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Experimental and theoretical determination of the dipole polarizability of dibenzothiophene

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ABSTRACT: The dipole polarizability of dibenzothiophene is reported, which was measured experimentally by refractometry techniques, and evaluated theoretically with *ab initio* and density functional theory (DFT) methods in the $^1A'$ electronic ground state. The experimental polarizability was determined from measurements of the refraction index of dibenzothiophene in CCl_4-diluted solutions at five different frequencies to obtain the dispersion curve. The static polarizability of dibenzothiophene was determinated to be 2.358×10^{-23} esu from the extrapolation of the dispersion curve to zero frequency. Theoretical calculations were performed with fully C_{2V} optimized geometries at both the HF/6-31G** and HF/6-31 + G(d,p) levels of theory, and we present comparisons with the crystal structure of dibenzothiophene and HF/6-31G** geometry of benzothiophene previously reported. We calculated the dipole polarizability by using the coupled perturbed Hartree–Fock analytical method, with both the STO/6-31 + G(d,p) and STO/6-31 + G(3d,3p) basis sets. We investigated the effects of exchange and electron correlation on these properties by using the BLYP and B3LYP hybrid approaches. The B3LYP/6-31 + G(3d,3p) average polarizability value of dibenzothiophene is 2.425×10^{-23} esu, which differs from the experimental static value by 3%. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: dibenzothiophene; dipole polarizability; refractometry; density functional theory

INTRODUCTION

The importance of sulfur-containing compounds in the design of molecular electronic devices, pharmacological molecules, and new kinds of polymer-conducting material has renewed interest in the study of their chemistry and electronic properties.[1–3] For example, molecular properties as diverse as dipole polarizabilities are currently being explored in thiophene monomers and polythiophenes by both experimental and theoretical methods.[4,5] In particular, new experimental determination[4a] and *ab initio* calculations of these properties have been reported recently for thiophene[4a,5] and benzothiophene molecules.[6] For thiophene, good agreement was found between the calculated and the measured properties, and prediction for the dipole polarizability of benzothiophene was reported.[6] We are currently interested in the *ab initio* determination and prediction of such optical properties in conjugated heterocyclic molecules obtained with the coupled perturbed Hartree–Fock method (CHF),[7] density functional theory (DFT) approach[8] and the family of diffuse and polarized STO/6-31 + G (md,mp) basis sets,[9] and in the corresponding comparison with available experimental data. Our aim is also to interpret the induced changes in these properties on heteroatom substitutions or by extension of the number of rings in the conjugated system.[5] In this context, we have studied benzene and naphthalene, monocyclic and bicyclic azines, five-membered heterocyclics and benzothiophene.[6] Recently, we have reported DFT dipole polarizabilities for acenaphthene and acenephthylene molecules.[8] Now, we extend these studies to the experimental and theoretical determination of dipole polarizability of the dibenzothiophene (DBT) molecule,

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where the experimental polarizability is determined by using refractometric techniques[10] and is supported with *ab initio* and DFT calculations. We have continued these studies with the dibenzothiophene compound because of the importance of this molecule as a model for understanding the hydrodesulfuration (HDS) process in catalysis, and also because DBT belongs to the class of bicyclic sulfur-conjugated polyenal compounds, which display the largest hyperpolarizabilities ever reported.[11]

This paper is organized as follows: following this Introduction we discuss the theoretical as per in the third section we give experimental and computational details. The fourth section deals with results and discussions; the fifth section gives the conclusions. We report the experimental determination in CCl_4 solution of the static and dynamic dipole polarizability of DBT, together with an *ab initio* and DFT study of the molecular geometry, electronic distribution and the static dipole polarizability α of DBT.

