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Excess polarizabilities upon the first dipole-allowed excitation of some conjugated oligomers

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This paper presents theoretical predictions for the excess polarizabilities upon excitation from the ground state to the first dipole-allowed excited state (1^1B_u) of some conjugated oligomers. The excess polarizability was obtained by simulating the Stark shift, which was predicted by the time-dependent density functional theory (TDDFT) with the hybrid Becke-3 Lee–Yang–Parr (B3LYP) potential. The Stark shift in solution was simulated by employing the non-equilibrium integral equation formalism polarizable continuum model (IEFPCM). All the model molecules considered in this study were fully optimized by the Hartree–Fock (HF) method and the density functional theory (DFT) with the B3LYP potential, respectively. For diphenylpolyenes, the excess polarizabilities displayed by the DFT/B3LYP-optimized geometries are more reasonable than those displayed by the HF-optimized geometries when compared with the experimental results. However, this feature is not clearly demonstrated by our results in the cases of oligo(phenylenevinylene)s (OPVs). Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: the excess polarizability; the Stark shift; diphenylpolyenes; oligo(phenylenevinylene)s

INTRODUCTION

Excited states of conjugated organic systems have attracted considerable interest in recent years, since they are closely related to the promising phenomena such as electroluminescence (EL) and nonlinear optical response (NLO).[1,2] It is noted that most existing quantum-chemical calculations are limited to the excited state in the absence of the electric field. Actually, the theoretical analysis on the excited state under the electric field is of the high demand in the design of the optoelectronic device.[3] It has been reported that the electric field applied to the organic light emitting diode (OLED) can beyond several MV/cm.[4] The Stark shift is the basic response of the excited state to the electric field. For centrosymmetric molecules, the Stark shift is dominated by the excess polarizability, which is defined as the difference between the ground- and excited-state polarizabilities. The excess polarizability has been found to contain the spatial information on the exciton.[5,6] For instance, Gelinck *et al*. suggested that the excess polarizability in units of Å^3 is an approximate measure of the volume enclosed by the wave function of the exciton.[5]

So far, the time-dependent density functional theory (TDDFT) approach has shown the great promise for investigating the excited-state electronic structures of organic oligomers. It has been found that the TDDFT/Becke-3 Lee–Yang–Parr (B3LYP) predictions for the 1^1B_u excitation energies of some short diphenylpolyenes and oligo(phenylenevinylene) (OPV) oligomers are in reasonable agreement with the experimental results.[7–9] Grozema *et al*. first calculated the excess polarizabilities of some organic oligomers by employing the TDDFT approach.[10] In their study, the molecular geometries and excited-state electronic structures were predicted by the Becke88-Perdew86 (BP) potential. One notes that the accuracy of the TDDFT calculation depends on two major factors, namely the molecular geometry and the selection of the exchange-correlation (xc) potential. We therefore present this theoretical work to gain a better insight into the performance of the TDDFT approach in predicting the excess polarizability for organic conjugated oligomers. We mention that we calculated the excess polarizability of the unrelaxed excited state in this paper. The evolution of the excess polarizability during the geometric relaxation process induced by the 1^1B_u excitation for diphenylpolyenes was discussed in our previous study.[11] Note that in that work the local field correction to the excess polarizability was not considered when comparing the theoretical predictions with the experimental results available. In this paper, the local field correction was calculated in a quantum-chemical way.

The model molecules studied in this study were sketched in Fig. 1. DPB, DPH, DPO, and DPD as a whole will be denoted diphenylpolyenes in discussion. For the model molecules, the 1^1B_u excitation is mainly built by the one-electron transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The excitation displays the large oscillator strength, arising from the strong coupling between the ground and 1^1B_u states.[1] One notes that the experimental information on the geometries of these model molecules is rather limited, so that it is relatively difficult to

