure 2 versus the number of six-membered rings, N , in the linear polyacenes. The N dependencies of $\langle\alpha\rangle$ in the present results show that $\langle\alpha\rangle$ increases linearly with the number of six-membered rings. Similar results were also revealed for the 1D conjugated system by Hurst et al. [15] as they increased the number of ethylene units in the linear polyenes. The second hyperpolarizabilities, $\langle\gamma\rangle$, of linear polyacenes were found to increase exponentially as N increases. Therefore, as the six-cycle number in the linear polyacenes increases, the mean value of $\langle\alpha\rangle$ and $\langle\gamma\rangle$ becomes larger, reflecting the stronger response of the delocalized π electrons to electric fields. The first hyperpolarizabilities, $\langle\beta\rangle$, of linear polyacenes are very small due to the existence of inversion symmetry.

The effect of π -delocalization on the linear and nonlinear responses in the polycyclic aromatics are further exploited by plotting $\log \langle\alpha\rangle$, $\log(-\langle\beta\rangle^*)$, and $\log \langle\gamma\rangle$ as functions of total resonance energy [53] in Figure 3. $\langle\alpha\rangle$ and $\langle\gamma\rangle$ are found to correlate very well with total resonance energy. In the case of first hyperpolarizabilities, symmetry is the dominating factor. Only those PAHs without inversion centers have large $\langle\beta\rangle$ values.

IV. Conclusions

Semiempirical methods have been found to be extremely useful in predicting the trend of the linear and nonlinear optical properties for large molecular systems, such as polycyclic aromatic compounds. In our work, the MNDO-FF calculation was tested successfully in computing $\langle\alpha\rangle$ for benzene, which is in satisfactory agreement with experimental values, and $\langle\beta\rangle$ of benzene is zero by symmetry. However, the computing values for $\langle\gamma\rangle$ of benzene are in marked discrepancy with the data determined by various experimental methods [54, 55]. The same scheme was then applied to study the structure-optical-property relationship in polycyclic aromatic hydrocarbons (PAHs).

From the above discussion, it is concluded that the 2D conjugations in PAHs are able to yield highly enhanced electronic linear and nonlinear optical polariza-

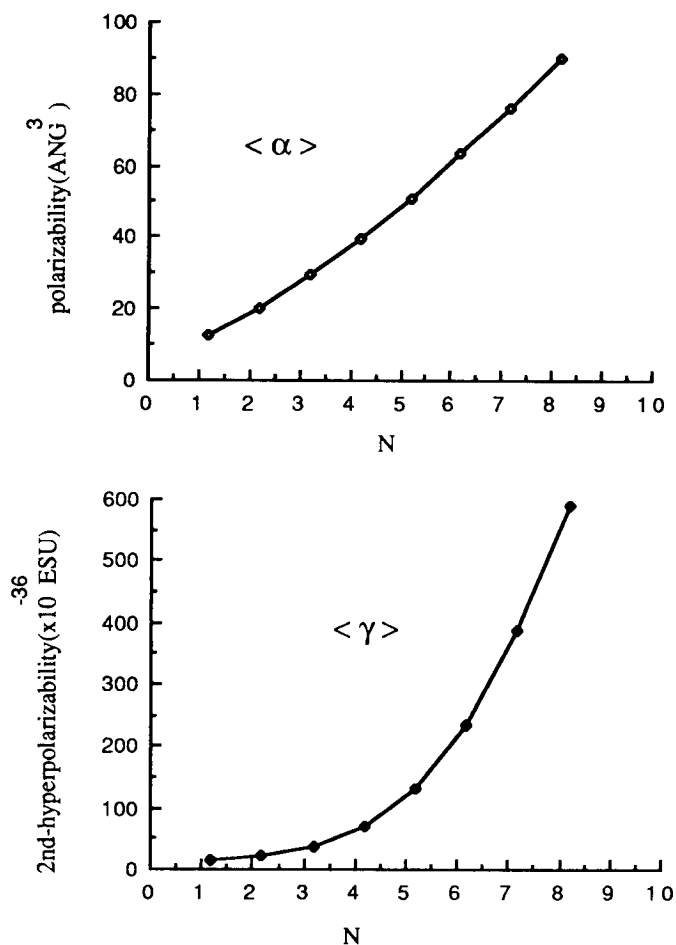


Figure 2. Plot of the mean quantities $\langle \alpha \rangle$ and $\langle \gamma \rangle$ vs. N . N is the number of the six-membered rings in the linear polyacenes.

tion responses. For linear polyacenes, we find that $\langle \alpha \rangle$ and $\langle \gamma \rangle$ are dependent on the number of six-membered rings. A similar trend, i.e., chain-length dependency, was revealed before in linear polyenes with 1D conjugation [15]. Only polycyclic aromatic hydrocarbons with noncentrosymmetric structure are found to have larger values of the mean hyperpolarizabilities.

Acknowledgment

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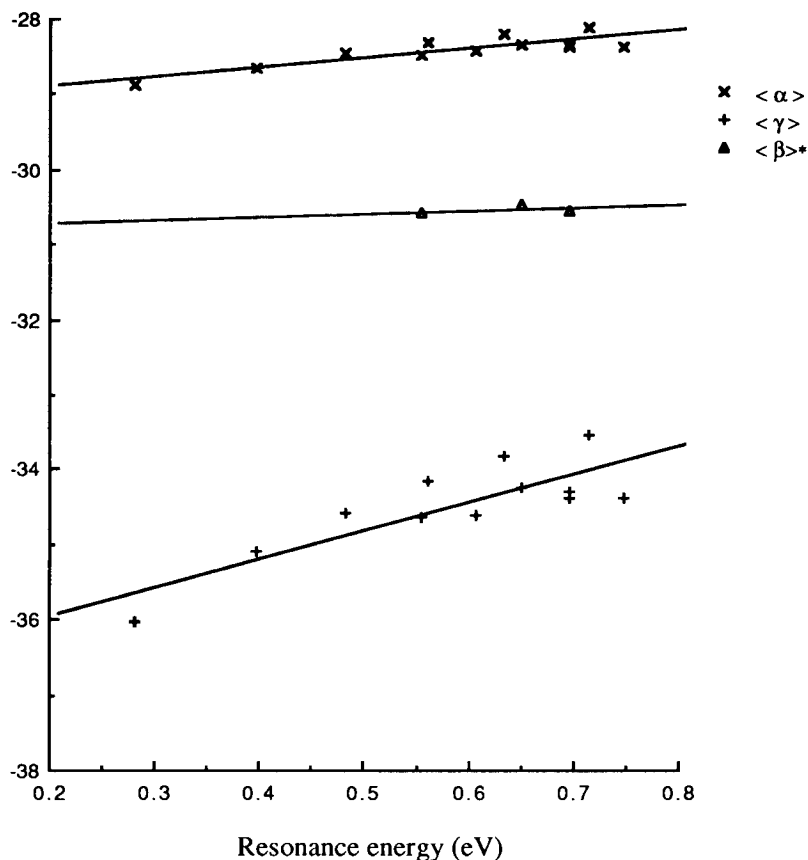


Figure 3. Plot of $\log \langle\alpha\rangle$, $\log(-\langle\beta^*\rangle)$, and $\log \langle\gamma\rangle$ vs. RE, the total resonance energies [53] of the polycyclic aromatic compounds studied. $\langle\beta^*\rangle$ refer to noncentrosymmetric molecules. The unit of $\langle\alpha\rangle$ is set at m^3 .

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