THEORY

The molecular dipole polarizability α is the linear response of a molecular electronic distribution to the action of an external electric field $\Im$. Such an external field causes charge rearrangements in the molecular structure that are reflected in changes in the permanent molecular dipole moment μ_e according to:[12]

$$\mu_e(\Im) = \mu_e(\Im = 0) + \alpha\Im + (1/2!)\beta\Im^2 + (1/3!)\gamma\Im^3 + \ldots \quad (1)$$

In this equation, $\mu_e(\Im = 0)$ is the dipole moment without perturbation, α is a second rank tensor that represent the dipole polarizability, and the higher-order tensors are the first and second hyperpolarizabilities respectively. Similarly, a Taylor expansion for the energy E of the system has been defined in terms of these tensor quantities and the field $\Im$ in the Cartesian axis system as

$$E(\Im) = E(0) - \mu_i\Im_i - \left(\frac{1}{2}\right)\alpha_{ij}\Im_i\Im_j - \left(\frac{1}{6}\right)\beta_{ijk}\Im_i\Im_j\Im_k - \left(\frac{1}{24}\right)\gamma_{ijkl}\Im_i\Im_j\Im_k\Im_l + \ldots \quad (2)$$

where $E(0)$ is the unperturbed energy.[12a] In polarizability studies, the quantities of experimental interest are the average polarizability

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

and the polarizability anisotropy

$$\Delta\alpha = \{(1/2)[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]\}^{\frac{1}{2}} \quad (4)$$

The mean polarizability can be determined from the refractive index η of a gas according to the equation

$$\eta = 1 + \frac{\langle\alpha\rangle\pi}{2\varepsilon_0 k_B T} \quad (5)$$

where π is the pressure, k_B the Boltzmann constant, T the thermodynamic temperature and ε_0 the permittivity of free space. Equation (5) has been derived with the assumption that the individual molecules do not interact with each other. In the condensed phase, the molecular interaction should be considered, where each molecule is polarized by the external field and the field due to the neighboring molecules. The resultant field is named the local field F, and is expressed in terms of the dielectric polarization P as

$$F = E + \frac{L}{\varepsilon_0}P \quad (6)$$

where L is the dimensionless Lorentz factor, which depends on the structure of the phase. L is a tensor the three principal components of which have the value of 1/3 for cubic and isotropic phases, giving the Lorentz local field

$$F = E + \frac{1}{3\varepsilon_0}P \quad (7)$$

From this equation can be derived the Lorenz–Lorentz equation

$$\frac{\eta^2 - 1}{\eta^2 + 2} = \frac{N\langle\alpha\rangle}{3\varepsilon_0 V} \quad (8)$$

which gives an expression for the molecular polarizability $\langle\alpha\rangle$. Here, N is the number of molecules in volume V.

For molecules with a permanent dipole moment μ_e, it is necessary to take account of the orientation polarization. The resulting Debye equation

$$\frac{M}{\rho}\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N_A}{3\varepsilon_0}\left(\langle\alpha\rangle + \frac{\mu_e^2}{3k_B T}\right) \quad (9)$$

permits the average polarizability $\langle\alpha\rangle$ and dipole moment μ_e to be determined from measurements of the relative permittivity ε_r and the density ρ as a function of the temperature T.[12b] M is the molar mass and N_A the Avogadro constant. The application regime of this equation is for pure compounds only.

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Usually, the dipole polarizability is determined experimentally at electric fields that depend on the frequency giving the dynamic property. At the regime of optical frequencies, Eqn. (9) is converted to Eqn. (8). From this equation and for binary mixtures, such as solvent and solute, the equation of Garito and Singer in the cgs system can be derived (Eqn. (10)).[13a]

$$\frac{4\pi}{3}N_{\mathrm{A}}\alpha^{\mathrm{e}}_{2_{(v)}} = \frac{3\mathrm{M}_2}{\rho_1(\eta_1^2(v)+2)^2}\left(\frac{\partial\eta^2_{(v)}}{\partial w}\right)_0 + M_2\left[\frac{1}{\rho_1}+\left(\frac{\partial V}{\partial w}\right)_0\right]\left(\frac{\eta^2_{1_{(v)}}-1}{\eta^2_{1_{(v)}}+2}\right) \tag{10}$$

