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Static and dynamic dipole polarizabilities of 2- and 3-methylthiophenes in solution: experimental and theoretical determination

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ABSTRACT: The dynamic and static dipole polarizabilities of 2-methythiophene (2MT) and 3-methylthiophene (3MT) molecules were investigated using refractometric and theoretical calculations. The experimental properties were studied within the Garito and Singer approach for dilute CCl_4 and CH_3CN solutions. The local field effects were tested with the Onsager and Lorentz local fields. The static dipole polarizabilities of 2MT and 3MT were obtained from extrapolation to zero frequency of the corresponding dispersion Cauchy-type curves, which gave a monotonic increase as a function of the squared frequency. The differences between these curves were analyzed as a function of the solvent effects and the local fields. The theoretical static properties were evaluated by using *ab initio* (Hartree–Fock) and density functional theory (DFT) (BLYP and B3LYP) methods with the 6–31 + G(d,p), 6–311 ++ G(3d,3p) and Sadlej basis sets. The dynamic polarizabilities were calculated with the time-dependent Hartree–Fock (TDHF) approach and the 6–31 + G(d,p) and Sadlej basis sets. In order to make a comparison with the experimental results, the solvent effects were studied at the TDHF level in both CCl_4 and CH_3CN solvents and the Onsager model. The calculations were performed with fully optimized geometries. The experimental values of the static dipole polarizabilities of the 2MT and 3MT were determined as 1.129×10^{-21} and 1.140×10^{-21} esu, respectively, whereas the corresponding B3LYP/6–311 ++ G(3d,3p) values were 1.151×10^{-21} and 1.139×10^{-21} esu, respectively. Additionally, for the B3LYP/Sadlej method the corresponding values were 1.176×10^{-21} and 1.174×10^{-21} esu, respectively. In general, there was good agreement between the experimental and the DFT theoretical results. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: methylthiophenes; dipole polarizability; solvent effects; electric local fields

INTRODUCTION

The field of linear and non-linear optical properties of molecules and polymers with delocalized π-electron systems has received considerable attention from both experimental and theoretical points of view during recent years.[1] Polythiophenes have a very special position in this respect, because these compounds are the starting point materials for the design of new electronic devices with technological applications. Despite the significant progress that has been achieved in the relations between the optical properties and electronic nature of these materials, the electronic structure of polythiophene and similar polymers has been difficult to study experimentally. However, monomer and oligomer 'building block' units are selected as samples, and their properties are often extrapolated to real polymers.[2,3] In this context, the determination of the optical response properties of thiophenes and their methyl derivatives are very important for understanding the electronic features of large molecules containing thiophenic units such as polythiophenes. Therefore, a knowledge of the linear response of electronic systems toward an external electric field can provide detailed information about the electronic structure of these molecules that can be extrapolated

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to large systems.[4,5] In fact, the molecular dipole polarizability α is a fundamental property of the matter. It describes the deformability of the charge distribution of an electronic system under the influence of a weak external electric field. This property, which can be determined experimentally and calculated theoretically, gives valuable information about the π-electron delocalization in conjugated molecules such as thiophenes.[6] The polarizability is measured experimentally at the frequencies of the external field, and it is referred as the dynamic polarizability, whereas the static property is obtained by extrapolating the dynamic polarizability to zero frequency. The behavior of the polarizability in the regime of frequencies is well known as the dispersion of the polarizability referred as the Cauchy curve.

The optical properties of thiophene have been extensively studied, both experimentally and theoretically.[6–9] However, little is known about its methyl derivatives, such as 2- and 3-methylthiophene. In fact, 3-methylthiophene (3MT) is the monomer species of regioregular (RR) and regiorandom (RRa) substituted polythiophene polymers, such as poly(3-methylthiophene) (P3MT). In particular, the (RR)-(P3MT) polymers form thin films with nanocrystalline lamellae with high hole mobilities, that are used to build integrated circuits.[10] In these compounds, the role of intermolecular interactions and the frequency dependence of the polarizability are unknown in solution, and no experimental measurements in solution and theoretical calculations on these electronic properties have been reported so far. The frequency dependence of the polarizability is important in many areas of chemical physics and physical chemistry, and has been related to concepts of chemical interest such as hardness, aromaticity and electronegativity.[6–8,11]

In order to gain an insight into the electronic properties of alkylthiophenes, we report the first measurement of the static and dynamic electronic mean polarizability and the dispersion of the polarizability of 2- and 3-methylthiophene compounds in solution, by using refractometric techniques. For these molecules we have studied the effect of solvents on their polarizabilities using CCl_4 and CH_3CN as solvents. Furthermore, we have performed theoretical calculations on the geometries, dipole moments and the static dipole polarizability at *ab initio* CPHF[12] and TDHF[13] levels of theory with standard[14] and polarized Sadlej[15] basis sets. Exchange and electron correlation effects on these properties were taken into account using density functional theory (DFT) methods with the BLYP and B3LYP schemes.[16] Finally, in order to make a comparison with the experimental dynamic properties, the theoretical solvent effects of CCl_4 and CH_3CN solvents on the polarizability of 3MT were evaluated with the TDHF method using the local field of the Onsager model.[17]

The accuracy of the theoretical and experimental methodologies used here was tested for the dipole polarizability determination of dibenzothiophene molecule in solution.[18] The difference between the measured and calculated static dipole polarizability for this molecule lies within a 3% experimental error. We expect the same accuracy for the results reported in the present work for 2MT and 3MT compounds.

