

Rotational Conformation Dependence of Second Hyperpolarizabilities; 1, 3-Butadiene, 3-Hexyn-1, 5-diene, and Dimers of Pyrrole, Cyclopentadiene, and Furan

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1, 3-Butadiene, 3-Hexyn-1, 5-diene 분자와 Pyrrole, Cyclopentadiene, Furan 이합체에 대한 이차 초편극도와 회전구조간의 관계

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Summary

The second hyperpolarizabilities of 1,3-butadiene, 3-hexyn-1,5-diene, dipyrrole, dicyclopentadiene, and difuran with respect to their conformational changes were calculated using a finite-field method in AM1, MNDO, and PM3 approximations. The maximum values are at their cis and trans structures, and the minimum values are at the conformations with about 90°-95° dihedral angle changes. The relative heats of formation of those molecules were also calculated and compared for the conformational dependence. The MOPAC program was used for all the computations performed in this paper.

Introduction

Nonlinear optical properties, especially for the second hyperpolarizabilities (χ), of organic molecules have been the hot subjects to the theoretical chemists as well as the experimentalists, and the studies have been recently stimulated by the tremendous development of

computational capabilities in scientific environment. Here the nonlinear optical property is meant by the nonlinear behavior of the polarization of a molecule when it is exposed to a high external electric field strength. The applications of those properties range from optical computing and optical communications by the fiber optics up to the laser industry (Shen, 1984). From the search for good nonlinear optical

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materials, it has been reported theoretically and experimentally that the organic molecules and polymers having high π electron delocalization show very large second hyperpolarizabilities [Chemla and Zyss, 1987; Prasad and Williams, 1991].

In this paper, it is intended to show how the second hyperpolarizabilities of molecules depend on the rotational conformation changes. Also the heats of formation of the molecules with respect to their conformational changes were relatively obtained and related with the second hyperpolarizability values. The molecules studied here are 1,3-butadiene, 3-hexyn-1,5-diene, dipyrrole, dicyclopentadiene, and difuran. The semi-empirical hamiltonian approximations used for this calculation are AM1 [Dewar et al., 1985], MNDO [Dewar and Thiel, 1977], and PM3 [Stewart, 1989]. The MOPAC program (version 5.0) was used for all the computations performed in this work, which has been modified with Finite-Field method for the nonlinear optical property calculations.

Computational Methods

The molecular polarizability and hyperpolarizability tensors relate the dipole moment induced in an isolated molecule to the applied electric fields as a power series :

$$\mu'_i = \alpha_{ij}E_j + (1/2)\beta_{ijk}E_jE_k + (1/6)\gamma_{ijkl}E_jE_kE_l + \dots$$

where μ'_i is the component of the induced dipole moment in the cartesian coordinate direction i , α_{ij} is the linear polarizability tensor, β_{ijk} and γ_{ijkl} are the first and second hyperpolarizability tensors, respectively, and E_j is a component of the applied electric field acting on the molecule. And the energy W of the molecule can be related to its dipole moment μ in an electric field E using the related $W = -\int \mu dE$ such as

$$W = W^0 - \mu_i^0 E_i - (1/2)\alpha_{ij}E_iE_j - (1/6)\beta_{ijk}E_iE_jE_k - (1/24)\gamma_{ijkl}E_iE_jE_kE_l \dots$$

where W^0 is the energy of the molecule in the absence of the external electric field, and μ_i^0 is a component of the permanent molecular dipole moment. The α_{ij} , β_{ijk} and γ_{ijkl} are all polar tensors fully symmetric in the permutation of cartesian indices, and allow the induced dipole moment to be in a direction other than that of the applied electric field. The coefficients are obtained by finite differencing successively at static field ($E_i=0$) such as

$$\begin{aligned} \mu_i^0 &= - \left(\frac{\partial W}{\partial E_i} \right) \\ \alpha_{ij} &= - \left(\frac{\partial^2 W}{\partial E_i \partial E_j} \right) \\ \beta_{ijk} &= - \left(\frac{\partial^3 W}{\partial E_i \partial E_j \partial E_k} \right) \\ \gamma_{ijkl} &= - \left(\frac{\partial^4 W}{\partial E_i \partial E_j \partial E_k \partial E_l} \right) \end{aligned}$$