where w is the weight fraction of solute, $\eta_{(v)}$ and $\eta_{1_{(v)}}$ are the refraction indexes of the solution and solvent respectively at optical frequency v, ρ_1 is the density of the solvent, N_{A} is Avogadro's number, M_2 is the molecular weight of solute, V is the specific volume of solution, and $\alpha^{\mathrm{e}}_{2_{(v)}}$ is the average of the molecular electronic dynamic polarizability of the solute. This equation assumes that solute and solvent are not interacting and, therefore, the different molecular polarizations are additive. To obtain the static mean molecular electronic polarizability, the polarizability is treated as a frequency-dependent quantity and calculated at different wavelengths according to Eqn. (10). The long-wavelength limit is obtained from an extrapolation to zero frequency of the plot between the dynamic mean polarizability $\alpha^{\mathrm{e}}_{2_{(v)}}$ versus the frequency v. This relationship is referred to as the Cauchy-type dispersion curve and gives the behavior of the dispersion of the polarizability in terms of the frequency of the field. This curve allows for the extrapolation of only the electronic part of this property, the limit value of which corresponds to the static dipole polarizability. Contributions from infrared-active modes (vibrational polarizability) are not considered here.[13b,c]

METHODS

Experimental section

The average electronic polarizability dispersion curve of dibenzothiophene was determined experimentally by using the refractometric technique, where the refractive index η of both solvent and solution were measured with a Bellingham + Stanley high-resolution ABBE refractometer 60/LR at 20 °C (±0.1 °C). Spectral lamps of sodium, mercury and cadmium were employed on the wavelength range 435.8–643.8 nm. Densities ρ were measured on a DMA-5000 Anton Paar densitometer.

DBT compound was purchased from Aldrich and sublimed prior to use. Carbon tetrachloride (Merck) was employed as solvent after drying ($\mathrm{CaCl_2}$), fractionation and storage over molecular sieves. The range of concentration used was (2.8–27.8) $\times 10^{-3}$ M.

The reproducibility for the various slopes of the concentration dependence for this data is very high and the uncertainties in dynamic mean electronic polarizabilities obtained in this work are between 0.9 and 2%.

Computational details

The calculations of the polarizability α were performed by using the analytical and direct CHF method[7] with a selection of diffuse and polarized basis sets, which were constructed by starting from the standard STO/6-31G frame and extending it with either sp diffuse functions plus d and p polarized functions, leading to the standard scheme denoted by STO/6-31 + G(d,p) and STO/6-31 + G(3d,3p) respectively.[9] These atomic functions have shown good performance for polarizability calculations of conjugated molecules.[6,8] Exchange and electron correlation effects on the dipole polarizability were determined by using DFT calculations at the BLYP and B3LYP hybrid approaches,[14] by using both the STO/6-31 + G(d,p) and STO/6-31 + G(3d,3p) basis sets.

Calculations were performed with optimized DBT molecular geometry, by using gradient techniques at the SCF MO STO/6-31G** and STO/6-31 + G(d,p)[9] levels subject to C_{2v} symmetry. Calculations of α were carried out by using direct techniques with the Gaussian 98[15] quantum chemistry package on an Intel dual Pentium III Graphic Workstation under Windows 98 operating system and Origin 2000 Silicon Graphics six R10000 MIPS processors.

RESULTS AND DISCUSSION

Geometry and electronic properties of DBT

Formally, the DBT molecule is constructed by the fusion of two benzene rings between a sulfur atom as bridge, giving a three fused-rings structure, where the S is located between these rings linked to two C atoms and each C atom belongs to each ring. This atomic conformation leads to a geometric structure known as DBT. Owing to the electronic pairs of the S atom, the linked C atoms form a C—S—C angular bond that is almost planar and whose angle should be about 90°, such as in thiophene. Furthermore, the electronic pairs of S are understood to be far away, oriented in the two corners of the tetrahedral positions that are located perpendicular to the C—S—C plane. In the present work, we report HF/6-31G**, HF/6-31 + G(d,p) and BLYP/6-31 + G(d,p) C_{2v} optimized structures for gaseous DBT, and comparison is made with selected theoretical parameters of thiophene, benzothiophene and in more detail with the crystal structure of DBT. With respect to the optimization

