



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 NO₂-Π-Y systems we find group polarizabilities in the order N(Et)₂ > NBr₂ > N(Me)₂ > NHMe > PH₂ > NHNH₂ > SH > Br ~ BH₂ ~ CHO ~ NHOH ~ NH₂ > CN ~ CH₃ ~ Cl > NF₂ ~ OCH₃ ~ OH > H ~ F. The study reveals inverse relationship between the E_{gap} and first static hyperpolarizabilities. Compounds with the N(Et)₂, NHNH₂, N(Me)₂, NHMe, NHOH, NH₂ 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.

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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 (Kan-

is 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

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optic effects. The design of most efficient organic materials 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; Poulsen 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 hyperpo-

larizabilities (β) are calculated using Ab initio method using Hartree-Fock level using HF/6-31G++ (d,p) basis set for twenty substituted PA $[\text{NO}_2-(\text{CH}=\text{CH})_4-\text{Y}]$ 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):

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

Here $\mu_{e(0)}$ is the dipole in the absence of a field and $\mu_e(E)$ is the dipole moment in the presence of the field. The six independent quantities α_{ij} ($j \geq i$) 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:

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

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:

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

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

$$\beta_{ijk} = \left(\frac{\partial^3 U}{\partial E_i \partial E_j \partial E_k} \right)_{E=0} \quad (5)$$