THEORY AND METHODS

Theoretical considerations

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 induces charge rearrangements that are reflected in changes in the permanent molecular dipole moment (μ_e) according to the equation[18]

$$\mu_e(\Im) = \mu_e(\Im = 0) + \alpha\Im + (1/2!)\beta\Im^2 + (1/3!)\gamma\Im^3 + \cdots \tag{1}$$

where $\mu_e(\Im = 0)$ is the dipole moment without perturbation, α is a second-rank tensor that represents 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 the dipole polarizabilities and the field $\Im$ as

$$E(\Im) = E(0) - \mu\Im - (1/2)\alpha\Im^2 - (1/6)\beta\Im^3 - (1/24)\gamma\Im^4 + \cdots \tag{2}$$

where $E(0)$ is the unperturbed energy. In polarizability studies, the quantities of experimental interest are the mean polarizability α_{ave}:

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

and the polarizability anisotropy $\Delta\alpha$:

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

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

$$\eta = 1 + \frac{2\pi\langle\alpha\rangle\sigma}{k_B T} \tag{5}$$

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

$$F = E + 4\pi LP \tag{6}$$

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

$$F = E + \frac{4\pi}{3}P \tag{7}$$

From this equation, it is possible to derive the Lorenz–Lorentz equation:

$$\frac{\eta^2 - 1}{\eta^2 + 2} = \frac{4\pi}{3}\frac{N\langle\alpha\rangle}{V} \tag{8}$$

which gives an expression for the mean molecular dipole polarizability $\langle\alpha\rangle$, and where N is the number of molecules in a volume V. For molecules with a permanent dipole moment (μ_e), it is necessary to take into account the orientational polarization. The resulting Debye equation:

$$\frac{M}{\rho}\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{4\pi N_A}{3}\left(\langle\alpha\rangle + \frac{\mu_e^2}{3k_B T}\right) \tag{9}$$

permit the polarizabilities $\langle\alpha\rangle$ 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.[19] M is the molar mass and N_A is Avogadro's constant. The application regime for this equation is only for pure compounds.

Experimental considerations

It is well known that the dipole polarizability is determined at electric fields that depend on the frequency and the dynamic property is obtained. In the range of optical frequencies, Eqn. (9) is converted into Eqn. (8). For binary mixtures, such as solvent and solute, the equation of Garito and Singer can be derived as[20]

$$\begin{aligned}\frac{4\pi}{3}N_A\alpha^e_{2_{(\nu)}} &= \frac{3M_2}{\rho_1[\eta_1^2(\nu)+2]^2}\left(\frac{\partial\eta^2(\nu)}{\partial w}\right)_0 \\ &\quad + M_2\left[\frac{1}{\rho_1} + \left(\frac{\partial V}{\partial w}\right)_0\right]\left(\frac{\eta^2_{1_{(\nu)}} - 1}{\eta^2_{1_{(\nu)}} + 2}\right)\end{aligned} \tag{10}$$

where w is the weight fraction of solute, $\eta_{(\nu)}$ and $\eta_{1_{(\nu)}}$ are the refractive indices of solution and solvent at optical frequency (ν), respectively, ρ_1 is the density of the solvent, N_A is Avogadro's number, M_2 is the molecular weight of the solute, V is the specific volume of solution and $\alpha^e_{2_{(\nu)}}$ is the average of the molecular electronic dynamic polarizability of the solute. This equation assumes that the 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 wave-numbers, and the limit is obtained from an extrapolation to zero frequency (infinite wavelength) of the plot between the dynamic mean polarizability $\alpha^e_{2_{(\nu)}}$ and the wavenumber, ν. This relationship, called the Cauchy-type dispersion curve, gives the dispersion of the polarizability as a function of the frequency of the field and allows for the extrapolation of the electronic part of this property, the limit value of which is the static dipole polarizability. Contributions from infrared-active modes (vibrational polarizability) are not considered here.[21]

Experimental methods

The dispersion curves were determined with the refractometric technique of Garito and Singer [Eqn. (10)] and the static polarizability was evaluated from extrapolation of these curves to zero wavenumber. The refractive index η of both solvent and solution were measured with Bellingham + Stanley high-resolution ABBE 60/LR and 60/LR refractometers with a CCD camera, thermostated on an LAUDA RM6 at 20 °C (±0.1 °C). Sodium, mercury and cadmium spectral lamps were employed in the wavelength range 435.8–643.8 nm. Densities ρ were measured on an Anton Paar DMA-5000 densitometer.

2MT and 3MT were purchased from Aldrich and purified rigorously prior to use. Carbon tetrachloride (Merck) and acetonitrile (Aldrich) were employed as solvents after drying over a $CaCl_2$ bed and storage over a molecular sieve. The concentration range used was 0.207–1.035 M.