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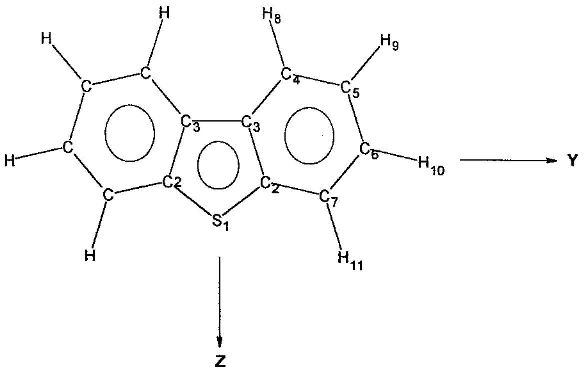

Figure 1. Atom numbering and orientation axis in DBT

geometry of DBT, a harmonic vibrational analysis showed that all eigenvalues of the Hessian matrix were positive, indicating that the reported structure is an absolute minimum of energy, where the electronic ground state of this molecule is $^1A'$.

The numbering and geometric parameters for DBT are presented in Fig. 1, and the optimized values are displayed in Table 1, together with those corresponding to the experimental crystal structure of this molecule.[16] Additionally, Table 1 shows selected optimized geometric parameters of thiophene and benzothiophene in parentheses for comparison. It is worth noting that the C—S bonds in DBT are similar to those reported for thiophene and benzothiophene.[5] In particular, the C—S bonds are typically larger than those of C—C. In this series of compounds, the C—S bond is slightly larger in DBT than in thiophene and benzothiophene. With respect to the bond angles, the C—S—C angle value in DBT is about of 90.9° and is similar to that reported for thiophene, 91.3°. The optimized C—S—C bond angle in DBT is independent of the basis sets and of the level of theory employed.

Analysis of the results in Table 1 indicates that the thiophene moiety is only slightly affected by the fusion of the two benzene rings when the DBT structure is formed. It is observed that the patterns of bond distance and bond angles of the heteroring are nearly similar to those in the thiophene and benzothiophene structures. The small differences between these geometric features suggest that the DBT structural–electronic properties can be

Table 1. C_{2V}-optimized geometry of DBT

R_{ij} (Å)	HF/6-31G**	HF/6-31 + G(d,p)	BLYP/6-31 + G(d,p)	Experiment
*d*C2S1	1.7591 (1.7434)[a] (1.7252)[b]	1.7585	1.7841	1.7345
*d*C3C2	1.3941	1.3951	1.4274	1.4073
*d*C4C3	1.3941	1.3957	1.4151	1.3915
*d*C5C4	1.3781	1.3804	1.4025	1.3625
*d*C6C5	1.3945	1.3968	1.4153	1.3900
*d*C7C6	1.379	1.3814	1.4047	1.3961
*d*C7C2	1.3885	1.3904	1.4077	1.3841
*d*H8C4	1.0754	1.0754	1.0933	
*d*H9C5	1.0753	1.0753	1.0929	
*d*H10C6	1.0755	1.0754	1.0931	
*d*H11C7	1.0752	1.0752	1.0927	
*d*C3C3	1.4622	1.4626	1.4624	1.4414
<*ijk* (°)				
*a*C3C2S1	112.52	112.57	112.34	112.86
*a*C4C3C2	119.07	119.11	118.61	119.35
*a*C5C4C3	119.72	119.71	119.94	119.50
*a*C6C5C4	120.49	120.48	120.56	121.06
*a*S1C2C7		125.96	125.96	
*a*C3C2C7		121.47	121.70	
*a*C7C6C5	120.64	120.61	120.67	121.06
*a*C2C7C6		118.62	118.52	117.47
*a*H8C4C3	120.29	120.34	119.99	
*a*H9C5C4	119.83	119.84	119.75	
*a*H10C6C5	119.75	119.76	119.85	
*a*H11C7C6	120.66	120.61	120.63	
*a*C2S1C2	90.91 (91.30)[a]	90.929	90.87	91.51
*a*C3C3C2		111.98	112.22	111.40

[a] Thiophene, Ref. 5.