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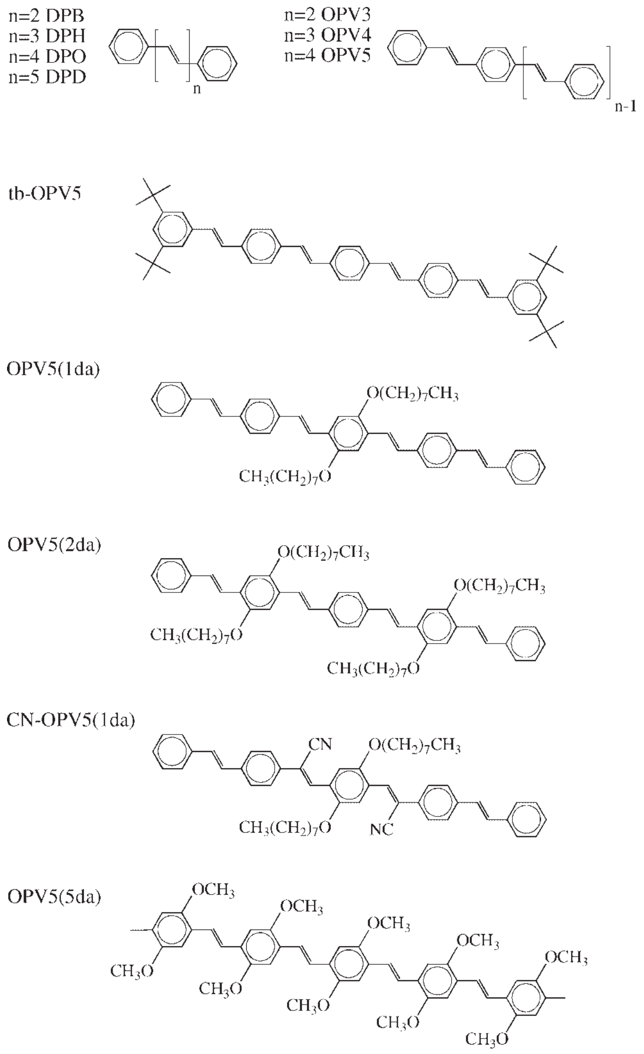

Figure 1. Model molecules considered in this study

evaluate the quality of the geometries optimized by currently used quantum-chemical methods. Therefore, we used two different sets of geometries, which were predicted at the density functional theory (DFT)/B3LYP[12] and Hartree–Fock (HF) theory levels, respectively, to calculate the excess polarizability.

COMPUTATIONAL METHODOLOGY

The Stark shift under the applied static electric field $\boldsymbol{F}$ is given by

$$\mathrm{Exc}(\boldsymbol{F}) = \mathrm{Exc}(0) - \sum_i \Delta\mu_i \boldsymbol{F}_i - \frac{1}{2}\sum_{i,j} \alpha_{i,j}\boldsymbol{F}_i\boldsymbol{F}_j \qquad (1)$$

where Exc stands for the vertical excitation energy and $\Delta\mu_i$ and $\Delta\alpha_{ij}$ are the elements of the increase in the dipole moment upon excitation and the excess polarizability in the *i*th and *ij*th directions, respectively. Centrosymmetric molecules will display the vanishing $\Delta\mu$, since they have no dipole moment in both the ground state and the unrelaxed excited state. The excess polarizability is often discussed via its isotropic value. In Cartesian coordinates, the isotropic value is defined as:

$$\Delta\alpha = (\Delta\alpha_{xx} + \Delta\alpha_{yy} + \Delta\alpha_{zz})/3 \qquad (2)$$

We presented the isotropic value of the excess polarizability in this work.

All the model molecules were fully optimized in the ground state in the gas phase. The DFT/B3LYP and HF approaches show the large difference in predicting the average bond length alternation (BLA) parameter,[13] that is, the average difference in length between the single carbon–carbon (C—C) bonds and the double carbon–carbon (C═C) bonds, for the conjugated linkage (the polyene linkage for diphenylpolyenes while the vinylene linkages for OPV molecules). The BLA parameters for the phenyl or phenylene rings of the model molecules were found to be on the order of 10^{-3} Å and insensitive to the selection of the geometry optimization method. This phenomenon is imposed by the widely delocalized π orbitals in the phenyl and phenylene rings. We mention that only the BLA parameter of the conjugated linkage will be discussed in the following. The model molecules were put in Cartesian coordinates with their long axes parallel to the *x* axis when calculating the excess polarizability. The other two diagonal components $\Delta\alpha_{yy}$ and $\Delta\alpha_{zz}$ thus approach to zero. To obtain the component $\Delta\alpha_{xx}$, we performed the parabolic fit to six excitation energies calculated at the TDDFT/B3LYP theory level under $\boldsymbol{F}_x$ ranging from 0 to 5×10^{-4} a.u. The fitting process is helpful to balance the errors generated in quantum-chemical calculations.