For the determination of the dynamic polarizabilities of 2MT and 3MT, the Lorentz–Lorentz[19] and Onsager[22] local field factors were employed within the Garito and Singer approximation [Eqn. (10)]. For the molar refraction and the Lorentz–Lorentz local field, Eqn. (10) remains unaltered. However, for the Onsager factor, Eqn. (10) at the infinite dilution limit becomes

$$\begin{aligned}&\frac{N_A}{M_2}\alpha^e_2(\nu)\left[\frac{\eta_1^2(\nu)[\eta_2^2(\nu)+2]}{2\eta_1^2(\nu)+\eta_2^2(\nu)}\right] \\ &\quad = \frac{1}{4\pi\rho_1}\left[\frac{\partial\eta^2(\nu)}{\partial w}\right]_{w\to 0} + \frac{\eta_1^2(\nu)-1}{4\pi}\left(\frac{\partial V}{\partial w}\right)_{w\to 0} \\ &\quad + \frac{\eta_1^2(\nu)-1}{4\pi\rho_1} - \frac{\eta_1^2(\nu)-1}{4\pi\rho_1}\left[\frac{1}{3\eta_1^2(\nu)}\right]\left[\frac{\partial\eta^2(\nu)}{\partial w}\right]_{w\to 0}\end{aligned} \tag{11}$$

where w is the solute weight fraction, $\eta_{(\nu)}$, $\eta_{1_{(\nu)}}$ and $\eta_{2_{(\nu)}}$ are the refractive indices at the optical frequency (ν) of the solution, solvent and solute, respectively, ρ_1 is the density of the solution, M_2 is the solute molecular weight, V is the specific volume of solution, N_A is Avogadro's number and $\alpha^e_2(\nu)$ is the electronic part of the mean dynamic polarizability of a molecule of solute. In this case, the $\eta_{2_{(\nu)}}$ values determined in the present work for pure 2MT and 3MT agree very well with previous values

Table 1. Dynamic electronic polarizabilities of 2MT and 3MT in CCl_4 solution[a]

	2MT		3MT	
Frequency ν (μm^{-1})	$\alpha_2^e(\nu)(10^{-23}$ esu)[b]	$\alpha_2^e(\nu)(10^{-23}$ esu)[c]	$\alpha_2^e(\nu)(10^{-23}$ esu)[b]	$\alpha_2^e(\nu)(10^{-23}$ esu)[c]
2.294631	1.226	1.227	1.227	1.227
1.966182	1.197	1.198	1.198	1.199
1.831166	1.188	1.188	1.189	1.190
1.696065	1.178	1.178	1.181	1.181
1.553277	1.170	1.170	1.174	1.174
0.00	1.130	1.128	1.147	1.141
	1.119[d]		1.119[e], 1.149[f] 1.107[g]	

[a] $T = 20 \pm 0.1\,°C$, $(\partial V/\partial w)_0 = 0.3543 \pm 0.003$, $\rho_1 = 1.5940\ g\ cm^{-3}$.

[b] Eqn. (10) using Lorentz local field.

[c] Eqn. (11) using Onsager local field.

[d] Neat 2-MT (Ref. 23a).

[e] Neat 3-MT (Ref. 23a).

[f] Empirical method, α(ahp) (Ref. 29).

[g] Empirical method, α(ahc) (Ref. 29).

reported in the literature for these compounds.[23] To minimize specific solute–solute interactions, the slopes of the dispersion curves were determined at infinite dilution, where it is assumed that no significant interactions between the solute and solvent occur, and therefore the molecular polarizations are additive. The reproducibility of the experimental parameters, and those from the corresponding slopes of the concentration dependence for the resultant data, is very high and the uncertainties in the dynamic mean electronic polarizabilities obtained in this work were in the range 0.6–1.1%.

To obtain the static mean molecular electronic polarizability, this property was treated as a frequency-dependent quantity and calculated at different wavelengths according to Eqns (10) and (11). The long-wavelength limit can be obtained from an extrapolation of the frequency dependence of the mean polarizability $\alpha_2^e(\nu)$ of the Cauchy-type dispersion curve to zero wavenumber. This dispersion curve allows only for an extrapolation of the electronic part of the polarizability. Contributions from infrared-active modes (vibrational polarizability) are not covered by these equations.[7,21]

Theoretical calculations

Theoretical calculations of the geometries and the static dipole polarizabilities of 2MT and 3MT were performed as support for the experimental determinations. The calculations were carried out at the Hartree–Fock CPHF SCF-MO[12] and the time-dependent Hartree–Fock[13] levels, by using the standard 6–311 ++ G(3d,3p)[14] and the specialized basis sets of Sadlej.[15] These basis sets have shown good performance for polarizability calculations.[18,24] However, for this kind of property, we took into account the electron correlation effects by using DFT methods with the BLYP and B3LYP hybrid schemes.[16] Recently, it has been shown that B3LYP approach is able to give accurate values of static dipole polarizabilities for conjugated molecules.[18,24] The calculations were carried out with the Gaussian quantum chemistry package.[25] The CCl_4 and CH_3CN solvent effects and the dynamic effects in 3MT were accounted for in the dipole polarizability of this compound by using the Onsager model[17] within the TDHF method and the 6–31 + G(d,p) and the Sadlej basis sets. These TDHF calculations were performed with the Gamess program.[26]