[b] Benzothiophene, Ref. 6; experiment Ref. 16.

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Table 2. Total energy, dipole moment and Mulliken atomic charge Q in the S and C atoms for DBT

	HF/6-31 + G(d,p)	BLYP/6-31 + G(d,p)
Total energy (a.u.)	−856.641381	−860.115938
Dipole moment (D)	1.16	0.71 (0.79)[a] (0.78)[b]
Q(S1)	+0.2474	−0.0590
Q(C2)	−0.6641	−0.7261
Q(C3)	−0.9862	0.9126
Q(C4)	−0.3199	−0.3090
Q(C5)	−0.1336	0.0093
Q(C6)	−0.2725	−0.2457
Q(C7)	−0.1613	−0.0524

[a] This work, with the B3LYP/6-31 + G(3d,3p) method.
[b] Experimental, Ref. 13d.

understood by extension of those for thiophene and benzene. Likewise, the differences in the properties of these compounds could be due to the charge rearrangements that occur in the DBT molecule by the effect of the added perturbation of the two benzene rings. The results in Table 1 show that the calculated geometry of DBT follows the geometric parameter pattern from the experimental structure.[16]

Table 2 shows the total energy, charge distribution and dipole moment of DBT. The charge distribution is calculated in terms of the Mulliken atomic population of the S (Q(S)) and C (Q(C)) atoms. An analysis of these populations, calculated at the HF/6-31 + G(d,p) level, indicates that very small changes in the charge distribution are induced when the benzene rings are fused with the S atom to form the DBT moiety. However, these charges are very sensitive to the level of calculations, which are reflected in the total dipole moment, as expected. For example, at the HF/6-31 + G(d,p) level the value of dipole moment is 1.16 D, whereas at BLYP/6-31 + G(d,p) it is 0.71 D and with B3LYP/6-31 + G(3d,3p) it is 0.79 D. This value is in excellent agreement with the experimental high accuracy dipole moment reported for this molecule by Nagai *et al.* of 0.79 D.[13d]

Polarizability of DBT

Experimental determination. No estimates for the molecular dipole polarizability of DBT have been reported so far. In the present work we report a static value of this property from refractometric measurements and using the limit relationship of Garito and Singer (see Eqn. (10)). The performance of this methodology has been reported elsewhere.[17] Prior to the refractometric measurements, the UV–VIS spectra of DBT was determined in the region between 200 and 450 nm, in order to explore the adsorption of this compound. It was found that the lower adsorption wavelength of adsorption of this molecule is 330 nm. With this result, we study the dispersion of the dipole polarizability of DBT in the region off-resonance. The experimental frequency-dependent results of the relevant terms of Eqn. (10) are reported in Table 3, and the corresponding Cauchy-type dispersion curve of dipole polarizability is displayed in Fig. 2. The dynamic results of the dipole polarizability show how this property increases monotonically with the frequency ν, giving a normal dispersion behavior for the DBT polarizability. From this relationship, the extrapolation to zero frequency gives a value of 2.358×10^{-23} esu for the static dipole polarizability of DBT in CCl_4. The uncertainty in this value, calculated from an analysis of propagation of random errors, is about 3%.[13b]

The static value determined for DBT of 2.358×10^{-23} esu lies in the range of dipole polarizabilities of aromatic molecules with three fused rings. For example, the dynamic average dipole polarizability of anthracene at 589.8 nm in benzene solution has the value of 2.54×10^{-23} esu,[18] which is only 8% higher than our experimental static value for DBT. This difference is expected because of the dynamic effects. For example, at 589.8 nm (1.696065 μm^{-1}) the DBT α mean has a value of 2.427×10^{-23} esu (see Table 3), which is 5% lower than that of anthracene. However, this difference is due to the fact that the DBT molecular size is smaller than the anthracene molecule. It is important to note that the dispersion behavior of dynamic polarizability of DBT, as can be seen in Fig. 2, shows that the molecular response is not enhanced by the effects of the frequency of the

Table 3. Results of least-squares fit to the concentration dependence of index of refraction, density of solutions and dipole polarizability of DBT in CCl_4