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

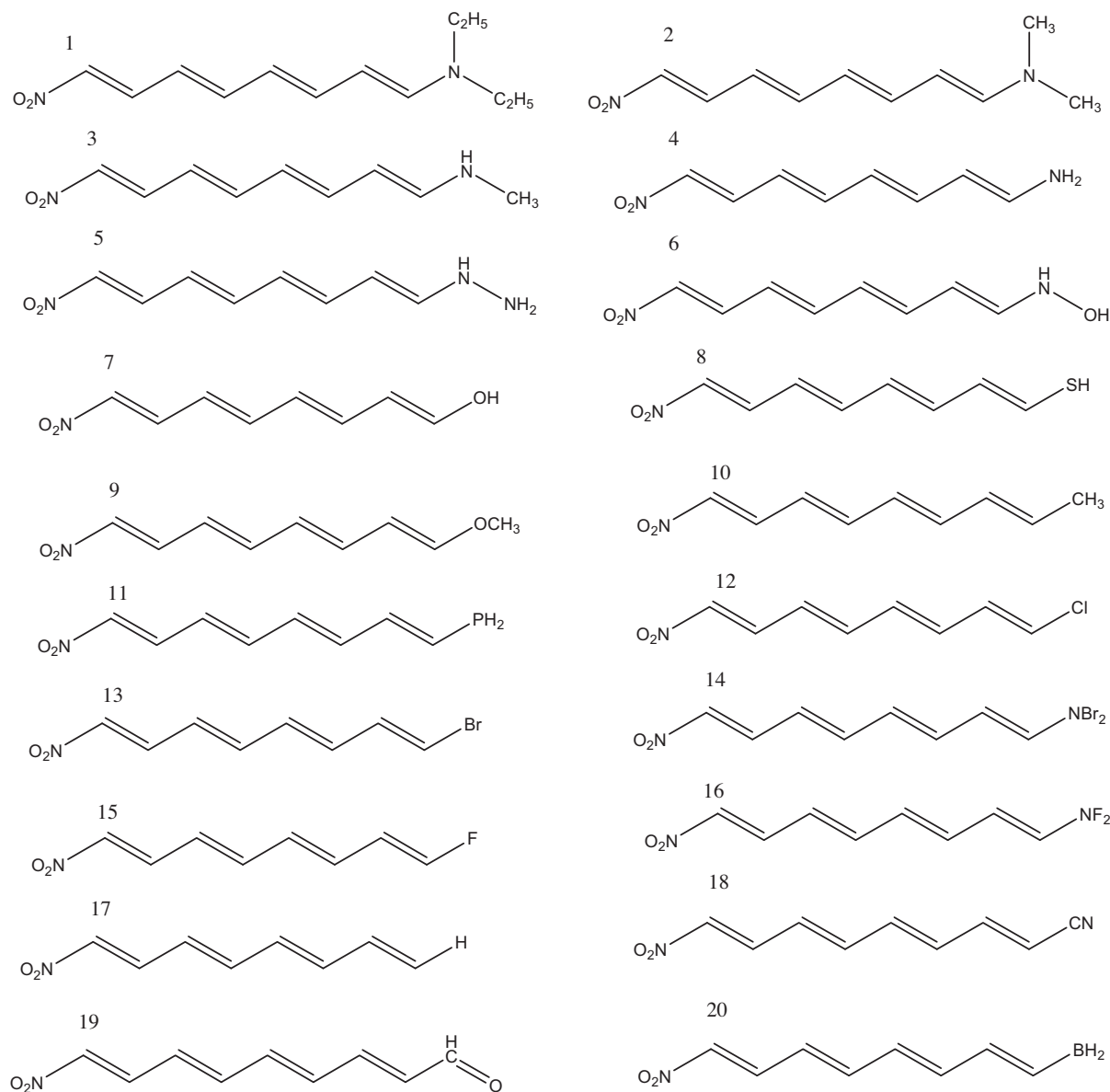


Figure 1 Structure of different substituted PA molecules $[\text{NO}_2-(\text{CH}=\text{CH})_4-\text{Y}]$.

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

$$\langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (6)$$

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:

$$\kappa = \frac{\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2 - 3 \langle \alpha \rangle^2}{6 \langle \alpha \rangle^2} \quad (7)$$

First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry (Kleinman, 1962) ($\beta_{xyy} = \beta_{yxy} = -\beta_{yyx} = \beta_{yyz} = \beta_{zyy} = \beta_{zyx} = \beta_{zyx} = \beta_{zyx} \dots$ likewise other permutations also take same value). It can be given in the lower tetrahe-

dral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrix (cube) is a tetrahedral. The output from Gaussian03 provides 10 components of this matrix as β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{xzz} , β_{yzz} , β_{zzz} , respectively. Many types of hyperpolarizabilities have been discussed in the literature in this investigation, we report β_{tot} for all the molecules listed in Fig. 1. The components of β can be calculated using the following equation:

$$\beta = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (8)$$

Using the x , y and z components of β , the magnitude of the first hyperpolarizability tensor can be calculated.

$$\beta_{\text{tot}} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{\frac{1}{2}} \quad (9)$$

The complete equation for calculating the magnitude of β from Gaussian03 output is given as follows. The values of the first hyperpolarizability tensors of the output file of Gaussian03 are reported in atomic units (a.u.).

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{\frac{1}{2}} \quad (10)$$

3. Methods

All Ab initio calculations were made using Gaussian03 (Frisch et al., 2003) and both geometries were optimized at the Hartree–Fock HF/6-311G++(d,p) level of theory. The semi empirical calculations using AM1, was performed using MOPAC 2000 (Stewart, 2002). No restrictions were imposed on the structure during the optimization and calculation of optical properties. Molecular volumes and empirical polarizabilities were found from optimized AM1 geometries using HyperChem v7 (Hypercube, 2000). The Miller–Savchik polarizabilities were also found using this software for all structures Fig. 1.

4. Results and discussion

4.1. Dipole polarizabilities

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

The HF/6-311G++(d,p) polarizabilities are generally a few percent higher than the corresponding values calculated at AM1 level. For all series, the smallest enhancement is due to the pair NO₂/H values of about 145.277au for $\langle\alpha\rangle$, and 0.211 for the anisotropy, and the largest enhancement due to the pair NO₂/N(Et)₂ values of about 229.229 au for $\langle\alpha\rangle$, and 0.201 for the anisotropy.

