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ORIGINAL ARTICLE

AM1 and DFT study of polarizability of nitrogen-containing octatetraene with donor substituents: Comparative investigation

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Abstract We report density functional theory (DFT) studies of the dipole polarizabilities of nitrogen-containing octatetraene with a number of Π-electron donor substituent at the end parts. All geometries were optimized at the B3LYP/6-311++G(d,p) level of theory and polarizabilities were done at the same level of theory. The results indicate that for the NO_2–$(CH{=}CH)_4$–**Y** systems we find group polarizabilities in the order: $N(Me)_2 > NBr_2 > OCH_3 > Br > NH_2 > OH > CH_3 > NF_2 > H \sim F$.

Semi empirical AM1 and QSAR-quality empirical calculations show poor quantitative agreement with the DFT results, but give excellent statistical correlation coefficients with the DFT values. This implies that the results of such cheaper calculations can suitably scaled for predictive purpose.

1. Introduction

In the last years, much attention has been devoted to the study of nonlinear optical (NLO) properties of conjugated organic polymers due to their importance as possible key materials for future nanotechnological applications. The nonlinear optical properties of conjugated polymers have been extensively studied as these compounds form a promising class of organic materials with interesting characteristics for photonic applications (Nalwa, 2001; Prasad and Williams, 1991; Kanis et al., 1994; Bourhill et al., 1994). The delocalization of Π-electrons in these systems leads to large non resonant optical molecular polarizabilities. Besides, a number of quantum mechanical and experimental studies have shown that geometric changes caused by incorporation of push–pull end groups can enhance the nonlinear polarizabilities of conjugated molecules (Sinclair et al., 1987; Chemla and Zyss, 1987).

A better understanding of the chemical substitutions effects on the NLO properties of new organic polymers constitutes an

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important step towards the advance of photonic technologies. Theoretical studies have drawn interesting conclusions on the side-substitution effects on the electric responses of trans PA chains. Marder et al. (1994a,b, 1994) have investigated, on the basis of semi-empirical calculations, relations between structure and polarizabilities in donor–acceptor polyene compounds and have shown that the NLO responses of these systems can be optimized by varying the geometric parameter defined as bond length alternation (BLA).

Hayashi et al. (1991) have calculated the linear and nonlinear polarizabilities in the side-chain direction (perpendicular to the main chain) of the PA chains with all H atoms substituted by fluoro, hydroxyl and cyano groups. Their HF/STO-3G results have shown that the coupling between electronic states of the side groups with those of the main chain increase the values of the perpendicular polarizabilities. Margulis and Gaiduk (1998) have investigated the influence of the phenyl side groups on the third-order nonlinear optical susceptibility of trans PA chains. In the context of the tight-binding approximation, they have shown that an appropriate selection of side groups attached to the main chain can lead to a change of the sign of this property. Besides, effects of the incorporation of terminal donor and acceptor groups as well as the inclusion of singly and doubly charged defects on the polarizabilities of PA chains have also been studied (Oliveira et al., 2003; Champagne et al., 2002; Fonseca et al., 2001; An and Wong, 2001; Champagne et al., 1997; de Melo and Fonseca, 1996; de Melo and Silbey, 1988; Zhu et al., 2002). These theoretical works have shown that, in general, such modifications increase the electric responses of conjugated polymers. Also general is the fact that the second hyperpolarizability is much more sensitive to substitution effects than the linear polarizability.

Clarification of the effects of nitrogen-atom substitution in Π-conjugated bridges is an important unsolved problem for establishing a useful guide to the design of a new molecular system. In this paper we perform DFT calculations on DA (donor/acceptor) octatetraene like model compounds for a practical system and investigate the unsolved effect on nitrogen atom substitution on the molecular polarizability (α) values .We also report AM1 (Dewar et al., 1985) semiempirical polarizability together with QSAR-quality empirical polarizability using Miller's scheme and molecular volume calculations from optimized geometries using HyperChem v7 (HyperChem, 2000).