Experimentally, the excess polarizability can be determined by analyzing the electroabsorption (EA) spectroscopy, which is obtained by using an external electric field to modulate the absorption spectrum.[14–19] The sample used in the EA measurement is prepared by dispersing the molecule of interest in solution. Due to the surrounding of the solvent molecule, the solute molecule feels the local field rather than the applied field. Therefore, the Stark shift in solution is written as:

$$\mathrm{Exc}(\boldsymbol{F}) = \mathrm{Exc}(0) - \sum_i \Delta\mu_i(\boldsymbol{I}\cdot\boldsymbol{F})_i - \frac{1}{2}\sum_{i,j} \Delta\alpha_{ij}(\boldsymbol{I}\cdot\boldsymbol{F})_i(\boldsymbol{I}\cdot\boldsymbol{F})_j \qquad (3)$$

where $\boldsymbol{I}$ is the local field factor. Since the local field factor can not be determined experimentally, the excess polarizability obtained via the EA measurement will involve the local field correction inevitably. In the following, the excess polarizability determined by the EA experiment will be denoted by the local-field-corrected excess polarizability $\Delta\alpha\boldsymbol{I}^2$.[19] In this study, the local-field-corrected excess polarizability was obtained by simulating the Stark shift in solution (Eqn (3)) via the integral equation formalism polarizable continuum model (IEFPCM) model.[20] We used the geometry optimized in the gas phase when calculating the local-field-corrected excess polarizability. One notes that the geometric relaxation upon solvation will be negligibly small for the model molecules, since these molecules possess the vanishing dipole moment.[21]

Quantum-chemical calculations were carried out using Gaussian03 package of codes.[22] In all cases, the basis set 6-311G was used. The keyword options UltraFine, BigAtoms, and BigShells, which actually increase the effective xc quadrature volume, were selected in the TDDFT calculation to improve the quality of the result. From now on, the abbreviations DFT and TDDFT will not be expressed explicitly. For instance, B3LYP//B3LYP

Table 1. Geometric parameters (in Å) of the model molecules

Molecule	B3LYP			HF			BP		
	r(C–C)	r(C=C)	BLA	r(C–C)	r(C=C)	BLA[c]	r(C–C)	r(C=C)	BLA
DPB[a]	1.457	1.354	1.03×10^{-1}	1.467	1.333	1.34×10^{-1}	1.457	1.368	8.9×10^{-2}
DPH[a]	1.452	1.357	9.5×10^{-2}	1.464	1.334	1.30×10^{-1}	1.451	1.372	7.9×10^{-2}
DPO[a]	1.448	1.359	8.9×10^{-2}	1.461	1.334	1.27×10^{-1}	1.446	1.374	7.2×10^{-2}
DPD[a]	1.445	1.361	8.4×10^{-2}	1.460	1.335	1.25×10^{-1}	1.443	1.377	6.6×10^{-2}
OPV3[a]	1.465	1.350	1.15×10^{-1}	1.473	1.331	1.42×10^{-1}	1.466	1.363	1.03×10^{-1}
OPV3[b]	1.464	1.350	1.14×10^{-1}	1.473	1.330	1.43×10^{-1}	1.465	1.363	1.02×10^{-1}
OPV4[a]	1.464	1.351	1.13×10^{-1}	1.473	1.331	1.42×10^{-1}	1.464	1.363	1.01×10^{-1}
OPV5[a]	1.464	1.351	1.13×10^{-1}	1.472	1.331	1.41×10^{-1}	1.463	1.364	9.9×10^{-2}

r(C–C) [r(C=C)] is the average value of all the single (double) carbon–carbon bonds in the conjugated linkage.

[a] C_{2h}.

[b] C_{2v}.

[c] Results for diphenylpolyenes are from Reference [11].

stands for the TDDFT/B3LYP calculation performed for the molecule with the DFT/B3LYP-optimized geometry.

RESULTS AND DISCUSSIONS

Diphenylpolyenes

This section involves two aspects: (i) the relation between the magnitude of the excess polarizability and the BLA parameter; (ii) the local field corrections to the excess polarizability in different solutions. The obtained conclusions hold true also for OPV molecules.

The B3LYP approach is found to predict the smaller BLA parameter than the HF approach, as shown in Table 1. For instance, the B3LYP-optimized DPO displays the BLA parameter 8.9×10^{-2} Å, which is $\sim 4 \times 10^{-2}$ Å smaller than that displayed by the HF-optimized DPO. One can expect that the influence on the geometry of the polyene linkage induced by the phenyl ring will decrease while the length of the polyene linkage increases. Therefore, we compare the geometric parameters of the polyene linkage in DPD with those of *trans*-polyacetylene. Experimental results for the C—C and C=C bonds in *trans*-polyacetylene were found to be 1.44 and 1.36 Å, respectively.[23] The corresponding BLA parameter is therefore 8×10^{-2} Å. From Table 1, one finds that the B3LYP-optimized DPD exhibits the geometric parameters $r(\text{C—C}) = 1.445$, $r(\text{C=C}) = 1.361$ Å, and BLA $= 8.4 \times 10^{-2}$ Å, respectively. These three data are in reasonable agreement with the experimental results mentioned above. We mention that the bond length r(C—C) [r(C=C)] listed in this study is the average value of all the C—C (C=C) bonds in the polyene linkage. The HF-optimized DPD displays the overestimated C—C bond 1.460 Å and the underestimated C=C bond 1.335 Å in comparison with the experimental values for the C—C and C=C bonds. Consequently, the BLA parameter 1.25×10^{-1} Å for the HF-optimized DPD shows the large deviation from the experimental result 8×10^{-2} Å.