There is poor absolute agreement between the HF/6-311G++(d,p) values and the AM1 results, but they give a

correlation coefficient of 0.88 which means that AM1 results cannot be accurately scaled for such molecules. In this work, the transverse static polarizabilities (α_{zz}) calculated at the HF/6-311G++(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}).

4.2. First static hyperpolarizabilities

The first static hyperpolarizability and dipole moments are given in Table 3.

As the molecules lie in the XZ plane, and the X-axis is directed along the charge transfer (CT) axis in all series, the largest component of the first hyperpolarizability tensor is β_{xxx} (Table 3), and all other components of the tensor are weak. As a result, the first hyperpolarizability tensor can be obtained by the following expression: $\beta_{\text{tot}} \sim \beta_{xxx}$. The change of sign of β_{xxx} (cf. N(Et)₂ vs. NHNH₂, N(Me)₂ vs. NHMe and NHOH vs. NH₂ and OH) arises from the direction of X-axis do not change as exchange of donor/acceptor. On the other hand, it can be seen that β_{tot} is strongly sensitive to the exchange of donor/acceptor. The compounds with end parts N(Et)₂, N(Me)₂, NHMe, NHNH₂, NHOH, NH₂ and OH provides an intrinsic enhancement of their second-order NLO response. The first hyperpolarizability tensor of molecule with NO₂/N(Et)₂ end parts is the largest relative to the other molecules. The first hyperpolarizability value of this molecule is about five times greater than that of NO₂/H group and 93times greater than that of trans hexatriene (Weast, 1985).

The results obtained for molecules containing a combination of NO₂/H, CN, CHO, BH₂ groups, respectively, show a decrease in first hyperpolarizability compared with all other molecules.

This means that the presence of the NO₂ group together with the CN, CHO and BH₂ in polyacetylene chains decreases the non linear optical properties of these types of oligomers.

The resultant dipole moment (μ) of the studied molecules is about 12 and 1.63Debyes. This value of dipole moment may

Table 1 HF/6-311++G(d,p) principal dipole polarizability tensor components.

Molecule NO ₂ -(CH=CH) ₄ -Y	α_{xx} /au	α_{yy} /au	α_{zz} /au	$\langle\alpha\rangle$ /au	κ
N(Et) ₂	433.702	148.123	105.864	229.229	0.201
NBr ₂	384.843	149.824	92.642	209.103	0.222
N(Me) ₂	387.021	126.158	86.568	199.915	0.182
NHMe	369.967	112.571	76.967	186.501	0.244
PH ₂	351.212	117.922	79.661	182.931	0.215
NHNH ₂	355.885	110.279	73.702	179.955	0.242
SH	345.272	111.806	74.029	177.035	0.229
Br	338.327	110.037	71.024	173.129	0.231
BH ₂	338.775	110.339	67.841	172.318	0.238
CHO	337.423	108.170	66.095	170.562	0.244
NHOH	325.545	112.669	69.100	169.104	0.219
NH ₂	334.327	104.359	66.800	168.495	0.246
CN	322.330	106.687	66.839	165.285	0.230
CH ₃	316.690	107.940	70.483	165.037	0.215
Cl	319.762	104.691	66.061	163.504	0.232
NF ₂	303.036	108.298	67.145	159.493	0.208
OCH ₃	277.864	121.866	78.325	159.351	0.144
OH	304.921	101.053	62.916	156.296	0.231
F	278.737	98.196	60.383	145.772	0.213
H	277.264	97.182	61.387	145.277	0.211

Table 2 AM1 principal dipole polarizability tensor components.

