濟大論文集(自然), 37, 125-132, 1993
Cheju Univ. Jour. (Natural Sci.),
37, 125-132, 1993

Finite-Field Calculations for the First Hyperpolarizabilities of Several Substituted Aromatic Compounds

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방향족 치환체의 일차 초편극도에 대한 유한장 계산

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Summary

The first hyperpolarizabilities (β) of several mono- and multi-substituted benzene derivatives and aromatic compounds were calculated by the Finite-Field method modified in MOPAC molecular orbital program. The AM1, MNDO, and PM3 semi-empirical hamiltonian approximations were used for all the calculations. The available experimental β values were also given, but the comparison was not made satisfactorily due to some experimental factors presented.

Introduction

The field of nonlinear optics did not develop as a well-defined scientific discipline until the 1960s, because the striking phenomena of nonlinear optics can readily be observed only at high electric field levels. With the advent of lasers, much higher electric field strengths became available. As soon as the first powerful ruby laser was developed, second harmonic generation (SHG) was observed in the ultraviolet at 3470 Å when the ruby laser with a 6940 Å wavelength traverses a quartz crystal [Franken et al., 1961]. This nonlinear optical phenomenon arises from interaction of the electric field of the laser beam with the first hyperpolarizability $\beta(-2\omega;\omega,\omega)$, where ω is the incident frequency and 2ω is the doubled-outcoming frequency of the nonlinear material. There have been discovered numerous nonlinear optical phenomena such as optical parametric up and down conversion, stimulated Raman and Brillouin scattering, self-focusing of light beams, and self-induced transparency, etc., and the details can be found elsewhere [Shen,

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1984; Prasad and Williams, 1991]. They have greatly induced a strong interest about nonlinear optical responses of materials theoretically and experimentally.

It has been known that, for conjugated molecules, the delocalization of the π electrons produces large nonlinear optical responses. However, most often, the contribution of the delocalized electrons to the first hyperpolarizabilities β vanishes in centrosymmetric nonsubstituted molecules. The β of conjugated molecules thus arises from the distortion of the π electron distribution caused by one or more electron donation and withdrawing substituent groups, thereby removing the center of symmetry [Chemla and Zyss, 1987]. In general, β increases with increasing donor and acceptor strength which is related to the ionization potentials of the filled donor and empty acceptor orbitals or the coulomb energies of independent electron theory [Ballhausen and Gray, 1964], and with increasing separation so long as there is strong electronic coupling through the conjugated bridge [Marder et al., 1991]. The close relationship which exists between the donor-acceptor character of a benzene substituent and β can be found in detail elsewhere [Levine, 1975; Oudar and Chemla, 1975; Chemla et al., 1975].

The purpose of this work was to calculate the first hyperpolarizabilities (β) of several substituted aromatic compounds in MNDO, AMI and PM3 semi-empirical hamiltonian approximations using the finite-field method modified in MOPAC molecular orbital program. The β values reported here are the calculated ones with a static electric field so that there are problems to directly compare with the experimental results of β due to their frequency-dependent nature, solvent effect, and other experimental factors.

Computational Background

The polarization, P, induced in a medium by an external electric field E is given by

$$P = P^{0} + \chi^{(1)} \cdot E + \chi^{(2)} \cdot E \cdot E + \chi^{(3)} \cdot E \cdot E \cdot E + \cdots \quad (1)$$

where $\chi^{(n)}$ are the n-th order susceptibility tensors of the bulk medium. Nonlinear optical properties of substances arise from nonzero values of terms higher than $\chi^{(1)}$. These bulk susceptibilities can be expressed in terms of the molecular induced dipole. The dipole moment of a system interacting with an electric field can be written as

$$\mu_i = \mu_i^0 + a_{ij}E_j + \frac{1}{2!}\beta_{ijk}E_jE_k + \frac{1}{3!}\gamma_{ijkl}E_jE_kE_l + \cdots \quad (2)$$

where μ_i^0 is the permanent dipole moment of a substance and a_{ij}, β_{ijk}, and γ_{ijkl} are tensor elements of the polarizability, first hyperpolarizability and second hyperpolarizability, respectively. In the above expression, i, j, k and l are the Cartesian coordinates, and the Einstein convention of summation over indices is assumed. From the finite-field procedure, after truncating the higher terms than γ_{ijkl}, the mean values of first hyperpolarizability are given as the component along the dipole moment direction by [Buckingham and Orr, 1967]

$$\langle\beta\rangle = \frac{3}{5}(\beta_{ixx} + \beta_{iyy} + \beta_{izz}) \quad (3)$$

where i is the major axis along the dipole moment direction. That is, the first hyperpolarizability is a vector quantity as same to the dipole moment.

