Aza-Substituted Thiophene Derivatives: Structures, Dipole Moments, and Polarizabilities

N. El-Bakali Kassimi*

Chemistry Department, University of New Brunswick, Fredericton, NB, Canada E3B 6E2

Zijing Lin

NumTek, 1839 E 11th Ave, Vancouver, BC, Canada V5N 1Y9

Received: May 27, 1998; In Final Form: September 16, 1998

Ab initio calculations of dipole moments and static dipole polarizabilities are reported for nine heteroaromatic five-membered rings—thiophene, thiazole, isothiazole, the four thiadiazoles, and the two thiatriazoles—all at their MP2/6-31G** geometries. Extensive basis sets have been used, and the approximate applicability of the variational principle to the Hartree−Fock polarizability has been discussed. Electron correlation effects have been investigated up to the MP4(SDQ) level for a representative subset of the series of the molecules considered. Our best polarizability determinations are expected to be accurate within a few percent.

Introduction

Polarizabilities characterize linear response to an electric field. The variety of circumstances in which atomic and molecular electronic clouds are slightly distorted under weak electric fields due to a molecular or atomic environment or to radiation demonstrates both the relevance and importance of these properties in many areas of chemical physics and physical chemistry such as optics, low-energy scattering, intermolecular forces, reactivity, and reaction kinetics.[1−4] New ideas, in fact, keep surging in the literature about using these properties to address interesting issues. For instance, a polarizability-based criterion for aromaticity in the case of π-conjugated aromatic molecules has been suggested.[5−7] A correlation between change in polarizability and dissociation energy has been explored,[8] and more recently polarizabilities have been used to measure the strength of hydrogen bonds in peptides.[9]

The five-membered heteroaromatic rings[10] form an interesting class of chemical compounds. In continuation of a previous work on azoles[11] and oxazoles,[12] we examine thiophene and its heteroaromatic aza-substituted derivatives, as shown in Figure 1: thiophene (**1**), isothiazole (**2**), thiazole (**3**), 1,2,3-thiadiazole (**4**), 1,2,5-thiadiazole (**5**), 1,3,4-thiadiazole (**6**), 1,2,4-thiadiazole (**7**), 1,2,3,4-thiatriazole (**8**), and 1,2,3,5-thiatriazole (**9**). Thiophene, thiazole, and thiadiazole are important building blocks for some organic materials of interest in nonlinear optics.[13,14] Thiadiazoles and their derivatives are of considerable biological and pharmacological interest.[15] Apart from thiophene, for which both ab initio[16−19] and experimental[16,20−22] determinations of polarizabilities are available, we could not trace any such data for the rest of the molecules. In this paper, we report electron-correlated ab initio calculations of these properties. But first we have determined the structures and dipole moments and compared them to experimental counterparts where available. Using a representative subset of the series, electron correlation effects at the fourth order of Møller−Plesset perturbation theory have been examined for dipole moments and polarizabilities. The basis sets have been also extended to include f Gaussian-type functions in an attempt to assess basis set completeness. The approximate applicability of the Hylleraas variational principle[23] to self-consistent-field polarizability has also been discussed in the context of comparing the performance of different one-particle basis sets.

Computational Methods

Details of the computational techniques used were given in an earlier work.[11] The finite-field approach[24,25] has been adopted. Both finite fields and the combinations of the corresponding energies have been chosen to achieve field convergence of the polarizability tensor components and avoid contamination by higher order polarization terms. In all our computations we used GAUSSIAN-94[26] utilizing both the Hartree−Fock (HF) self-consistent-field (SCF) and valence, second-, and fourth-order Møller−Plesset (MP) perturbation theory methods.[25,27]

Adequate description of the outer part of the electron density distribution is necessary to compute reliable polarizabilities. The basis set must, therefore, contain suitable diffuse sp-type and polarization functions. Energy-optimized substrates are usually supplemented with, or modified to include, such functions according to relatively systematic procedures and/or according to experience.[28,25,29] Perhaps the most theoretically well-founded procedure in choosing the diffuse polarization functions is the one approximately based on the Hylleraas variation principle.[23]

Our preliminary and smallest basis of Gaussian-type functions (GTF), denoted B1, is constructed in exactly the same way as in refs 11 and 12. The exponent of the diffuse d function on sulfur was chosen to maximize the mean dipole polarizability of thiophene. Schäfer et al.'s split-valence set[30] was augmented by a set of diffuse and polarization functions.[11] To generate the other basis sets, we used (11s6p)/[5s3p] for carbon and nitrogen, (14s9p)/[5s4p] for sulfur, and (5s)/[3s] for hydrogen. The last outermost s and p functions for carbon and nitrogen in the TZV (triple-ζ valence) set of Schäfer et al.[30] were replaced by two diffuse s and p functions in geometric sequence with the last unmodified TZV exponents using the ratios 0.29 and 0.22, respectively, whereas we supplemented the TZV set of sulfur with extra diffuse s and p functions in geometric sequence

---

* Corresponding author. E-mail nkassimi@unb.ca; FAX (506) 453-4981.