RESULTS AND DISCUSSION

Experimental results

Tables 1 and 2 give the results of the experimental measurements of the dynamic electronic polarizabilities for 2MT and 3MT in dilute solutions of CCl_4 and CH_3CN solvents, respectively. These tables display the dynamic results of the average electronic dipole polarizabilities $\alpha_2^e(\nu)$, obtained from the Lorentz [Eqn. (10)] and Onsager [Eqn. (11)] local fields, in the range of optical frequencies represented as wavenumbers, for the 2MT and 3MT molecules. The corresponding dispersion Cauchy curves of $\alpha_2^e(\nu)$for these compounds in solutions of CCl_4 are displayed in Fig. 1 and the corresponding results in CH_3CN solution in Fig. 2. These dispersion curves, in the different solvents and with the local fields, show a monotonic increase in the electric polarizability with increase in wavenumber, where the frequency dependences on the electronic part of the mean polarizability $\alpha_e(\nu)$ follow Cauchy-type curves. It is observed that $\alpha_2^e(\nu)$ is a function of the square of frequency, ν^2 (see Figs 1 and 2). A fit of this kind of curve allows for a precise extrapolation of the dynamic mean dipole polarizability to the static one at zero wavenumber that will be referred as $\alpha_2^e(0)$.The corresponding static values

Table 2. Dynamic electronic polarizabilities of 2MT and 3MT in CH_3CN solution[a]

	2MT		3MT	
Frequency ν (μm^{-1})	$\alpha_2^e(\nu)(10^{-23}$ esu)[b]	$\alpha_2^e(\nu)(10^{-23}$ esu)[c]	$\alpha_2^e(\nu)(10^{-23}$ esu)[b]	$\alpha_2^e(\nu)(10^{-23}$ esu)[c]
2.294631	1.229	1.215	1.236	1.223
1.966182	1.203	1.190	1.205	1.192
1.831166	1.194	1.182	1.194	1.182
1.696065	1.185	1.173	1.185	1.172
1.553277	1.177	1.165	1.177	1.165
0.000	1.135	1.123	1.141	1.131

[a] $T = 20 \pm 0.1\,°C$, $(\partial V/\partial w)_0 = -0.5584 \pm 0.004$, $\rho_1 = 0.781983$ g cm^{-3}.
[b] Eqn. (10), using Lorentz local field.
[c] Eqn. (11), using Onsager local field.

are reported in Table 1 for CCl_4 and for CH_3CN in Table 2. In particular, the values of $\alpha_2^e(0)$for 2MT in CCl_4 are 1.130×10^{-23} esu (Lorentz local field) and 1.128 $\times 10^{-23}$ esu (Onsager local field). These values are comparable to the experimental value for neat 2MT of 1.119×10^{-23} esu. For 3MT, the corresponding values of $\alpha_e(0)$ are 1.147×10^{-23} and 1.141×10^{-23} esu, respectively, and that for neat 3MT is 1.119×10^{-23} esu. Furthermore, the corresponding static values of $\alpha_e(0)$ for 2MT and 3MT in CH_3CN solvent with the Lorentz field are 1.135×10^{-23} and 1.141×10^{-23} esu, whereas for the Onsager field, the corresponding values are 1.123×10^{-23} and 1.131×10^{-23} esu. It is important to note that the values of the dipole polarizabilities of neat 2MT and 3MT were obtained from extrapolation of the molar refraction dynamic values in the literature.[23]

From the results in Fig. 1, it can be seen that the dynamic dipole polarizabilities of 2MT and 3MT in the non-polar solvent are slightly affected by the nature of the local fields, mainly at lower wavenumbers and the static case, where the effects of the local fields are greater than for higher wavenumbers. However, the differences between these effects are less than 0.5% for both molecules in the static region. In this region, the dipole polarizability of 3MT is relatively higher than that of 2MT. For higher wavenumbers in CCl_4 solvent, the $\alpha_2^e(\nu)$ value for 2MT approaches the 3MT polarizability. This tendency is independent of the local fields considered and tends to the value of 1.227×10^{-23} esu.

The dynamic dipole polarizabilities of 2MT and 3MT in CH_3CN solvent are reported in Table 2, and the corresponding dispersion curves are depicted in Fig. 2. The behavior of this property for the molecules studied in CH_3CN is different from that observed with CCl_4 solvent. Figure 2 shows the polarizability dispersion curves of 2MT and 3MT, where the differences between these properties can be observed, mainly in the region of lower and higher wavenumbers. The effect of the local fields is observed in the overall range of wavenumbers. In particular, for the intermediate optical region of 1.5–2.0 μm^{-1}, the polarizabilities of 2MT and 3MT are

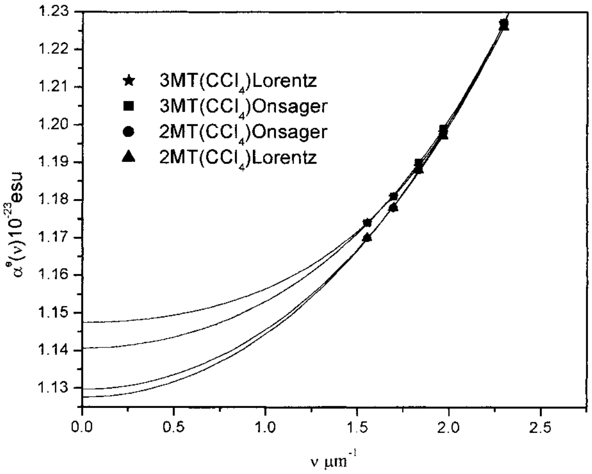


Figure 1. Experimental dispersion curves of 2MT and 3MT molecules in CCl_4 solution obtained using the Onsager and Lorentz local fields