Table 2 shows that the excess polarizability calculated using the B3LYP-optimized geometry is smaller than that calculated using the HF-optimized geometry. In the case of DPO, the excess polarizability of the B3LYP-optimized geometry is 24 Å^3 smaller than that of the HF-optimized geometry.

We now use DPO as an example to have an in-depth investigation of the relation between the excess polarizability and the BLA parameter. Table 3 collects the geometric parameters optimized at different theory levels, that is, HF, AM1,[24] BHandH, B3LYP, PBE1PBE,[25] BLYP,[26,27] and BP.[26,28] From the table, one finds that the excess polarizability decreases while the BLA parameter becomes small. For instance, the HF-optimized geometry has the largest BLA parameter 1.27×10^{-1} Å and the largest excess polarizability 127 Å^3, while the BP-optimized geometry has the smallest BLA parameter 7.2×10^{-2} Å and the smallest excess polarizability 88 Å^3. The excess polarizability considered here is the difference between the ground- and 1^1B_u excited-state polarizabilities. Therefore, our finding implies that the ground- and 1^1B_u excited-state polarizabilities have the different responses to the change in the BLA parameter. It is worthwhile to mention the theoretical work provided by Jonsson *et al.*, who calculated the ground- and 1^1B_u excited-state polarizabilities of some polyenes fully analytically.[29] They found that the ground-state polarizability increases whereas the 1^1B_u excited-state polarizability decreases with decreasing BLA parameter. Their finding suggests the same relation between the excess polarizability and the BLA parameter as that found by us.

The DPO molecules optimized at different theory levels have no dipole moment in both the ground state and the 1^1B_u state due to their C_{2h} symmetries. In our previous work, we used a strong static electric field, which was added along the long axis of the polyene linkage during the ground-state geometry optimization process, to change the BLA parameter of DPH.[11] The DPH molecule optimized under the electric field has the C_s symmetry, and therefore it displays the dipole moment in the ground state and $\Delta\mu$ upon the 1^1B_u excitation.

To investigate the local field correction to the excess polarizability, we tested three solvents, that is, benzene, toluene, and chloroform. For the IEFPCM model, the solvent effect is mainly characterized by the dielectric constant ε and the fast

Table 2. Electronic properties of the model molecules

Molecule	Exc (Osc)		$\Delta\alpha$		
	B3LYP//B3LYP	B3LYP//HF[c]	B3LYP//B3LYP	B3LYP//HF[c]	BP//BP[d]
DPB[a]	3.61 (1.54)	3.80 (1.50)	45	61	65
DPH[a]	3.27 (2.03)	3.49 (1.97)	73	91	100
DPO[a]	2.99 (2.51)	3.24 (2.40)	103	127	145
DPD[a]	2.77 (2.96)	3.04 (2.80)	145	209	265
OPV3[a]	3.23 (1.83)	3.42 (1.78)	142	158	351
OPV3[b]	3.26 (1.85)	3.45 (1.80)	145	160	
OPV4[a]	2.85 (2.58)	3.06 (2.49)	391	421	1283
OPV5[a]	2.63 (3.25)	2.86 (3.13)	781	821	

Exc in eV, oscillator strength (Osc) in a.u., $\Delta\alpha$ in Å^3.

[a] C_{2h}.

[b] C_{2v}.

[c] Results for diphenylpolyenes are from Reference [11].

[d] Reference [10].