In the finite-field method, the perturbed hamiltonian for the molecule can be written as

$$H' = H - \sum_i E r_i$$

where E is a finite electric field, and r_i is the position operator for the i -th electron. From the variational Hartree-Fock procedure, this perturbation term results in a modified form for the standard Hartree-Fock matrix elements as

$$F_{\mu\nu} = F_{\mu\nu}^0 + \sum_i E_i D_{\mu\nu}^i$$

where $F_{\mu\nu}^0$ is the unperturbed zero field H-F matrix element and $D_{\mu\nu}^i$ is the i -th component of the dipole moment matrix element between atomic orbitals ϕ_μ and ϕ_ν . In the semi-empirical calculations used here, $D_{\mu\nu}^i$ is neglected unless ϕ_μ and ϕ_ν are atomic orbitals on the same atom. From the resulting perturbed wavefunctions, all

the tensor components including the hyperpolarizabilities are obtained by successively computing $\bar{W}(E)$ for a series of positive and negative electric field strengths of the same magnitude.

In order to get the orientationally averaged values, the mean values for the polarizability and hyperpolarizability tensors are necessary such as (Buckingham and Orr, 1967).

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

$$\langle\beta\rangle = \frac{3}{5}(\beta_{xxx} + \beta_{yyy} + \beta_{zzz})$$

$$\langle\gamma\rangle = \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx})$$

where x, y, z denote Cartesian components, and i is the major symmetry axis that coincides with the dipole moment vector. The second hyperpolarizability values of the molecules reported here are therefore the average values of $\langle\gamma\rangle$.

For the proper achievement of nonlinear optical responses from a molecule, the applied electric field strength should be high enough, but not exceed to the limit over which the molecular electronic structure distortion would occur. Also, too high field strength may cause the terms following after the γ term in the above energy expression to be significant so that they would not be truncated in the finite-field method. The electric field strength used in this study was 0.001 a.u. which is equivalent to 5.1423×10^8 V/cm, and this choice was shown quite reasonable (Kim, 1991).

The finite-field procedure has been modified in MOPAC program, which allows the calculation of nonlinear optical properties as well as geometry optimization of a molecule on each AM1, MNDO, and PM3 hamiltonians. The molecules studied in this paper were fully optimized in three semi-empirical levels and then taken to the nonlinear

optical property calculations.

The atomic unit (a.u.) of second hyperpolarizability was used here, where one a.u. of γ equals 6.2356×10^{-45} C⁴m⁴J⁻³, which is equivalent to 5.0509×10^{-49} esu.

Results and Discussion

The second hyperpolarizabilities for 1,3-butadiene were calculated with respect to changes in the C-C-C-C dihedral angle, and their semi-empirical results are shown in Fig. 1. The 5°

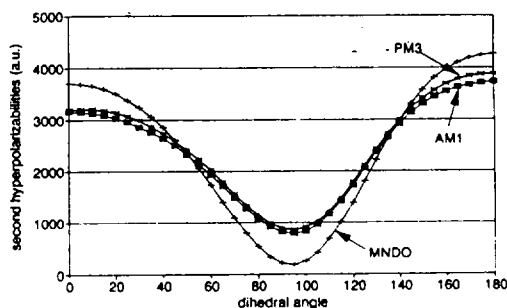


Fig. 1. Second hyperpolarizabilities (in a.u.) for 1,3-butadiene with respect to the C-C-C-C dihedral angle changes.