Molecule NO ₂ -(CH=CH) ₄ -Y	α_{xx}/au	α_{yy}/au	α_{zz}/au	$\langle \alpha \rangle / \text{au}$	κ
N(Et) ₂	335.974	87.083	104.494	175.850	0.208
NBr ₂	385.103	127.502	24.729	179.111	0.358
N(Me) ₂	388.681	114.912	32.358	178.650	0.363
NHMe	384.554	108.141	25.2284	172.641	0.395
PH ₂	336.690	108.100	31.960	158.917	0.331
NHNH ₂	368.251	107.053	19.476	164.927	0.403
SH	355.919	104.082	16.635	158.879	0.409
Br	313.165	99.1121	15.5015	142.592	0.386
BH ₂	321.942	94.564	27.333	147.946	0.362
CHO	326.395	100.952	17.087	148.145	0.388
NHOH	338.107	105.785	22.166	155.352	0.370
NH ₂	343.238	97.085	16.842	152.388	0.415
CN	316.467	96.238	20.661	144.455	0.377
CH ₃	310.432	99.040	23.109	144.194	0.355
Cl	319.559	94.2257	15.1422	142.975	0.406
NF ₂	318.436	104.333	18.036	146.935	0.369
OCH ₃	348.621	100.537	23.530	157.562	0.387
OH	318.939	95.091	15.282	143.104	0.403
F	294.216	92.907	15.147	134.090	0.384
H	277.120	91.475	14.996	127.864	0.370

seem large for molecules with ends substituted (N(Et)₂, N(Me)₂, NHMe, NHNH₂, NHOH, NH₂ and OH). This high dipole moment, especially for compounds N(Et)₂ and N(Me)₂ ($\mu = 12$ and 10D , respectively), may make them reactive and attractive for NLO proprieties. Compounds with CN and CHO end parts have the lowest μ values respectively 1.63D and 3.15D (see Table 4).

The value change of the first hyperpolarizability also depends on the change of transition moment of the molecule. As the molecule has greater change of transition moment, the charge transfer is clearer and the value of dipole moment is becoming larger. Accordingly, the values of the dipole moment and first hyperpolarizability are influenced by the differently substituted ones. The values of the dipole moment and polarizability are larger in compounds NO₂-(CH=CH)₄-Y (Y = N(Et)₂, N(Me)₂, NHMe, NHNH₂, NHOH, NH₂ and OH) compared with (BH₂, Cl, CN, NF₂, CHO, Br, NBr₂).

4.3. Effect of HOMO–LUMO energies

The Ab initio calculated HOMO–LUMO gaps at HF/6-311G++(d,p) level of theory for all substituted polyacetylene are shown in Table 5.

As shown in Table 5, substitution of different groups on NO₂/N(Et)₂, N(Me)₂, NHMe, NH₂, NHNH₂, NHOH and OH increases the energy of the HOMO, while leaving the LUMO energy essentially changed. Thus, the energy gap decreases with substitution in order respectively N(Et)₂, N(Me)₂, NHMe, NH₂, NHNH₂, NHOH and OH and produces a larger first hyperpolarizability β_{tot} .

The replacement of compounds by (SH, OCH₃, CH₃, PH₂, Cl, Br, NBr₂, F, NF₂, H, CN, BH₂, CHO) groups changed considerably both HOMO and LUMO energies, this has led to a larger energy gap than that of the other molecules and give a decrease in β_{tot} value.

Fig. 2 shows the variation of first hyperpolarizability of the selected molecules. It clearly shows the inverse relationship

with the E_{gap} ($E_{\text{LUMO}} - E_{\text{HOMO}}$) energy. The HF/6-311G++(d,p) calculated β_{tot} and E_{gap} values for selected compounds show that it could be interesting to synthesize compounds with end parts in polyacetylene (NO₂/N(Et)₂, N(Me)₂, NHMe, NH₂, NHNH₂, NHOH and OH) groups having the greatest and the lowest, respectively β_{tot} and E_{gap} values.

4.4. QSAR-quality calculations

Dipole polarizabilities are often used in QSAR studies, where the aim is to give a reliable but quick estimate of $\langle \alpha \rangle$, as part of the process of high-throughput screening. DFT polarizability calculations are prohibitively expensive in a QSAR context, even for such simple molecules. One therefore looks to less rigorous but reliable procedures.