Table 3. Excess polarizabilities predicted by the B3LYP potential *versus* the BLA parameters optimized at different theory levels for DPO

Method	r(C–C)[a]	r(C=C)[a]	BLA	BLA[b]	Exc (Osc)	$\Delta\alpha$
HF	1.461	1.334	1.27×10^{-1}	3.07×10^{-3}	3.24 (2.40)	127
AM1/sto-3g	1.447	1.346	1.01×10^{-1}	1.99×10^{-3}	3.08 (2.42)	118
BHandH	1.435	1.337	9.8×10^{-2}	2.65×10^{-3}	3.12 (2.48)	107
B3LYP	1.448	1.359	8.9×10^{-2}	2.09×10^{-3}	2.99 (2.51)	103
PBE1PBE	1.444	1.355	8.9×10^{-2}	1.84×10^{-3}	3.01 (2.51)	102
BLYP	1.450	1.376	7.4×10^{-2}	1.87×10^{-3}	2.89 (2.54)	91
BP	1.446	1.374	7.2×10^{-2}	1.84×10^{-3}	2.87 (2.54)	88

All geometries possess the C_{2h} symmetry, geometric parameters in Å, Exc in eV, Osc in a.u., $\Delta\alpha$ in Å^3.

[a] Average values were presented.

[b] The average bond length alternation parameter for the phenyl ring.

dielectric constant ε_f.[30] In the case of the electronic excitation, the fast dielectric constant is approximately equal to the square of the refractive index n.[30] Table 4 collects the dielectric constants and refractive indices of these three solvents. One finds that these three solvents have the near refractive indices whereas their dielectric constants show the trend benzene ≈ toluene < chloroform.

Table 5 indicates that the magnitude of the local field correction to the excess polarizability increases with the delectric constant. For instance, the local-field-corrected excess polarizabilities of the B3LYP-optimized DPH were calculated to be 83 Å^3 in benzene, 84 Å^3 in toluene, and 100 Å^3 in chloroform, respectively. Note that the difference between the local field correction in benzene and toluene is very small. This finding is consistent with the fact that benzene and toluene are close in the dielectric constant. Compared with the excess polarizability of the isolated molecule, the local-field-corrected excess polarizability is relatively large. In the case of DPH, the excess polarizability of the B3LYP-optimized geometry was predicted to be 73 Å^3 (Table 2), which is 10, 11, and 27 Å^3 smaller than the local-field-corrected excess polarizabilities in benzene, toluene, and chloroform, respectively. This indicates that the DPH molecule will display the larger Stark shift in solution than in vacuum when under the same applied field. Consequently, one can conclude that the local field, which affects the DPH molecule in solution directly, is stronger than the applied field.

The local-field-corrected excess polarizabilities of diphenylpolyenes were measured in dioxane at room temperature.[16] It is worthwhile to note that the local field corrections in dioxane and benzene will be of similar magnitude. As shown in Table 4, dioxane and benzene are alike in the dielectric constant and refractive index. Besides, these two solvents were found to be close in the dispersion radius at the B3LYP theory level, 3.61 Å for dioxane while 3.94 Å for benzene.

For convenience of comparison, the local-field-corrected excess polarizabilities calculated in benzene and the EA

Table 4. Dielectric constants and refractive indices for the solvents considered in this study

Property	Benzene	Toluene	Chloroform	Dioxane	PMMA
ε	2.247[a]	2.379[a]	4.9[a]	2.217[b]	3.1[b]
n	1.501[c]	1.497[c]	1.489[c]	1.422[c]	1.490[c]

[a] Default values provided by Gaussian 03.
[b] Refference [16].
[c] *n*D20.

Table 5. Local-field-corrected excess polarizabilities (in Å^3) in different solvents

Method	Solvent	DPB[a]	DPH[a]	DPO[a]	DPD[a]	OPV3[a]	OPV3[b]
B3LYP//B3LYP	Benzene	60	83	121	163	159	162
	Toluene	61	84	122	167	162	165
	Chloroform	71	100	143	194	182	184
B3LYP//HF	Benzene	70	104	156	221	175	177
	Toluene	71	106	157	224	178	180
	Chloroform	82	121	169	258	197	205
EA Expt	Dioxane[c]	53 ± 2	91 ± 9	116 ± 8	140 ± 10		
	Toluene[d]					47 ± 7	
	PMMA[e]					420	

[a] C_{2h}.
[b] C_{2v}.
[c] At room temperature (Reference [16]).
[d] At 77 K (Reference [17]).
[e] At 77 K (Reference [18]).

experimental results measured in dioxane were presented in Fig. 2. From the figure, one finds that the B3LYP//B3LYP results are in reasonable agreement with the experimental results considering the experimental uncertainties. In comparison, the B3LYP//HF results exhibit relatively large deviations from the experimental data. For instance, the B3LYP//B3LYP, B3LYP//HF, and experimental results for DPO are 121, 156, and 116 ± 8 Å^3 (Table 5), respectively. In the case of DPD, the B3LYP//B3LYP result 163 Å^3 is much closer to the experimental result 140 ± 10 Å^3 than the B3LYP//HF result 221 Å^3. This is consistent with the conclusion obtained previously, namely the C—C and C═C bonds as well as the BLA parameter of the polyene linkage in the B3LYP-optimized DPD are more reasonable than those in the HF-optimized DPD.