When a molecule with a center of symmetry

such as benzene is considered, alternating the sign of the applied electric field in the i coordinate direction causes the elimination of odd terms in the dipole moment expression in equation (2), so that the energy associated with it can be written

$$W = W^0 - (1/2)\alpha E^2 - (1/24)\gamma E^4 \cdots\cdots \quad (4)$$

where W^0 is the energy of the molecule in the absence of an electric field. The inclusion of only even terms in equation (2) results in a symmetric potential, and W(E) and W(-E) are equal. If an odd-order term such as one with β in equation (2) had been included, the potential energy would be different for the +i and -i direction, but this is inconsistent with the symmetry of the molecule. In molecules with a inversion symmetry, all the tensor elements β_{ijk} are equal to zero and no first hyperpolarizabilities. On the other hand, a molecule without a center of symmetry will exhibit an asymmetric potential in the +i and -i directions so that the energy is

$$W = W^0 - (1/2)\alpha E^2 - (1/6)\beta E^3 - (1/24)\gamma E^4 \cdots\cdots (5)$$

and W(E) is obviously different for E than for -E. In order to observe the first hyperpolarizabilities, therefore, this symmetry nature should be distorted and this is mostly done by introducing the electron-donating and withdrawing substituents.

For the calculation of frist hyperpolarizabilities in finite-field method, the applied electric field strength should be chosen properly. It must be small enough to allow all terms after the γ in equation (2) and (5) to be truncated as well as not to change the electronic configuration of the molecule, but large enough to provide the nonlinear optical effects with sufficient numerical accuracy by dipole or energy differences. Usually high field strengths tend to retard convergence in the self-consistent field step. Fig. 1 and 2 show the variation of the calculated values of first hyperpolarizabilities for nitrobenzene and phenol, respectively, with field strengths from 0.0001 to 1 a.u. At the field strength of range about 0.001 a.u. in both cases, the energy based and the dipole based β can be seen to give the same results, so this field value (0.001 a.u.) is used for the calculations done in this work. The dramatic changes of β values at higher field strengths (above 0.01 a.u.) can be

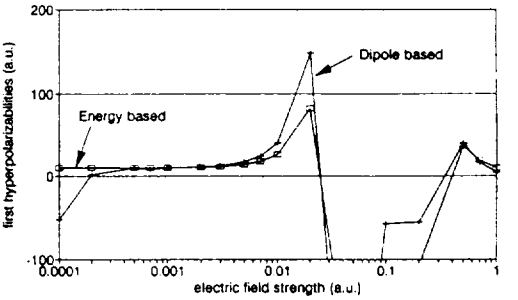

Fig. 1. Variation of the first hyperpolarizabilities with electric field strength for nitrobenzene from the dipole-based and energy-based expressions. The values were obtained using PM3 method.

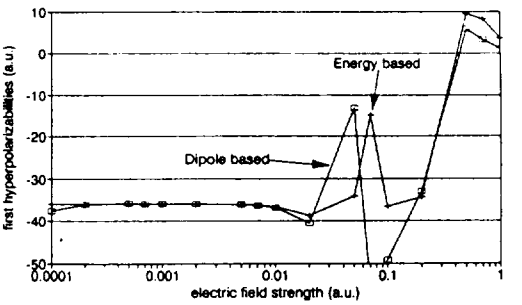

Fig. 2. Variation of the first hyperpolarizabilities with electric field strength for phenol from the dipole-based and energy-based expressions. The values were obtained using PM3 approximation.

attributed to the significance of higher order terms that were neglected in the finite-field expansion and the electronic configuration changes of molecules as well. On the other hand, erratic deviations of β values below 0.001 a.u. are due to the onset of numerical errors in the differentiation.

The unit of first hyperpolarizabilities reported in this paper is the electrostatic unit (esu), and 1 esu is equivalent to $3.7037\times10^{-21}C^3m^3J^{-2}$ in SI unit or 1.1551×10^{32} a.u..