ν (μm^{-1})	$\left(\frac{\partial n^2_{(\nu)}}{\partial w}\right)_0$ (at 20 ± 0.1 °C)	n_1 (at 20 ± 0.1 °C)	$\alpha_2^e(\nu) \times 10^{-23}$
2.294631	1.245 ± 0.011	$1.472384 \pm 5 \times 10^{-5}$	2.590
1.966182	1.125 ± 0.010	$1.464933 \pm 3 \times 10^{-5}$	2.483
1.831166	1.091 ± 0.012	$1.462519 \pm 1 \times 10^{-5}$	2.452
1.696065	1.065 ± 0.011	$1.460000 \pm 1 \times 10^{-5}$	2.427
1.553277	1.047 ± 0.012	$1.457779 \pm 2 \times 10^{-5}$	2.407
0.00000			2.358

$\left(\frac{\partial \nu}{\partial w}\right)_0 = 0.158745 \pm 0.004$ at 20 ± 0.1 °C.
$\rho_1 = 1.593995 \pm 6 \times 10^{-6}$ g cm^{-3} at 20 ± 0.1 °C.

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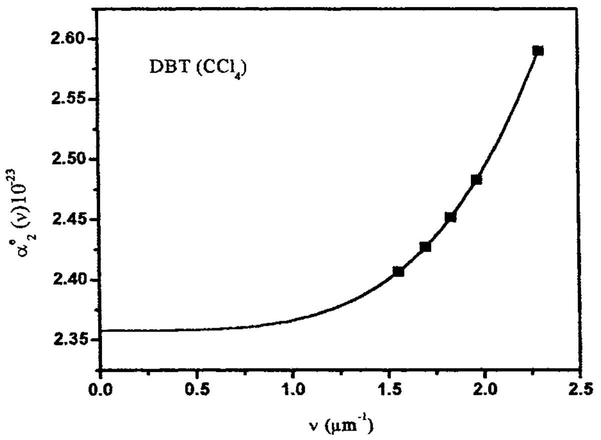

Figure 2. Frequency dependence of the mean dipole-polarizability $\alpha(\nu)$ of DBT in CCl$_4$

electric field, as expected for conjugated systems of three fused rings. For example, the variation of polarizability at 435.8 nm with respect to the static value for dibenzothiophene is 9% whereas for anthracene the corresponding variation is 25%.[19] These results indicate that despite DBT having a static polarizability close to the anthracene molecule, the electric deformability of the sulfur compound is much less than for the three fused ring hydrocarbon compound, which suggests a bigger contribution of the delocalized π electrons in this molecule than for the title molecule. Further studies in this context are being performed in our laboratory.

Theoretical calculations. In the present work, the dipole polarizability components (α_{xx}, α_{yy} and α_{zz}) have been calculated independently using *ab initio* (HF) and DFT (BLYP, B3LYP) methods with the STO/6-31 + G(d,p) and STO/6-31 + G(3d,3p) extended basis sets. These calculations were performed with DBT optimized geometries at HF and BLYP respectively, with the orientation of the molecular axis system as shown in Fig. 1. This orientation follows the order of polarizabilities $\alpha_{xx} < \alpha_{yy} < \alpha_{zz}$. From these independent components, the corresponding average polarizability α_{ave} and the polarizability anisotropy $\Delta\alpha$ of DBT were calculated. The results are reported in Table 4.

The predicted static average polarizability value for the DBT molecule at the HF/6-31 + G(d,p) level is 2.173×10^{-23} esu. The comparison of this value with our experimental measurement indicates that, at the HF level, the theoretical property value is lower than the experimental one, with a difference of 8%. These results show that for DBT the HF calculations underestimate the experimental dipole polarizability, which is as expected.