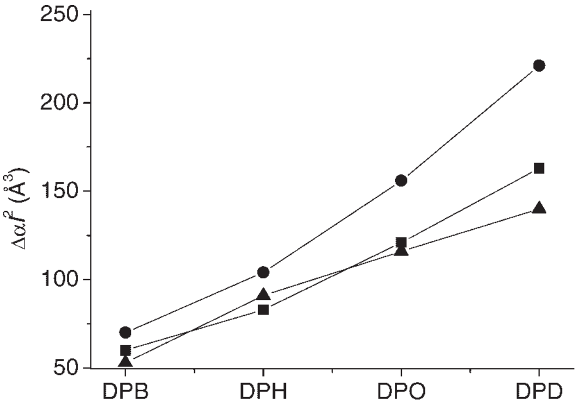

Figure 2. Local-field-corrected excess polarizabilities calculated in benzene and the EA experimental results measured in dioxane for diphenylpolyenes. Closed circles, squares, and triangles stand for the B3LYP//HF, B3LYP//B3LYP, and experimental results, respectively

Figure 2 shows that both the B3LYP//B3LYP and B3LYP//HF results rise more quickly than the experimental data. This implies that the B3LYP potential is too sensitive to the increase in the chain length in predicting the excess polarizability. Consequently, the B3LYP potential is expected to overestimate the excess polarizability for long oligomers systematically, independent of the method used for the geometry optimization. Note that in our study the excess polarizability was calculated by determining the trend of the excitation energy under the external electric field. Therefore, our results indicate that the B3LYP potential will predict the overestimated slope of the excitation energy under the external electric field for long oligomers. This phenomenon is actually due to the inherent errors in treating the long-range electron correlation of the currently available xc potentials,[31] which draw excess charges to the ends of the chain so that the external field is not properly screened.[32]

It should be mentioned that the local field correction to the excess polarizability has been investigated non-quantum-chemically by employing the Onsager model.[15,16,33] In comparison with the IEFPCM model, the Onsager model predicts the

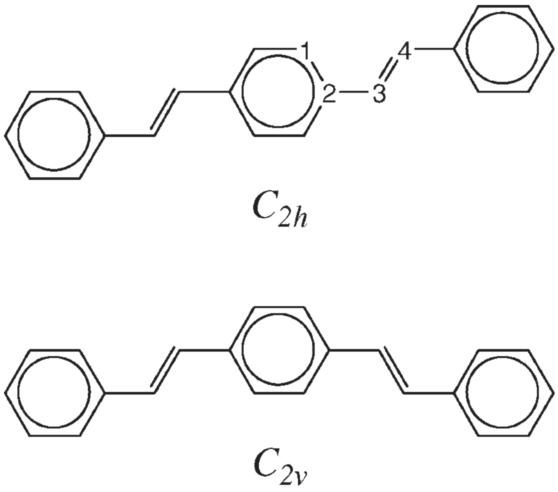

Figure 3. C_{2h} and C_{2v} geometries for OPV3

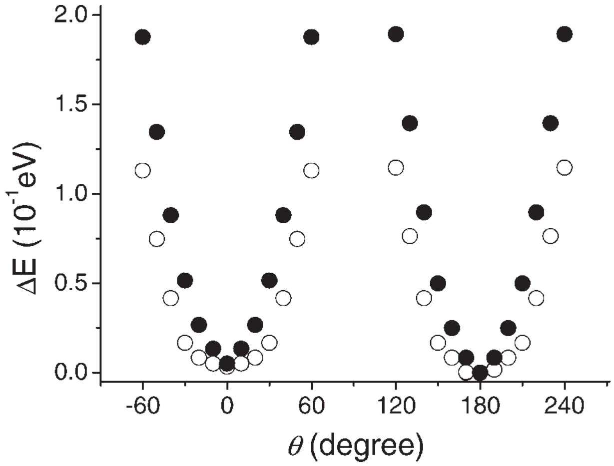

Figure 4. A plot of the total ground-state electronic energy of OPV3 as a function of the dihedral angle $\theta = \angle C1C2C3C4$ (carbon numbers were labeled in Fig. 3). Open circles were predicted at the HF theory level while closed circles at the B3LYP theory level

relatively large local field correction. For instance, the excess polarizability of the isolated DPH was calculated to be 42 Å^3 by the Onsager model based on the experimental result measured in dioxane (91 Å^3).[16] Therefore, for DPH the difference between the isolated excess polarizability and the local-field-corrected excess polarizability amounts to 49 Å^3. However, the corresponding difference is ~10 Å^3 at the B3LYP//B3LYP theory level according to the IEFPCM calculation.