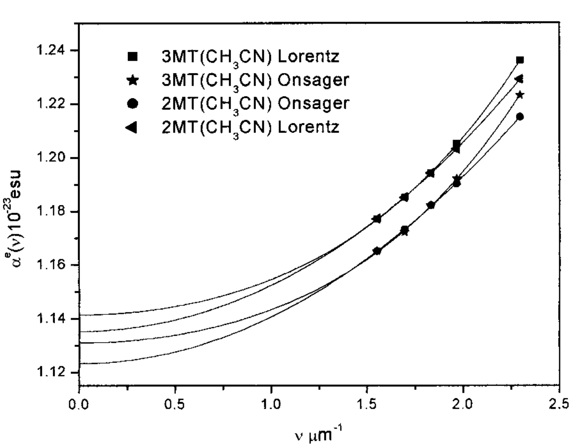


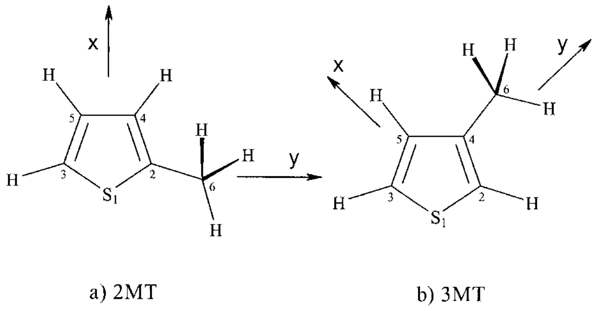
Figure 2. Experimental dispersion curves of 2MT and 3MT molecules in CH_3CN solution obtained using the Onsager and Lorentz local fields

similar for each local field curve, but the observed differences between the curves in Fig. 2 are due to the differences in the local fields. For example, with the Onsager local field the 2MT and 3MT values of $\alpha_2^e(\nu)$ are identical, but are lower than the 2MT and 3MT $\alpha_2^e(\nu)$ values with the Lorentz local field.

On the other hand, for the CH_3CN solvent, the dipole polarizability of 2MT is lower than that of 3MT, and is clearly differentiated from the static region and also at higher wavenumbers. The effect of the local fields at lower optical frequencies gives a significant difference between the response properties for these molecules. The results show that the static dipole polarizability of 2MT is 1.135×10^{-23} esu with the Lorentz local field, whereas with the Onsager local field the corresponding value is 1.123×10^{-23} esu, i.e. a difference of 0.012×10^{-23} esu. Additionally, for 3MT, the corresponding values are 1.141×10^{-23} and 1.131×10^{-23} esu. These results give slight differences of about 1.5% and 1.2% between the static polarizability of 3MT and 2MT if the Lorentz and Onsager local fields are used, respectively. However, there is no significant difference between the polarizabilities of 2MT and 3MT if the dynamic region is considered. The observed variations are due to the effects of the Lorentz and Onsager local fields only, where the structural and electronic differences between the 2MT and 3MT seem not to be significant. These last results indicate that in the region of optical frequencies, the dynamic polarizabilities of 2MT and 3MT are sensitive only to the local field factors, where the electronic deformability of the thiophene moiety in 2MT and 3MT is not affected by the position of substitution of the methyl group in the hetero-ring. In conclusion, the Onsager local field always gives lower polarizability values than the Lorentz local field.

Although the static $\alpha_2^e(0)$ is an important value for a molecule in solution and comparison with the gas-phase values is significant for considering the role of the effects of intermolecular forces,[27] no experimental static polarizability data for 2MT and 3MT molecules in the gas phase appear to have been published. In this context, a theoretical analysis is required for this property. It is important to remember that for both neat 2MT and 3MT the value of $\alpha_2^e(0)$ is of 1.119×10^{-23} esu.[23] This value is lower than our static values for 2MT and 3MT, in either carbon tetrachloride or acetonitrile solution (see Tables 1 and 2). The difference between the values of these properties is less than 2.5%, and this variation lies in the range generally observed between the gas and liquid phases for pure compounds.[28]

Miller obtained a series of average electronic polarizabilities for 300 aliphatic, aromatic and heteroaromatic compounds using an empirical method.[29] This method uses atomic hybrid parameters, which are based on a theoretical interpretation of variational perturbation in terms of molecular orbital theory and reproduces the experimental dynamic dipole polarizabilities at 589.3 nm with an average error of 2.2 and 2.8% for the optimized atomic hybrid polarizabilities method α_e(ahp) and the not optimized atomic parameters method α_e(ahc), respectively. To verify if this method is able to reproduce empirically our static electronic polarizabily value for 3-MT, we estimated the electronic polarizability by using the optimum set of α_e(ahp) and α_e(ahc) parameters.[29] Examination of Table 1 shows that the empirical α_e(ahp) value for the dipole polarizability of 3MT is in excellent agreement with our corresponding static experimental value, whereas the predicted dipole polarizability value with the ahc method gives a deviation of about 3% when compared with the experimental data obtained in this work. We suggest that the ahc empirical method does not reproduce the static dipole polarizability of 3-MT, because it underestimates the dipole polarizability of the S heteroatom with respect to other atom values. It is important to note that these methods are not able to discriminate between isomers, and in consequence the same value of the dipole polarizability is predicted for 2MT and 3MT. In conclusion, the dipole polarizabilities of 2MT and 3MT are overestimated by the α_e(ahp) method in CCl_4 by about 1.7%, whereas the α_e(ahc) method underestimates them by about 2% compared with our static experimental values.