Table 1. First hyperpolarizabilities of several substituted benzene derivatives (in unit of 10^{-30} esu)

compounds	MNDO	AM1	PM3	Experimental[a]
fluorobenzene	-0.649	-0.703	-0.338	0.44, 0.53, -0.70, 1.06
chlorobenzene	-0.757	-0.979	-2.408	0.22, 0.28, -0.33
bromobenzene	-0.612	-0.919	-0.631	0.04, 0.02, -0.20
iodobenzene	-1.379	-0.995	-1.497	0.46, -0.28, -0.70
phenol	-0.397	-0.509	-0.312	0.36, -0.17
nitrobenzene	-1.295	0.016	0.090	1.1, 2.0, 2.2, 2.3
benzonitrile	0.427	0.407	0.307	0.48
aniline	-0.188	0.832	0.493	0.79, 0.89, 1.23, 1.48, 1.1
methoxybenzene	-0.083	-0.010	0.095	
benzoic acid	-0.084	0.979	0.844	
biphenyl	0	0	0	
toluene	-0.253	0.501	0.465	0.18
ethylbenzene	-0.183	0.575	0.313	
n-propylbenzene	-0.234	0.692	0.524	
N, N-dimethylaniline	-0.255	2.198	1.348	1.51, 1.75, 1.27
o-xylene	-0.381	0.772	0.772	
m-xylene	-0.242	0.466	0.437	
p-xylene	-0.001	0.005	0.019	
resorcinol	-0.356	-0.454	-0.308	0.2
m-aminophenol	0.507	1.099	1.485	1.2
p-tolunitrile	1.046	1.527	1.373	2.86
p-aminobenzonitrile	3.434	4.509	5.720	13.4
p-methoxybenzonitrile	3.017	2.841	2.968	4.8
p-toluidine	-0.067	0.444	-0.146	
o-nitroaniline	-1.818	0.780	0.076	6.4, 10.2
m-nitroaniline	-0.148	1.584	1.992	4.2, 6.0
p-nitroaniline	1.263	5.425	6.295	6.4, 9.6, 21.1, 34.5
p-phenylenediamine	-0.943	-0.918	-1.507	
p-N, N-dimethylaminobenzonitrile	0.913	6.086	7.187	14.3
2, 4-dinitroaniline	0.260	2.654	3.268	21.0
3, 5-dinitroaniline	1.380	2.519	3.777	
2, 4, 6-trinitroaniline	2.031	2.490	2.509	

a) The experimental results are based on dc electric-field-induced second harmonic generation (EFISH) in solution [Nicoud and Twieg, 1987].

Results and Discussion

In order to evaluate the computation of first hyperpolarizabilities (β), a series of substituted benzenes were chosen and their calculated semi-emporical β results were collected in Table 1. In each of these calculations the optimized structures for the selected molecules were empolyed by each MNDO, AM1 and PM3 approximation. The different β values between these semi-empirical methods are due to the different optimized geometries from each procedure. Since the geometries optimized from MNDO are not quite reliable due to, in many cases, the poor computed results for the heats of formation by overestimated repulsions between atoms in a molecule (Dewar et al., 1985; Stewart, 1989), the β values from AM1 and PM3 optimized geometries are more preferable. When a geometry is optimized in AM1 or PM3 hamiltonian and taken to the β calculation in MNDO, it gives better β result than the one which is optimized in MNDO (Kurtz, 1990). The available experimental β values were also given and compared with the calculated values. This comparison does not seem to be very exciting, since the large variations are found in experimental values. The experimental β results are based on dc electric-field-induced second harmonic generation (EFISH) measurements, in which solvent effects are also involved (Levine et al., 1978;Chemla and Zyss, 1987). In addition, it must be underlined that the experimental results are frequency dependent properties and the calculated values are static field properties. Also, it should be noted that a factor of 2 is involved in macroscopic experimental results. This is due to a difference in definition used by experimentalists who follow the Bloembergen model (Bloembergen, 1965) in a perturbation expansion of the energy, in which the numerical factor in front of the second-order susceptibilily χ_{ijk} term is $\frac{1}{3}$, and by theoreticians who adopt 1/6 as the numerical factor in front of the first hyperpolarizability β_{ijk} term based on a Taylor series expansion in equation (5).

It has been known that the sign of the nonlinearity is directly related to the nature of the substituent group such that β is negative for withdrawing groups that induce a flow of electrons from the benzene ring toward the substituent group and it is positive for donor groups that produce an opposite charge flow (Chemla and Zyss, 1987). However, as can be found in Table 1, the semi-empirical results for β did not always follow this general trend, possibly due to different dipole orientations induced by the substituents in each semi-empirical method used. Most often, only the magnitudes of β are taken to be considered for the nonlinearity calculations, where its magnitude is mostly governed by the strength of the substituent and by the length of the molecule.