The definitive reference in this field appears to be that due to (Miller, 1990). Miller pointed out the need to take account of the atomic environment in molecular calculations, and this is usually done by assigning parameters in which each atom is characterized by its state of atomic hybridization. Miller and Savchik (1979) proposed a functional form:

$$\langle \alpha \rangle = 4\pi\epsilon_0 \frac{4}{N} \left(\sum_A \tau_A \right)^2 \quad (11)$$

where τ_A is an atomic hybrid component for each atom A in a given state of hybridization.

N is the total number of electrons. In fact, Miller and Savchik omitted the factor $4\pi\epsilon_0$ and so most computer packages quote the results as polarizability volumes (typically Å³).

These are shown in Table 6.

The Miller method gives mean polarizability volumes (Å³) in much better agreement with the HF/6-311G++(d,p) value than the crude molecular volume. It is clear that polarization volumes are not to be interpreted as molecular volumes. A linear regression between the Miller polarizabilities and the Ab initio $\langle \alpha \rangle$ values gives a regression coefficient of 0.91. A lin-

Table 3 HF/6-311G++(d,p) calculated static components β and β_{tot} (a.u) value for all compounds.

NO ₂ ,Y	β_{xxx}	β_{xyx}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_{tot}
N(Et) ₂	−8598.761	−990.048	368.581	−1.984	220.972	15.432	−33.342	78.238	2.515	−60.348	8212.7643
N(Me) ₂	−6884.275	766.819	271.097	15.010	60.731	0.1494	21.421	107.744	−9.712	117.313	6554.1301
NHMe	6202.845	877.6346	−204.066	1.169	70.946	−14.060	3.596	−67.516	18.008	65.561	6000.3148
NH ₂	−5379.167	678.419	207.870	−14.240	28.315	2.050	0.955	29.384	−7.824	11.762	5183.7973
NHNNH ₂	−5321.421	733.206	190.567	3.032	81.449	7.258	8.205	56.285	15.027	42.393	5131.5758
NHOH	4709.129	405.661	−20.671	32.648	−43.385	2.344	3.871	−14.467	−4.731	2.040	4694.2063
OH	−3926.528	507.652	171.480	−3.317	−0.0521	−0.114	−0.015	11.467	−4.456	−0.163	3776.8067
SH	3547.722	362.433	−185.848	−11.124	4.078	24.862	0.7400	−81.649	−5.042	3.455	3298.4610
OCH ₃	−3233.158	100.862	188.674	21.017	179.457	39.061	12.764	59.537	6.199	46.627	2997.2255
CH ₃	−3108.121	416.130	159.029	−28.4813	0.0392	−0.0013	0.009	42.565	1.783	0.010	2932.4994
PH ₂	3075.757	379.790	−194.137	−8.246	−1.748	1.500	−12.972	−87.195	5.842	−38.902	2820.3025
Cl	−2800.218	326.358	130.493	−19.7457	−0.0451	0.0371	0.011	12.0185	−5.605	0.029	2674.6980
Br	2826.806	292.600	−150.001	−14.061	−0.0763	−0.052	0.001	−42.677	−5.951	0.029	2648.1943
NBr ₂	−2914.622	−657.630	364.620	−15.870	−131.658	−15.078	−22.952	70.981	−6.204	−50.379	2578.6746
F	2566.208	374.833	−138.555	−13.578	−0.0168	−0.0396	0.005	−23.090	−1.513	0.0299	2431.3235
NF ₂	−2043.303	246.305	104.541	−4.050	43.932	−13.828	−7.271	13.526	0.903	−9.232	1940.7232
H	1790.809	348.753	−126.457	−17.034	1.361	2.341	0.2.668	−91.980	−1.734	−0.341	1606.6252
CN	−759.739	−53.508	−54.5623	34.538	−0.026	−0.082	−0.014	19.655	−6.819	0.058	795.06445
CHO	856.075	154.810	−94.627	−47.590	−0.057	−0.047	0.0080	−15.805	−10.124	0.036	751.93794
BH ₂	−8.5872	151.398	147.691	−25.770	0.009	0.028	0.006	89.679	4.487	−0.011	263.1957

Table 4 Ab initio calculated electric dipole moment μ (Debye) for selected molecules.