2. Theory

The electric dipole moment μ_e of a molecule is a quantity of fundamental importance in structural chemistry. When a molecule is subject to an external electric field E, the molecular charge density may rearrange and hence the dipole moment may change (Hinchliffe and Munn, 1985). This change can be described by the tensor Eq. (1):

$$\mu_{e,j}(E) = \mu_{e,j}(0) + \sum_{j=x}^{z} \alpha_{ij} E_j + \frac{1}{2} \sum_{j=x}^{z} \sum_{k=x}^{z} \beta_{ijk} E_j E_k + \cdots \tag{1}$$

Here μ_e *(0)* is the dipole in the absence of a field and μ_e *(E)* is the dipole moment in the presence of the field. The six independent quantities α_{ij} $(j \geqslant i)$ define the dipole polarizability tensor. The polarizability can be deduced as the gradient of the induced dipole.

$$\alpha_{xx} = \frac{\partial \mu_{e,x}}{\partial E_x} \tag{2}$$

For a molecule with symmetry, the principal axes of the polarizability tensor correspond to the symmetry axes; and so the principal values of the tensor are written α_{xx}, α_{yy} and α_{zz}, where, α_{xx}, α_{yy}, and α_{zz} are the diagonal elements of the polarizability tensor matrix. The average static polarizability $\langle\alpha\rangle$ tensor is defined (Buckingham, 1967) in terms of Cartesian components as:

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

The anisotropy κ gives a measure of deviations from spherical symmetry since it would be zero for a spherically symmetric charge distribution. Usually defined as:

$$\kappa = \frac{\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2 - 3\langle\alpha\rangle^2}{6\langle\alpha\rangle^2} \tag{4}$$

The average polarizability and κ the anisotropy are quantities of great experimental interest in theories of optoelectronics and intermolecular forces (Hinchliffe and Munn, 1985).

3. Methods

All DFT calculations were made using GAUSSIAN 98 (Frisch et al., 1998) and both geometries were optimized at the B3LYP/6-311++G(d,p) level of theory. All AM1 semi empirical calculations were made with MOPAC (MOPAC 93.00 Manual, 1993). Molecular volumes and The Miller–Savchik polarizabilities were found from optimized MM+ geometries using HyperChem v7 (HyperChem, 2000).

4. Results and discussion

4.1. Polarizabilities

Dipole polarizabilities calculated at the B3LYP/6-311++G(d,p) level of theory for all compounds Fig. 1 are shown in Table 1. The corresponding results at AM1 level are shown in Table 2.

The B3LYP/6-311++G(d,p) polarizabilities are generally a few percent higher than the corresponding values calculated at AM1 level (31.99% for NMe_2, 31.45% for NBr_2, 31% for OCH_3, 35.6117% for Br, 29.43% for NH_2, 32.19% for OH, 30.66% for CH_3 and 24.90% for NF_2). For all series, the smallest enhancement is due to the pair NO_2/F values of about 180.079 a.u. for $\langle\alpha\rangle$, and 0.305 for the anisotropy, and the largest enhancement due to the pair NO_2/NMe_2 values of about 262 a.u. for $\langle\alpha\rangle$, and 0.331 for the anisotropy. As regards to these substituted octatetraene, we are able to propose a decreasing classification, relatively to the $\langle\alpha\rangle$ polarizability. The established order is as follows: $NMe_2 > NBr_2 > OCH_3 > Br > NH_2 > OH > CH_3 > NF_2 > H{\sim}F$.

AM1 results for the title molecules are collected in Table 2. There is a poor quantitative agreement between the B3LYP/6-311++G(d,p) values and the AM1 results, but they give a correlation coefficient of 0.95 which means that AM1 results cant be accurately scaled for such molecules Fig. 2. In this work, the transverse static polarizabilities α_{zz} calculated at the B3LYP/6-311++G(d,p)and at AM1 level of theory show a similar trend and the absolute values are as usual extremely low in comparison to those of the axial components α_{yy} and α_{xx}.