intervals of the dihedral angle changes have been made and the smooth curves were shown through a minimum from 0° to 180° angle changes. Here assigned the molecular structure with 0° dihedral angle as the cis, and that with 180° angle as the trans. As expected, the value of the second hyperpolarizabilities is a maximum at the trans and cis structures, (the trans form has a little higher values than the cis one in all three semi-empirical methods), due to the fact that the fully extended conjugation of the delocalized π electrons allows larger responses to the external electric field. It is a minimum at about 95° dihedral angle at which conjugation is weakest. The relative heats of formation (ΔH_f) in units of kcal/mol for 1,3-butadiene are also shown in Fig. 2. These values were obtained by the

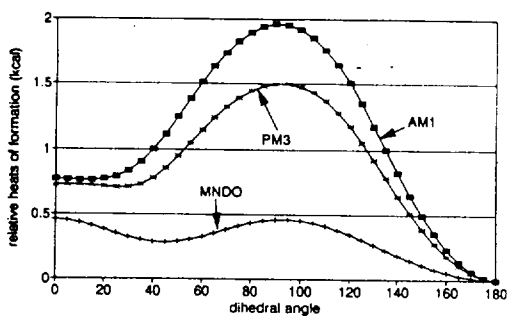


Fig. 2. Relative heats of formation (kcal/mol) for 1,3-butadiene with respect to the C-C-C dihedral angle changes.

difference of the heats of formation of this molecule between each dihedral angle and 180°. From these figures, an inverse relation can be seen between τ and ΔH_f for AM1 and PM3 results. That is, when a maximum delocalization of π electrons is achieved, its second hyperpolarizability value is maximum and ΔH_f is minimum with which the molecule has most stable geometry. When conjugation of the π system is broken, its second hyperpolarizability is minimum and ΔH_f is maximum that is, the molecule has most unstable geometry. This relation is not valid for the MNDO results. In MNDO case, a stable geometry was also obtained at 40°-45°, so that it may be assumed some possible contributions exist from other factors such as steric effects. Also the ΔH_f is a little higher at 0° than at 180° for all MNDO, AM1 and PM3 results, although the differences are less than 1 kcal/mol. Therefore, it is concluded that the π electron delocalization can be directly related to the second hyperpolarizability behavior but not to the heats of formation where several additional factors might be important.

Fig.3 shows the second hyperpolarizability values for 3-hexyn-1,5-diene versus its C1-C2-C5-C6 dihedral angle changes, where C1 and C2 are the carbon atoms at an end of the molecule, and C5 and C6 are those at the other end of the

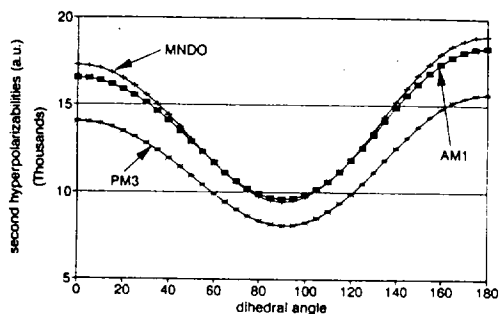


Fig. 3. Second hyperpolarizabilities (in a.u.) for 3-hexyn-1,5-diene with respect to the C1-C2-C5-C6 dihedral angle changes.

molecule. Again the values are maximum at the 180° (trans) and 0° (cis), and minimum at about 95° by the same reason as in case of 1,3-butadiene. And the maximum values for 3-hexyn-1,5-diene are about 5 times larger than those of 1,3-butadiene, because of its extended conjugation as well as larger molecular size. Fig. 4 gives the relative heats of formation for 3-hexyn-1,5-diene by subtracting the heat of formation of the molecule at 0° (cis) from that of its each rotation. The inverse relation between the second hyperpolarizabilities and the relative heats of formation can be seen very well from these figures. This is because 3-hexyn-1,5-diene has a longer chain length so that the π electron conjugation plays a major role for the rotational ΔH_f changes.