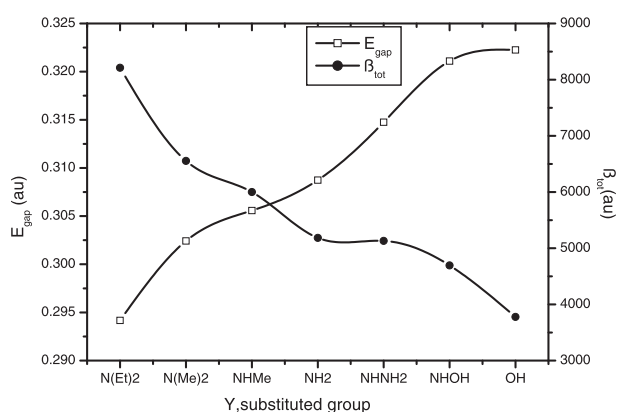
Molecule NO ₂ -(CH=CH) ₄ -Y	μ_x	μ_y	μ_z	μ
N(Et) ₂	12.1159	0.5424	−0.5818	12.1420
N(Me) ₂	10.9081	−0.7970	0.4084	10.9448
NHMe	−10.5964	−1.1206	0.6574	10.6758
NH ₂	10.1325	−0.8173	0.9239	10.2073
NHNNH ₂	8.5172	−0.2932	0.5588	8.5406
NHOH	−9.1389	−0.0245	0.4231	9.1487
OH	8.5151	0.8049	−0.0081	8.5530
CHO	−1.9461	−2.4812	0.0013	3.1534
CN	1.5750	−0.4386	0.0025	1.6349

ear regression between the molecular volumes and the Ab initio mean polarizabilities gives a correlation coefficient of 0.93. Although there is poor absolute agreement between these values and the HF/6-311G++(d,p) level of theory ones, there is an excellent correlation coefficient of 0.96 between the two sets of data. This is to be expected, since the method was first parameterized for hydrocarbons.

Finally we consider the likely reliability of various easily-computed indices such as the molecular volume, the Miller empirical volume polarizabilities and AM1 polarizabilities discussed above. Linear regressions were done for each of these quantities against the HF/6-311G++(d,p) mean Polarizabilities $\langle \alpha \rangle$, and the regression coefficients R are given in Table 7.

Table 5 HF/6-311++G(d,p) energy gap calculated for substituted compounds.

Molecule NO ₂ -(CH=CH) ₄ -Y	HOMO	LUMO	$E_{\text{gap}}(E_{\text{LUMO}} - E_{\text{HOMO}})$
N(Et) ₂	-0.26636	0.02781	0.29417
N(Me) ₂	-0.27526	0.02716	0.30242
NHMe	-0.27809	0.02749	0.30558
NH ₂	-0.28285	0.02589	0.30874
NHNH ₂	-0.28680	0.02795	0.31475
NHOH	-0.29253	0.02857	0.3211
OH	-0.29755	0.02470	0.32225
SH	-0.30636	0.02295	0.32931
OCH ₃	-0.30466	0.02938	0.33404
CH ₃	-0.30478	0.02998	0.33476
PH ₂	-0.30826	0.02260	0.33086
Cl	-0.31789	0.01979	0.33768
Br	-0.31765	0.01855	0.3362
NBr ₂	-0.30714	0.01411	0.32125
F	-0.31653	0.02441	0.34094
NF ₂	-0.32688	0.01525	0.34213
H	-0.31442	0.02854	0.34296
CN	-0.33002	0.00470	0.33472
CHO	-0.32982	0.00584	0.33566
BH ₂	-0.32240	0.00474	0.32714

**Figure 2** Variation of β_{tot} and E_{gap} values for some selected compounds.

The correlation coefficients are well below 0.95, which value is often taken to justify a straight line relationship. It therefore seems that none of the three simpler procedures gives a reliable estimate of $\langle \alpha \rangle$ for these series of molecules.