Scheme 1. Structures and geometric parameters of (a) 2 MT and (b) 3 MT

In order to test our experimental dipole polarizability results for 2MT and 3MT, *ab initio* and DFT calculations were performed on optimized geometries.

Theoretical results

Static dipole polarizabilities. The theoretical calculations were performed at the SCF level and DFT level with the BLYP and the B3LYP hybrid approaches, by using the 6–311 + G(3d,3p) (A) and the Sadlej (B) basis sets. The geometry of 2MT and 3MT molecules were fully optimized by using these methods, and employed for the dipole polarizability calculations. Scheme 1 shows the structures and atomic numbering for the geometric parameters of the 2MT and 3MT molecules used in the present work.

Table 3. Optimized relevant geometric parameters of 2MT and 3MT using the B3LYP and the 6–311 ++ G(3d,3p) (A) and Sadlej (B) basis sets

	2MT			3MT		
	B3LYP/A	B3LYP/B	Exp.[a]	B3LYP/A	B3LYP/B	Exp.[b]
Bond lengths (Å)—						
C2—S1	1.736	1.753	1.722	1.724	1.740	1.719
C3—S1	1.725	1.741	1.729	1.721	1.738	1.717
C4—C2	1.368	1.373	1.374	1.368	1.374	1.370
C5—C3	1.364	1.370	1.374	1.364	1.370	1.368
C5—C4	1.425	1.431	1.429	1.431	1.424	1.441
C6—C2	1.499	1.498	1.505			
C6—C4				1.503	1.504	1.497
C2—H				1.078	1.089	1.102
C3—H	1.077	1.087	1.098			
C4—H	1.081	1.091	1.098	1.081	1.092	1.102
C5—H	1.080	1.091	1.098	1.077	1.087	1.102
C6—H	1.090	1.099	1.114	1.092	1.102	1.119
C6—H′	1.092	1.101		1.089	1.098	
Bond angles (°)—						
C3—S1—C2	92.4	92.1	92.7	91.55	91.26	91.6
S1—C2—C4	110.1	110.1	110.5	112.36	112.34	113.5
C5—C3—S1	111.2	111.2	111.0	111.45	111.42	111.3
S1—C2—C6	121.4	121.3				
C2—C4—C6				124.81	124.74	123.2
C2—C6—H	109.7	109.8				
C2—C6—H′	111.9	112.0				
C4—C6—H				111.15	111.34	
C4—C6—H′				111.32	111.37	
S1—C3—H	120.2	120.0		120.24	120.00	
C2—C4—H	122.6	122.5				
C3—C5—H	123.4	123.3		123.16	122.99	
S1—C2—H				119.92	119.63	

[a] Ref. 30a.
[b] Ref. 30b.

Table 3 displays the optimized bond distances and bond angles of the compounds studied and a comparison with the experimental results. Experimentally, the molecular structure of 2MT has been determined by electron gas diffraction,[30a] and the 3MT structure has been studied more recently by a combined study of electron gas diffraction and microwave spectroscopy.[30b] The agreement between the theoretical geometry and the experiment is good.

Table 4 reports the dipole polarizability components α_{ii} ($i = x$, y and z), the average polarizability α_{ave} and the anisotropy of the polarizability $\Delta\alpha$ of the molecules studied. In addition, the theoretical and experimental[31] dipole moment μ, the total energy $-E$ and the experimental values of the static dipole polarizability obtained in the present work with the different solvents and the local fields are reported. Table 4 shows how the calculations of the molecular properties are affected by the basis sets. Also, the effect of correlation with the BLYP and B3LYP methods with respect to the HF approach can be observed from these results.

In the present work, we considered that our best set of dipole polarizability values is that obtained with the B3LYP method, because this method overestimates this property. For both 2MT and 3MT molecules, the B3LYP theoretical dipole polarizabilities are slightly larger than the experimental static values, with either the 6–311 ++ G(3d,3p) or Sadlej basis sets. Also, it is important to note that at the *ab initio* and DFT levels of theory, the results with the A basis show that the 2MT molecule is more polarizable than the 3MT molecule, whereas with the Sadlej (B) basis both molecules have similar values of polarizabilities. These results are in contrast with the experimental values discussed above. Despite these findings, the difference between the larger theoretical value of α for 2MT with the B3LYP/B method, 1.176×10^{-23} esu, and the smaller static experimental value of 1.123×10^{-23} esu for 2MT (using the Onsager local field and CH_3CN as solvent) is less than 4.7%.