Exchange and electron correlation in DBT dipole polarizability. The contribution of exchange and electron correlation effects for polarizabilities has not yet been rationalized for heteroaromatic molecules. In this context, an accurate estimate at the DFT level of these effects on the polarizabilities of conjugated and heterocyclic molecules is being carried out in our laboratory. It is important to note at this point that DBT is a fairly large molecule, where an adequate basis set and a good level of exchange-correlation are determining factors in the requirement for high accuracy in the theoretical determination of dipole polarizabilities, which is a demanding computational task for the molecule studied in this work. With respect to these requirements, we have shown that though the family of 6-31 + G(md,np) with (m = 1,2,3; n = 1,2,3) is not a specialized basis set for polarizability calculations, these atomic functions within the BLYP approach constitute a reasonable methodology for good values of polarizabilities in conjugated molecules.[6,8,20] In the present work, in order to explore the performance between the B3LYP and BLYP approaches, we have accounted for the exchange and electron correlation effects for the dipole polarizability of DBT at these two levels of the DFT hybrid approaches. The BLYP level was calculated with the STO/6-31 + G(d,p) basis set and the extension of the basis was considered by using the STO/6-31 + G(3d,3p) atomic function. Results are depicted in Table 4. The results show that the BLYP values, compared with the corresponding HF polarizability, are increased in the three main components of α, giving a value for α_{ave} of

Table 4. Components α_{ii} (i = x, y, z) and average α_{ave} of the dipole polarizability of DBT (10^{-23} esu)

	α_{xx}	α_{yy}	α_{zz}	α_{ave}
		Geometry HF/6-31 + G(d,p)		
HF/6-31 + G(d,p)	1.171	2.264	3.085	2.173
		Geometry BLYP/6-31 + G(d,p)		
BLYP/6-31 + G(d,p)	1.234	2.546	3.724	2.501
BLYP/6-31 + G(3d,3p)	1.283	2.538	3.665	2.495
B3LYP/6-31 + G(3d,3p)	1.260	2.485	3.524	2.425
Static experimental (this work)				2.358

2.501×10^{-23} esu, which is 18% higher than for the HF approach. At the BLYP level, the effects of extension of the STO/6-31 + G(d,p) basis set with additionally included polarized functions as STO/6-31 + G(3d,3p) produce a slight increasing in α_{xx} component, but the other components are decreased, giving $\alpha_{\text{ave}} = 2.495 \times 10^{-23}$ esu. The overall effect of this extension of the basis set is relatively small, leading to a reduction in the polarizability of about 0.24%. In the application of the B3LYP method with the STO/6-31 + G(3d,3p) basis, it is observed that the three main components of α are decreased, giving a value of 2.425×10^{-23} esu for α_{ave}, which is a difference with respect to the corresponding BLYP of 2.8%. We consider that the value of α_{ave} calculated with the B3LYP/6-31 + G(3d,3p) approach is our best theoretical estimated for the static dipole polarizability of the DBT molecule. The comparison between the experimental static results and the best theoretical value show that the α_{ave} at B3LYP/6-31 + G(3d,3p) is 2.8% higher than the experimental one.

The comparison of the DBT polarizability with that of anthracene, whose average polarizability has recently been reported at BLYP/6-31 ++ G(3d,2p) as 2.58×10^{-23} esu,[20] is relatively higher for DBT with comparable calculations, which is 2.495×10^{-23} esu at BLYP/6-31 + G(3d,3p) (see Table 4).

CONCLUSIONS

We have reported refraction measurements of the average dipole polarizability α_{ave} of DBT in CCl_4 solution, and we have performed *ab initio* and DFT calculations about this property as support for the experimental results. Additionally, a study of the geometry and other electronic properties of DBT is reported, and comparison with the crystal structure of DBT was undertaken. The technique of Garito and Singer at limit dilution was employed for the experimental determination of α_{ave}, giving a static value of 2.358×10^{-23} esu. On the other hand, our best estimated value of this property has been chosen as 2.425×10^{-23} esu from B3LYP/6-31 + G(3d,3p) calculations with the BLYP/6-31 + G(d,p) optimized geometry. The differences between these experimental and theoretical values are less than 3%. Comparison was made with the experimental and theoretical polarizabilities of anthracene.

The effects of the frequency on the dipole polarizability of DBT were compared with those for anthracene. The results showed that the DBT electronic deformability is less than that of anthracene when the frequency of the field is taken into consideration.

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