5. Conclusion

Polarizability is strongly dependent on the extent of the electronic communication between the push-pull groups through the end parts. We have also observed that molecular polarizabilities are slightly dependant on the variation of dipole moment for NO₂-II-Y systems. There are good least squares correlations between the Ab initio results and those given by cheaper procedures such as the calculated molecular volume, the Miller empirical polarizability models. Semiempirical AM1 models grossly underestimate the normal component of the polarizability tensor.

It is evident that the first hyperpolarizability tensor of substituted linear polyacetylene strongly depends on the electronic structure of the molecule. The end parts group

Table 6 Various quantities for the NO₂-(CH=CH)₄-Y series.

Molecule NO ₂ -(CH=CH) ₄ -Y	Volume/Å ³	Miller/Å ³
N(Et) ₂	780.83	25.22
NBr ₂	709.96	23.13
N(Me) ₂	686.29	21.55
NHMe	635.38	19.71
PH ₂	608.64	16.91
NHNH ₂	619.70	19.23
SH	599.26	19.53
Br	609.45	19.15
BH ₂	597.10	18.19
CHO	602.29	18.45
NHOH	607.06	18.52
NH ₂	581.69	17.88
CN	594.19	18.38
CH ₃	599.68	18.36
Cl	589.06	18.46
NF ₂	608.63	17.70
OCH ₃	628.77	19.00
OH	567.59	17.16
F	553.09	16.44
H	543.75	16.53

Table 7 Linear regression coefficients R for the NO₂-(CH=CH)₄-Y series.

Correlation of $\langle \alpha \rangle$ HF/6-311G++(d,p) with		
Molecular volume/Å ³	$R = 0.939$ ($Y = 178.96775 + 2.51361 * X$)	
$\langle \alpha \rangle_{\text{Miller}}$	$R = 0.918$ ($Y = 2.07227 + 0.09719 * X$)	
$\langle \alpha \rangle_{\text{AM1}}$	$R = 0.881$ ($Y = 44.87162 + 0.6265 * X$)	

linked together through the linear chain tend to rotate about carbon-carbon σ bond. This will increase the overlap of interacting orbitals, which eventually increase the CT from donor to acceptor through the linear chain. The HOMO-LUMO calculations show that the first hyperpolarizability of these

derivatives is directly related to the HOMO–LUMO energy gap. This is the highest in molecules with end parts: (NO₂/N(Et)₂, N(Me)₂, NHMe, NHNH₂, NHOH, NH₂ and OH) while the smallest was observed in the other molecules, which had the highest energy gap. The study reveals that the selected substituted PA molecules 1–7 have important first hyperpolarizability. They have potential applications in the development of NLO materials.