With respect to the anisotropy of the polarizability, the values of $\Delta\alpha$ indicate that 2MT is more anisotropic than

Table 4. Static dipole polarizability components, average and anisotropy polarizability, dipole moment and total energies of 2MT and 3MT molecules, calculated with the CPHF method, using the Hartree–Fock (HF), BLYP and B3LYP levels of theory[a]

		HF		BLYP		B3LYP	
Compound	Parameter	A[b]	B[c]	A[b]	B[c]	A[b]	B[c]
2MT	α_{xx}[d]	1.239	1.255	1.347	1.378	1.297	1.323
	α_{yy}	1.245	1.269	1.434	1.480	1.365	1.404
	α_{zz}	0.768	0.775	0.816	0.829	0.790	0.800
	α_{ave}	1.084	1.100	1.199	1.229	1.151	1.176
						1.130[d]	
	Experiment					1.128[e]	
	α_{ave} (this work)					1.135[f]	
						1.123[g]	
	$\Delta\alpha$	0.474	0.487	0.579	0.606	0.544	0.567
	μ(D)	0.893	0.935	0.688	0.701	0.700	0.720
							(0.67)[h]
	$-E$ (hartree)	590.41447	590.39138	592.30210	592.26087	592.41557	592.37936
3MT	α_{xx}[d]	1.113	1.147	1.204	1.290	1.236	1.234
	α_{yy}	1.370	1.376	1.451	1.555	1.393	1.483
	α_{zz}	0.771	0.779	0.794	0.834	0.790	0.805
	α_{ave}	1.085	1.101	1.150	1.226	1.139	1.174
						1.147[d]	
	Experiment					1.141[e]	
	α_{ave} (this work)					1.141[f]	
						1.131[g]	
	$\Delta\alpha$	0.368	0.368	0.406	0.447	0.383	0.420
	μ(D)	1.228	1.281	0.933	0.907	0.932	0.955
							(0.82)[h]
	$-E$ (hartree)	590.41440	590.39139	592.30205	592.26110	592.41557	592.37961

[a] Polarizability values in 10^{-23} esu.
[b] A = 6–311 ++ G(3d,3p) basis (Ref. 14).
[c] B = Sadlej basis (Ref. 15a).
[d] Using Lorentz local field and CCl_4 as solvent.
[e] Using Onsager local field and CCl_4 as solvent.
[f] Using Lorentz local field and CH_3CN a solvent.
[g] Using Onsager local field and CH_3CN as solvent.
[h] Experimental (Ref. 31).

3MT, which is as expected from the different asymmetry between these molecules. In fact, as the position of the methyl group in 2MT is closer to the S atom than it is in 3MT, a larger anisotropy is induced in 2MT with respect to 3MT. Despite this anisotropy behavior, the dipole moment of 2MT is lower than that of 3MT. The higher value of μ for 3MT can be interpreted in terms of the charge separation in this molecule, which should be greater than that in 2MT. In this context, it is important to mention that the theoretical methods used are able to reproduce satisfactorily the experimental dipole moments of the two molecules.

With respect to the stabilities of the molecules studied, Table 4 shows that there is no definite pattern for the total energy values of the 2MT and 3MT isomers. From energetic considerations the A basis gives lower total energies than the B basis at all the theoretical levels studied. Despite these results, no energetic differences are observed with the B3LYP/A method between 2MT and 3MT However, with the B3LYP/B method 3MT is more stable than 2MT, with an energy gap of 0.25 kcal mol^{-1}. It is worth noting that in the 3MT molecule the repulsion between the CH_3 group and the S atom of the ring is much less than in 2MT, and for this reason 3MT is expected be more stable than 2MT.

Frequency-dependent polarizabilities and solvent effects. In studies of dipole polarizability in solution, the frequency and the solvent effects are important, as was discussed in the previous section at experimental level. In order to make a comparison with the refractometric results, an *ab initio* time-dependent Hartree–Fock TDHF calculation with the 6–311 ++ G(d,p) and the Sadlej basis sets was performed for the 3MT molecule, using CCl_4 and CH_3CN solvents. The results are shown in Fig. 3, together with the experimental results obtained with the Onsager local field. The experimental results clearly show the similarity that exists between the dispersion curves of 3MT with CCl_4 and CH_3CN solvents.

On the other hand, it is observed that the TDHF method is not able to differentiate between the properties of these solvents in the dynamic polarizability of 3MT. Also, this method gives values of the polarizability of 3MT lower than the experimental ones. This result can be

