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ORIGINAL ARTICLE

Semi empirical and Ab initio methods for calculation of polarizability (α) and the hyperpolarizability (β) of substituted polyacetylene chain

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Abstract We report accurate Ab initio studies of dipole polarizabilities and the first static hyperpolarizabilities (β) of polyacetylene with a number of substituents at the end part of the linear system. Geometries of all molecules were optimized at the Hartree–Fock level with the 6-311G++(d,p) basis set. The results indicate that for the NO_2-Π-**Y** systems we find group polarizabilities in the order $N(Et)_2 > NBr_2 > N(Me)_2 > NHMe > PH_2 > NHNH_2 > SH > Br \sim BH_2 \sim CHO \sim NHOH \sim NH_2 > CN \sim CH_3 \sim Cl > NF_2 \sim OCH_3 \sim OH > H \sim F$. The study reveals inverse relationship between the E_{gap} and first static hyperpolarizabilities. Compounds with the $N(Et)_2$, $NHNH_2$, $N(Me)_2$, NHMe, NHOH, NH_2 and OH end parts have large β values. A poor agreement results between the Ab initio and the AM1 values which give a correlation coefficient of 0.88.

1. Introduction

NLO materials have been attractive in recent years with respect to their future potential applications in the field of optoelectronics such as optical communication, optical computing, optical switching, and dynamic image processing (Kanis et al., 1994; Prasad and Williams, 1991). Due to their high molecular hyperpolarizabilities, organic materials display a number of significant nonlinear optical properties. NLO materials were categorized as multilayered semi-conductor structures, molecular based macroscopic assemblies and traditional inorganic solids. A variety of inorganic, organic and organometallic molecular systems have been studied for NLO activity (Kanis et al., 1994). The design strategy, used by many with success involves connecting donor (D) and acceptor (A) groups at the terminal positions of a Π-bridge to create highly polarized molecules that could exhibit large molecular nonlinearity (Masraqui et al., 2004).

Prasad and Williams (1991) explained that certain classes of organic materials exhibit extremely large NLO and electro optic effects. The design of most efficient organic materials

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for the non linear effect is based on molecular units containing highly delocalized Π-electron moieties and extra electron donor (D) and electron acceptor (A) groups on opposite sides of the molecule at appropriate positions on the ring to enhance the conjugation. The Π-electron cloud movement from donor to acceptor makes the molecule highly polarized.

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 fluorine, 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 the 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; Zhu et al., 2002).

Marder et al. (1994) and Meyers et al. (1994) have investigated, on the basis of semiempirical 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). Several authors have used Ab initio techniques to study molecular polarizabilities. It is usually possible to obtain respectable agreement with experiments at the HF level of theory for the dipole polarizability tensor α provided that a careful choice of atomic orbital basis set is made. It is common knowledge that polarizabilities can only be calculated accurately from calculations employing extended basis sets. In particular, these basis sets have to include diffuse functions that can accurately describe the response of a molecular charge distribution to an external electric field. These diffuse (s and p) functions are needed in addition to the normal polarization functions; they are denoted by + and ++ in packages such as Gaussian03 (Hinchliffe, 1987; Chopra et al., 1989; Maroulis and Thakkar, 1991; Archibong and Thakkar, 1993; Nalwa et al., 1995; Jacquemin et al., 1997; Champagne et al., 1998; Kirtman et al., 2002; Paula et al., 2003; Poulsena et al., 2001).

Experimental measurements and theoretical calculations on molecular hyperpolarizability become one of the key factors in the second-order NLO materials design. Theoretical determination of hyperpolarizability is quite useful both in understanding the relationship between the molecular structure and nonlinear optical properties. It also provides a guideline to experimentalists for the design and synthesis of organic NLO materials given in Fig. 1 (Rao and Bhanuprakash, 2000; Lipinski and Bartkowiak, 1999; Cundari et al., 2000; Brasselet and Zyss, 1998; Cardelino et al., 1991).

Our objective is to design a range of novel molecular systems, which show NLO activity. The approach is based on the concept of charge transfer (CT) between the donor and acceptor through a polyacetylene system end parts. In this research work, molecular polarizability (α) and first hyperpolarizabilities (β) are calculated using Ab initio method using Hartree–Fock level using HF/6-31G++ (d,p) basis set for twenty substituted PA [NO_2–$(CH{=}CH)_4$–**Y**] chain using Gaussian03 (Frisch et al., 2003). The designing of systems with high CT is key to this part, as intra molecular CT between the donor and acceptor will lead to a very large value for β.

The other objective is to compare the Ab initio results with the semi empirical results employing AM1 (Dewar et al., 1985). We also consider AM1 semiempirical polarizability together with QSAR-quality empirical polarizability using Miller's scheme and molecular volume calculations from optimized geometries using HyperChem v7 (Hypercube, 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. This change can be described by the tensor Eq. (1):

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

Here $\mu_{e\,(0)}$ 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 ten independent quantities β_{ijk} define the first dipole hyperpolarizability and so on.

The energy U of the molecular charge distribution also changes when an electrostatic field is applied. This change can be written as:

$$U(E) = U(0) - \sum_{i=x}^{x} \mu_{e,i} - \frac{1}{2} \sum_{i=x}^{z} \sum_{j=x}^{z} \alpha_{ij} E_i E_j - \frac{1}{6} \sum_{i=x}^{z} \sum_{j=x}^{z} \times \sum_{k=x}^{z} \beta_{ijk} E_i E_j E_k - \quad (2)$$

Eqs. (1) and (2) are the key equations for the calculation of molecular polarizabilities and hyperpolarizabilities by gradient techniques (Zhu et al., 2002). The dipole polarizability is obtained as the first derivative of the energy with respect to a component of the electric field that gives a component of the electric dipole moment, while the second derivative gives the polarizability, in symbols:

$$\mu_{e,i} = -\left(\frac{\partial U}{\partial E_i}\right)_{E=0} \quad (3)$$

$$\alpha_{ij} = \left(\frac{\partial^2 U}{\partial E_i \partial E_J}\right)_{E=0} \quad (4)$$

$$\beta_{ijk} = \left(\frac{\partial^2 \mu_i}{\partial E_i \partial E_j \partial E_k}\right)_{E=0} \quad (5)$$

Where the subscript '0' means evaluated at zero electric field $E(0)$. Equally, the polarizability can be deduced as the gradient of the induced dipole.

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 $<\alpha>$ tensor is defined (Jacquemin et al., 1997) in terms of Cartesian components as:

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