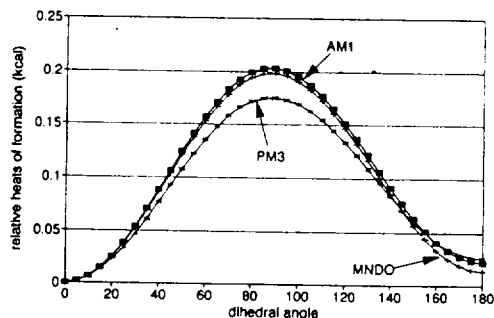


Fig. 4. Relative heats of formation (kcal/mol) for 3-hexyn-1,5-diene with respect to the C1-C2-C5-C6 dihedral angle changes.

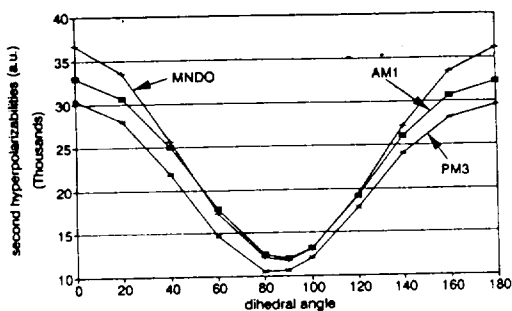


Fig. 5. Second hyperpolarizabilities (in a.u.) for dipyrrole with respect to the dihedral angle changes between the rings.

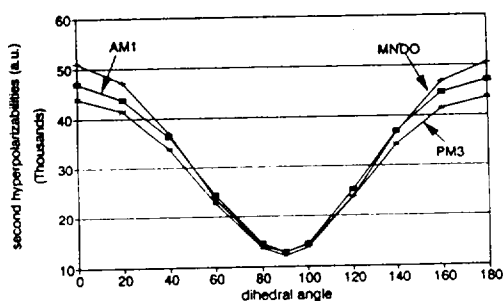


Fig. 6. Second hyperpolarizabilities (in a.u.) for dicyclopentadiene with respect to the dihedral angle changes between the rings.

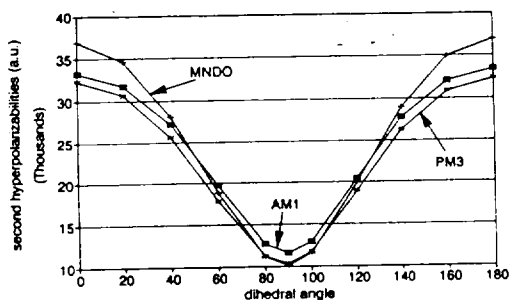


Fig. 7. Second hyperpolarizabilities (in a.u.) for difuran with respect to the dihedral angle changes between the rings.

The second hyperpolarizabilities of dimers of pyrrole, cyclopentadiene and furan were calculated for the conformational effect on the γ values, and Fig. 5, 6 and 7 show their semi-empirical results. Here, the dihedral angles have

been assigned for X-C-C-X in those dimers, where X indicates N, C, and O atoms for dipyrrole, dicyclopentadiene and difuran, respectively. Again it is evident that the γ values for the dimers are maximum at 0° and 180° dihedral angles due to the fully extended π electron delocalization and minimum at about 90° due to the breakage of π electron delocalization. The discrepancies between the semi-empirical γ results may be explained due to the different optimized geometries between each method, but they are still quite small. The relative heats of formation for the dimers were also calculated and are given in Fig. 8, 9 and 10. As shown in Fig. 8, the heat of formation for dipyrrole is a minimum at its trans structure in AM1 and PM3 as

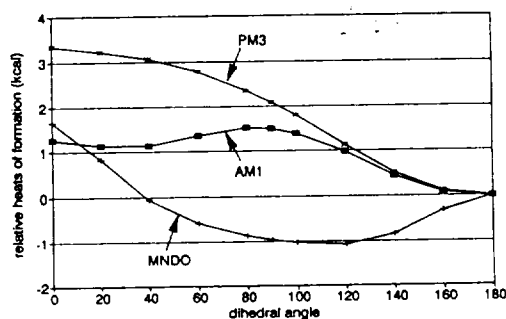


Fig. 8. Relative heats of formation (in kcal/mol) for dipyrrole with respect to the dihedral angle changes between the rings.