References

- An, Z., Wong, K.Y., 2001. *J. Chem. Phys.* 114, 1010.
- Archibong, E.F., Thakkar, A.J., 1993. *J. Chem. Phys.* 98, 8324.
- Brasselet, S., Zyss, J., 1998. *J. Opt. Soc. Am. B: Opt. Phys.* 15, 257.
- Cardelino, B.H., Morre, C.E., Stickel, R.E., 1991. *J. Phys. Chem.* 95, 8645.
- Champagne, B., Deumens, E., Ohrn, Y., 1997. *J. Chem. Phys.* 107, 5433.
- Champagne, B., Perpete, E., Jacquemin, D., Van Gisbergen, S., Baerends, E.J., Soubra-Ghaoui, C., Robins, K.A., Kirtman, B., 2000. *J. Phys. Chem.* 104, 4755.
- Champagne, B., Spassova, M., Jadin, J.B., Kirtman, B., 2002. *J. Chem. Phys.* 116, 3935.
- Chopra, P., Carlucci, L., King, H.F., Prasad, P.N., 1989. *J. Phys. Chem. A* 93, 7120.
- Cundari, T.R., Kurtz, H.Z., Zhou, T., 2000. *J. Phys. Chem. A* 104, 4711.
- De Melo, C.P., Fonseca, T.L., 1996. *Chem. Phys. Lett.* 28, 261.
- Dewar, M.J.S., Zebisch, E.G., Healy, E.F., Stewart, J.J.P., 1985. *J. Am. Chem. Soc.* 107, 3902.
- Fonseca, T.L., Castro, M.A., Cunha, C., Amaral, O.A.V., 2001. *Synth. Met.* 123, 11.
- Frisch et al., 2003. Gaussian03, Revision B.03, Pittsburgh PA, 2003.
- Hayashi, S., Yabushita, S., Imamura, A., 1991. *Chem. Phys. Lett.* 179, 405.
- Hinchliffe, A., 1987. *Ab Initio Determination of Molecular Properties*; Adam Hilger, Institute of Physics Publishing, Bristol UK.
- Hypercube, 2000. Hyper. Chem. Molecular Modelling System Inc., 1115 NW 4th Street, Gainesville, FL 32601, USA.
- Jacquemin, D., Champagne, B., Andre, J.M., 1997. *Int. J. Quantum Chem.* 65, 679.
- Kanis, D.R., Ratner, M.A., Marks, T.J., 1994. *Chem. Rev.* 94, 195.
- Kirtman, B., Champagne, B., Gu, F.L., Bishop, D.M., 2002. *Int. J. Quantum Chem.* 90, 709.
- Kleinman, D.A., 1962. *Phys. Rev.* 126, 1977.
- Lipinski, J., Bartkowiak, W., 1999. *J. Chem. Phys.* 245, 263.
- Marder, S.R., Gorman, C.B., Meyers, F., Perry, J.W., Bourhill, G., Bredas, J.L., Pierce, B.M., 1994. *Science* 265, 632.
- Margulis, V.A., Gaiduk, E.A., 1998. *Synth. Met.* 97, 175.
- Maroulis, G., Thakkar, A.J., 1991. *J. Chem. Phys.* 95, 9060.
- Masraqui, S.H., Kenny, R.S., Ghadigaonkar, S.G., Krishnan, A., Bhattacharya, M., Das, P.K., 2004. *Opt. Mater.* 27, 257.
- Meyers, F., Mader, S.R., Pierce, B.M., Bredas, J.L., 1994. *J. Am. Chem. Soc.* 116, 10703.
- Miller, K.J., 1990. *J. Am. Chem. Soc.* 112, 8533.
- Miller, K.J., Savchik, J.A., 1979. *J. Am. Chem. Soc.* 101, 7206.
- Nalwa, H.S., Mukai, J., Kakuta, A., 1995. *J. Phys. Chem. A* 99, 10766.
- Oliveira, L.N., Amaral, O.A.V., Castro, M.A., Fonseca, T.L., 2003. *Chem. Phys.* 289, 221.
- Paula, M.S., Qin, W., Weitao, Y., 2003. *J. Chem. Phys.* 119, 11001.
- Poulsen, T.D., Mikkelsen, K.V., Fripiat, J.G., Jacquemin, D., Champagne, B., 2001. *J. Chem. Phys.* 114, 5917.
- Prasad, P.N., Williams, D.J., 1991. *Introduction to nonlinear optical effects in molecules and polymers*. Wiley, New York.
- Rao, L.J., Bhanuprakash, K., 2000. *Indian J. Chem. A* 39, 114.
- Stewart, J.J.P., 2002. MOPAC, Fujitsu Limited, Tokyo, Japan.
- Weast, C.R. (Ed.), 1985. *CRC Hand Book of Chemistry and Physics*, 66th ed. CRC Press, Boca Raton, Fla. P.C., p. 308.
- Zhu, W., Wu, G.S., Jiang, Y., 2002. *Int. J. Quantum Chem.* 86, 390.