OPV molecules

This section mainly considers the cases of OPV3 and five OPV5 derivatives, whose excess polarizabilities were investigated experimentally.

The vinylene linkages in OPV3 may have the *trans* and *cis* configurations,[34] as sketched in Fig. 3. The *trans* configuration can lead to the C_{2h} symmetry while the *cis* configuration to the C_{2v} symmetry. One finds that the C_{2v} geometry can be obtained from the C_{2h} geometry by rotating one terminal phenyl ring and the adjoining vinylene linkage together along the C2—C3 bond (carbon numbers were labeled in Fig. 3), namely changing the dihedral angle $\theta = \angle C1C2C3C4$. Figure 4 illustrates the variation of the total ground-state electronic energy of OPV3 as a function of θ within the rigid-rotor approximation. Such an approximation presumes that the bond lengths and bond angles remain unchanged during the artificial rotation.[35] Note that the relative values with respect to the total electronic energy of the optimized C_{2v} geometry were presented in the figure. The optimized C_{2h} and C_{2v} geometries were located at $\theta = 0$ and 180°, respectively. It is interesting to find that these two geometries are very close in energy at both the B3LYP and HF theory levels. Besides, one notes that small deviations from $\theta = 0^\circ$ or $\theta = 180^\circ$ will increase the total electronic energy. Consequently, the optimized C_{2h} and C_{2v} geometries actually stay at the centers of two different potential wells, respectively. Table 2 indicates that the difference in the configuration of the vinylene linkages has the negligible influence on the value of the excess polarizability. For instance, the B3LYP-optimized C_{2h} and C_{2v} geometries display the excess polarizabilities 142 and 145 Å^3, respectively.

The EA experimental results measured by different groups show the relatively large discrepancy. As shown in Table 5, the EA result measured in toluene at 77 K is 47 Å^3,[17] whereas the result measured in PMMA at the same temperature is 420 Å^3.[18] From Table 5, one finds that the calculated local-field-corrected excess polarizabilities for OPV3 in toluene are overall larger than the experimental result 47 Å^3. For instance, the theoretical results in toluene for the B3LYP-optimized OPV3 were calculated to be 162 Å^3 for the C_{2h} geometry and 165 Å^3 for the C_{2v} geometry, respectively. It can be expected that the local field correction in PMMA will be weaker than that in chloroform, since the dielectric constant of PMMA is 3.1 while the dielectric constant of chloroform is 4.9 (Table 4). However, the local-field-corrected excess polarizability 420 Å^3 measured in PMMA is much larger than the theoretical results in chloroform. For instance, the experimental result is 238 Å^3 larger than the B3LYP//B3LYP result 182 Å^3 for the C_{2h} OPV3. Based on the theoretical results, one finds that the selection of different solvents in the EA experiment will not be the main reason for the large discrepancy between the experimental results. Actually, it has been pointed out that the errors in determining the absorption intensity and thickness of the sample are two main factors influencing the value of the EA result.[19]

The excess polarizabilities of some OPV5 derivatives were measured by the flash photolysis time-resolved microwave-conductivity technique (FP-TRMC),[5,36] which offers another opportunity to evaluate the performances of the B3LYP//B3LYP and B3LYP//HF approaches in predicting the excess polarizability. It should be emphasized that the excess polarizability determined by the FP-TRMC technique involves no local field correction, since what is investigated in the FP-TRMC measurement is the transient change in the microwave dielectric constant of the sample upon excitation[5,37,38] rather than the Stark shift under the electric field. The FP-TRMC technique measures the excess polarizability of the relaxed excited state. For long OPV molecules, the geometric relaxation induced by the 1^1B_u excitation was found to be insignificant.[39]

The calculated excess polarizabilities of OPV5 derivatives were collected in Table 6, together with the FP-TRMC results measured in benzene. For tb-OPV5 and OPV5(2da), the excess polarizability calculated using the B3LYP-optimized geometry is superior to that calculated using the HF-optimized geometry when

Table 6. Excess polarizabilities for OPV5 derivatives

Molecule	Exc (Osc)		$\Delta\alpha$		
	B3LYP//B3LYP	B3LYP//HF	B3LYP//B3LYP	B3LYP//HF	Expt
tb-OPV5	2.60 (3.50)	2.83 (3.35)	859	909	810 ± 100^{a}
OPV5(1da)	2.48 (2.91)	2.69 (2.68)	563	583	590^{b}
OPV5(2da)	2.42 (2.90)	2.63 (2.70)	754	809	660 ± 80^{a}
CN-OPV5(1da)	2.26 (2.29)	2.47 (2.10)	492	498	210^{b}
OPV5(5da)	2.26 (3.12)	2.47 (2.90)	790	864	860^{b}