The first hyperpolarizability values for xylenes give a good example of the β behavior with the distortion of inversion symmetry, depending on the relative orientation of the substituents. As can be found in Table 1, for instance, the β values of o-xylene (0.772×10^{-30} esu in PM3, 0.772×10^{-30} esu in AM1) are greater than those of m-xylene (0.437×10^{-30} esu in PM3, 0.466×10^{-30} esu in AM1) which is even much larger than those of p-xylene (0.019×10^{-30}esu in PM3, 0.005×10^{-30} esu in AM1). It is because the symmetry is being broken as the methyl groups are oriented to ortho position from para position. However, the β values of nitroanilines show opposite behavior due to two substituents which allow charge transfer by electron donating amino group and electron

withdrawing nitro group on the same conjugated beenzene ring. This charge transfer is the most effective when two substituents are at opposite position, so that it is clear the β values of p-nitroaniline are much larger than those of o-nitroaniline as given in Table 1.

The β calculations for other substituted aromatic compounds having extended conjugation were also carried out and their results are given in Table 2. Due to lack of experimental data and even large variations in the available values, the comparison can not be made at this point. Again, it can be noticed among the semi-empirical results that the MNDO results are much smaller than the AM1 and PM3 β values because of its poor geometry optimization. The β values from AM1 and PM3 agree very well, especially for the molecules having larger sizes.

Table 2. First hyperpolarizabilities of substituted aromatics with extended conjugation (in unit of 10^{-30} esu)

compounds	MNDO	AM1	PM3	Experimental[a]
trans-stilbene	-0.004	-0.107	0	
cis-stilbene	-0.042	-0.031	0.055	
4-amino-trans-stilbene	-0.008	7.882	5.436	12±7
4-amino-cis-stilbene	-0.167	2.924	1.107	
4-amino-4'-cyano-trans-stilbene	4.565	24.606	22.786	
4-N, N-dimethylamino-4'-cyano-trans-stilbene	1.503	25.507	26.692	115±23
4-N, N-dimethylamino-4'-nitro-trans-stilbene	-0.255	36.894	37.334	450±90, 39, 55[b]
styrene	-0.015	0.018	-0.006	
p-aminostyrene	-0.025	2.651	1.854	
1-(p-dimethylaminophenyl)-4-(p-cyanophenyl)-buta-1, 3-diene	2.503	33.495	35.371	265
1-(p-dimethylaminophenyl)-4-(p-nitrophenyl)-buta-1, 3-diene	1.126	50.091	50.485	

a) The experimental results are based on dc electric-field-induced second harmonic generation (EFISH) in solution [Nicoud and Twieg, 1987].

b) Marder et al., 1991.

Conclusion

So far, the calculated first hyperpolarizabilities of several organic compounds were obtained and the available experimental β values were also collected. These were not compared satisfactorily due to frequency dependence nature, solvent effects, different coefficients adoption, and other factors presented in experimental system. There- fore, the primary purpose of this work is only on the calculation and collection of β values for many interesting molecules, and the comparison between the semi-empirical methods with geometric aspects. Most often, the AM1 and PM3 approximations gave better results than from MNDO due to its inferiority on the structure optimization. Also, the molecules with strong charge transfer characters, asymmetric arrangement and effective delocalization of π

electrons have shown quite large nonlinear optical responses. In future, it is hoped that the computational method should include the frequency dependency and other factors so that the direct comparison with experimental data could be possible.

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〈국문초록〉

방향족 치환체의 일차 초편극도에 대한 유한장 계산

MOPAC 프로그램을 이용하여 치환기를 가진 벤젠 유도체와 방향족 화합물들의 일차 초편극도(β)를 유한장 방법으로 계산하였다. 이 계산을 위해서 AM1, MNDO, PM3 세가지 반경험적 hamiltonian 근사법이 사용되었다. 일차 초편극도의 vector적 성질에 기인하여, 전하 전이를 유도하는 전자주기, 전자받기 치환기를 가지므로서 구조적 대칭성을 깨뜨리는 분자들이 큰 β값을 나타냈다. 한편 실제실험에 포함되는 여러 요인들의 영향으로 인하여, 알려진 실험값과 계산된 이론값 간의 직접적인 비교는 할 수가 없었다.