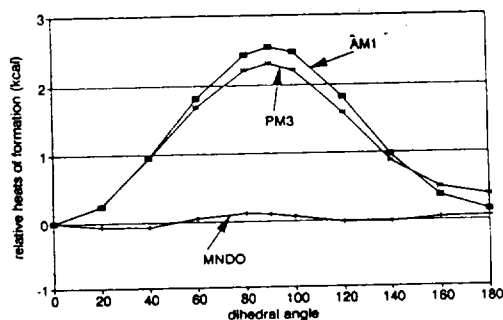


Fig. 9. Relative heats of formation (in kcal/mol) for dicyclopentadiene with respect to the dihedral angle changes between the rings.

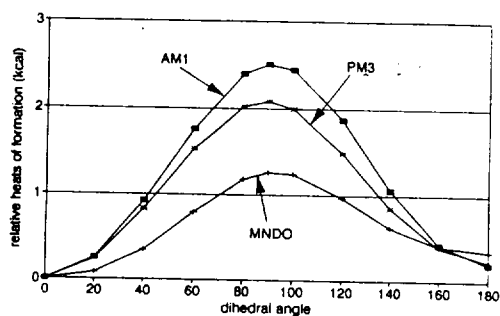


Fig. 10. Relative heats of formation (in kcal/mol) for difuran with respect to the dihedral angle changes between the rings.

expected, but no minimum at the cis form. It can only be guessed that there may be some optimizing problems for cis-dipyrrole in these two semi-empirical methods, especially in PM3. The MNDO predicts its minimum between 100° and 120° which is not true stable conformation for the molecule. It has been expected that the MNDO procedure gives poor optimized geometries in many cases, and it is inferior to AM1 and PM3 procedures in geometry optimization respects. In Fig. 9, the AM1 and PM3 methods show the energy minimum for dicyclopentadiene at 180° and 0°, while MNDO shows almost no minimum surface. In Fig. 10, all AM1, MNDO and PM3

show a minimum at 0° and 180° for difuran. Therefore, it can be eventually predicted that the second hyperpolarizability values can be directly related to the delocalization of π electron system.

Conclusion

For 1,3-butadiene, 3-hexyn-1,5-diene, dipyrrole, dicyclopentadiene, and difuran, the second hyperpolarizability values with respect to their dihedral angle changes showed a common pattern that there was a maximum at 0° and 180°, and a minimum at about 90°-95° dihedral angle changes. From this fact, the delocalization of π electron systems is directly related to the second hyperpolarizability of a molecule. When the π electron delocalization is fully extended the second hyperpolarizability has a maximum value, but it has a minimum value when the π electron delocalization is broken. The relative heats of formation with respect to the dihedral angle changes did not show such a common relation. It seemed to be some geometry optimization discrepancies between the semi-empirical approaches.

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〈국문초록〉

1, 3-Butadiene, 3-Hexyn-1, 5-diene 분자와 Pyrrole, Cyclopentadiene, Furan 이합체에 대한 이차 초편극도와 회전구조간의 관계

AM1, MNDO PM3 세가지의 반경험적 근사법을 조건으로 하여 1,3-butadiene, 3-hexyn-1,5-diene과 pyrrole, cyclopentadiene, furan 이합체의 회전구조적 변화에 대한 이차 초편극도를 계산하였다. 모든 계산은 유한장 방법으로 행해졌으며 MOPAC 프로그램이 이용되었다. 이 분자들의 회전구조가 cis와 trans의 형태일때 이차 초편극도값은 최대치를 가지며, 90°에서 95°의 이면각을 갖는 구조일때 그 값은 최소치를 나타냈다. 이러한 결과는 이차 초편극도가 π 전자의 비편재성에 직접적인 관계를 가짐을 보이는 것이다. 한편 이 분자들의 회전구조에 대한 상대적인 생성열도 계산, 비교되었다.