All geometries possess the C_{2h} symmetry, Exc in eV, Osc in a.u., $\Delta\alpha$ in Å^3.
[a] In benzene (Reference [5]).
[b] In benzene (Reference [36]).

compared with the experimental result. For instance, the excess polarizabilities for tb-OPV5 were found to be 859 Å^3 for the B3LYP-optimized geometry while 909 Å^3 for the HF-optimized geometry. The former value is more reasonable with respect to the experimental result 810 ± 100 Å^3. Comparing the excess polarizability of tb-OPV5 with that of OPV5 (Table 2), one notes that the tertiary butyl groups on the terminal phenyl rings of OPV5 can increase the excess polarizability by ~10%. For OPV5(1da), the excess polarizabilities predicted at the B3LYP//B3LYP and B3LYP//HF theory levels are 563 and 583 Å^3, respectively. These two results are of similar quality with respect to the experimental result 590 Å^3. In the case of CN-OPV5(1da), the theoretical predictions 492 Å^3 (B3LYP//B3LYP) and 498 Å^3 (B3LYP//HF) are much larger than the experimental result 210 Å^3. This implies that the B3LYP//B3LYP and B3LYP//HF approaches are likely to underestimate the decreasing effect of the cyano group on the excess polarizability when the group substitutes on the vinylene linkage.

The OPV5(5da) molecule studied in the experiment possesses long side alkoxy chains, namely 2-methyl-butyloxy groups.[36] In our calculations, we used the —OCH$_3$ group instead. The repeat unit —CH$_2$— in the alkoxy group will have the insignificant contribution to the excess polarizability. Table 6 indicates that the B3LYP//HF result 864 Å^3 is closer to the experimental finding 860 Å^3 than the B3LYP//B3LYP result 790 Å^3. However, the difference between the B3LYP//B3LYP result and the experimental result is small, within 10% with respect to the experimental result.

Differences between the B3LYP and BP results

It is worthwhile to compare the excess polarizabilities predicted by the B3LYP potential with those by the BP potential for the BP-optimized geometries reported by Grozema *et al.*[10] The BP potential is a typical generalized gradient approximation (GGA) potential, which mainly feels the local electronic density. Different from the BP potential, the B3LYP potential is formed using a linear combination of the exact HF exchange energy functional and the usual GGA energy functional. The addition of the orbital-dependent HF exchange energy can make the B3LYP potential more nonlocal and therefore improve the quality of the result.[32,40,41]

From Table 2, one finds that the excess polarizability predicted at the BP//BP theory level is larger than those predicted at the B3LYP//B3LYP and B3LYP//HF theory levels. This phenomenon is distinct in the cases of OPV3, OPV4, and DPD, which have the relatively large size. For instance, the B3LYP//B3LYP, B3LYP//HF, and BP//BP results for the excess polarizability of OPV4 were calculated to be 391, 421, and 1283 Å^3, respectively. We mention that the BP approach gives the smaller BLA parameter than the B3LYP and HF approaches, as shown in Table 1. It has been demonstrated that the smaller BLA parameter will lead to the smaller excess polarizability. Consequently, one concludes that the BP potential will predict the much larger excess polarizability than the B3LYP potential for large-sized molecules. One finds that the excess polarizabilities of diphenylpolyenes predicted at the BP//BP theory level are overall larger than the corresponding EA experimental results. For instance, the BP//BP result for DPO is 145 Å^3 (Table 2), while the corresponding EA experimental result is 116 Å^3 (Table 5). It can be expected that the difference between the BP//BP result and the EA experimental result will become even large when the local field correction is considered in quantum-chemical calculations.

CONCLUSIONS

This study indicates that TDDFT is a promising approach to predict the 1^1B_u excess polarizabilities of conjugated oligomers. For diphenylpolyenes, the excess polarizabilities calculated at the B3LYP//B3LYP theory level were found to be superior to those at the B3LYP//HF theory level when compared with the experimental results available. However, for OPV molecules this feature is not clearly revealed by our results. The B3LYP potential was found to be too sensitive to the increase in the chain length in predicting the excess polarizability due to the overestimate of the long-range electron correlation. The local field correction to the excess polarizability in solution was calculated to be positive. This implies that the molecule will display the larger Stark shift in solution than in vacuum when under the same applied field.

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