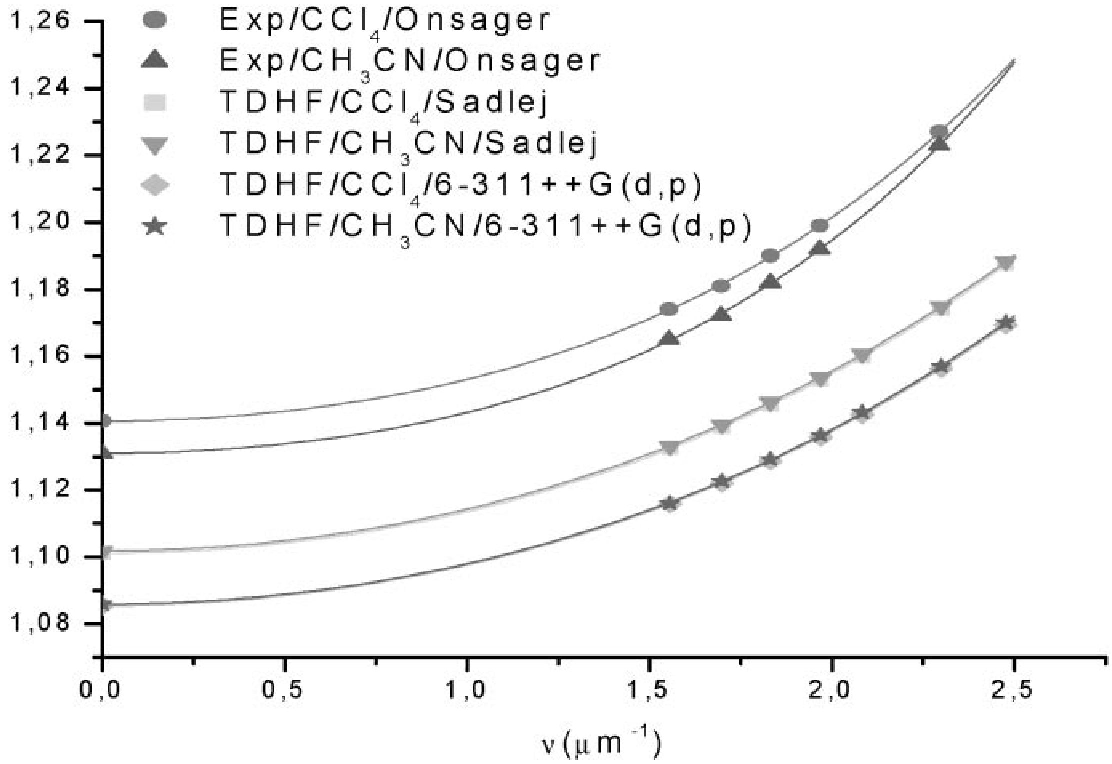


Figure 3. Theoretical dispersion curves of 3MT in solutions of CCl_4 and CH_3CN

explained because of the lack of electronic correlation effects in the TDHF calculations. Also, with respect to the atomic functions, it is important to note that although the TDHF results parallel the experimental values for the dipole polarizability, the Sadlej basis set gives a much better representation of the dynamic behavior of the dipole polarizability than the 6–311 ++ G(d,p) basis set. At this point, we can say that TDHF/Sadlej methodology gives a qualitative representation of solvent effects at the dynamic level, and no significant differences were observed for the CCl_4 and CH_3CN solvents. Because of this result, which is probably due to the simple nature of the Onsager model for solvation, we are performing further studies in order to explore the solvent effects on the dynamic dipole polarizabilities of sulfur compounds. We are trying to evaluate the performance of other solvent models and the effects of larger basis sets, including correlation effects, in order to make comparisons with the experimental results.

CONCLUSIONS

We have reported experimental and theoretical determinations of the dipole polarizability of 2MT and 3MT molecules. The experimental polarizability was determined by refractometric techniques in dilute CCl_4 and CH_3CN solutions, by using the Garito and Singer method with the Lorentz and Onsager local fields. The dispersion of the dynamic polarizability showed a Cauchy behavior, and the corresponding static dipole polarizabilities were analyzed considering the different local fields and the solvent effects and compared with experimental values extracted from refraction measurements. According to the refractive index values reported in the literature, the electronic dipole polarizabilities of 2MT and 3MT are identical in the liquid phase, and are lower than the values measured in the present work in solutions of CCl_4 and CH_3CN solvents. Furthermore, the static and dynamic polarizabilities calculated with the Onsager local field were lower than those obtained with the Lorentz local field. Additionally, 3MT in solution became slightly more polarizable than 2MT. On the other hand, the dispersion of the electronic polarizability for both species showed a strong dependence on the dielectric nature of the media, where these properties are similar at high frequencies in a non-polar solvent such as CCl_4, whereas at lower frequencies and in the static region the polarizabilities tend to be different for the two isomers. The influence of the local field becomes important in this region. With respect to the CH_3CN solvent, the values of the polarizabilities of 2MT and 3MT are very close and are not influenced significantly by the local field in the region of intermediate frequencies. However, for the static and higher frequency region, the electronic dipole polarizability of 3MT is higher than that of 2MT. In conclusion, the averages of the static values obtained for the electronic polarizability of 2MT and 3MT are 1.129×10^{-21} and 1.140×10^{-21} esu, respectively.

With respect to the semiempirical values obtained with the Miller parameters, the α(ahp) method was more appropriate than the α(ahc) method for the dipole polarizabilities of 2MT and 3MT. On the other hand, the B3LYP DFT method showed that the Sadlej basis (B) set gives very similar α values for 2MT and 3MT, whereas the 6–311 + G(3d,3p) (A) basis set with this DFT method yield values of α that differ by about 1.05% for the two isomers. The corresponding static B3LYP values of the dipole polarizability for 2MT and 3MT are 1.151×10^{-21} and 1.139×10^{-21} esu, respectively, with the A basis, whereas with the B basis they are 1.176×10^{-21} and 1.174×10^{-21} esu, respectively. In general, there is good agreement between the experimental and the DFT theoretical results.

The TDHF method was able to gives a qualitative description of the dynamic behavior of the dipole polarizability of 3MT, but the dynamic and static polarizability values for this molecule were underestimated, as expected at this level of calculation, however. For these dynamic properties, the Sadlej basis set gives a better performance than the 6–311 + G(d,p) basis set.

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