10.1021/jp9823749 CCC: $15.00

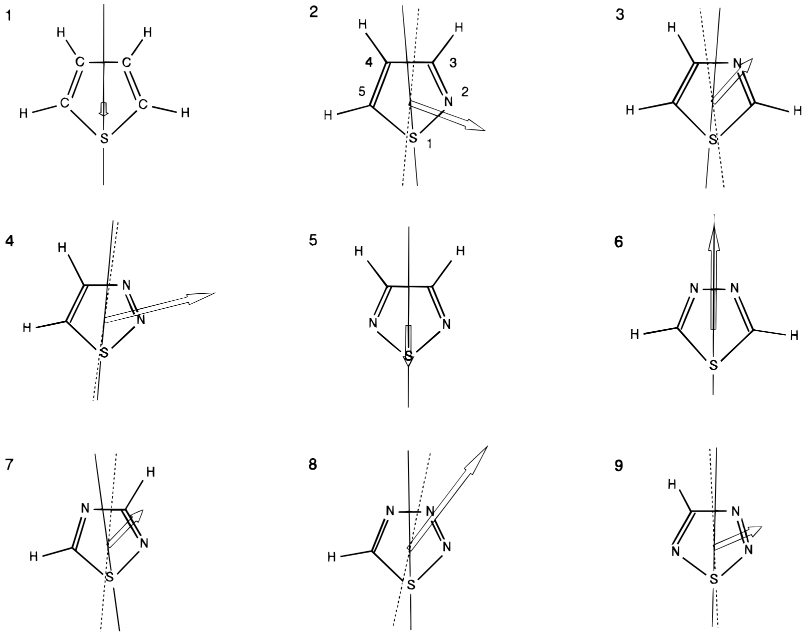

Figure 1. Aza-substituted thiophene derivatives at MP2/6-31G** geometries. MP2/C3 dipole moments are shown to scale pointing to the negative end. The dotted line is the highest eigenvalued polarizability axis, and the solid line is the *A*-axis of inertia.

TABLE 1: Details of the GTF Basis Sets

label	description
B0	(7s4p,4s)/[3s2p,2s], ref 30
F1	dC(0.10) + dN(0.15) + dS(0.15) + pH(0.05)
P	dC(0.55) + dN(0.817) + dS(0.7) + pH(0.727)
B1	B0 + F1 + P
C0	(11s6p)/[5s3p] for C and N, (14s9p)/[5s4p] for S, and (5s)/[3s] for H (see text)
C1	C0 + F1 + P
F2	dC(0.022) + dN(0.033) + dS(0.052) + pH(0.2)
F3	fC(0.10) + fN(0.15) + fS(0.15)
C2	C1 + F2
C3	C2 + F3

with the last two diffuse s and p functions. This was done based on preliminary calculations on thiophene aiming at producing a better balanced[31] and suited basis for our polarizability calculations. Finally, the hydrogen (5s)/[3s] basis set is the DZ of ref 11 augmented with the same s diffuse function. The basis set thus generated is enlarged to include d, f, and p polarization and diffuse functions on C, N, and S and a semidiffuse p on H to obtain basis sets C1, C2, and C3 as shown in Table 1.

Equilibrium Geometries

We optimized the geometries of all nine molecules at the MP2/6-31G** level of theory. On one hand, this permits us to systematize our polarizability calculations within the set of molecules under consideration, since gas-phase determinations are not available for the two thiatriazoles. On the other hand, this preserves the ground for comparison with previous sets of heteroaromatic molecules, the structures of which have been optimized at a very similar level of theory.[11,12]

Substitution r_s structures obtained by microwave spectroscopy are available for thiophene,[32] thiazole or 1,3-thiazole,[33] 1,2,3-thiadiazole,[34] 1,3,4-thiadiazole,[35] 1,2,4-thiadiazole,[36] and 1,2,5-thiadiazole.[37] The agreement with the MP2/6-31G** structures is good and comparable to that obtained for the oxazoles.[12] The average deviation from these experimental determinations of calculated bond lengths and bond angles is 0.7 pm and 0.3°, respectively. For bond lengths, the largest average discrepancy for a single molecule is 1.1 pm occurring for both 1,2,3-thiadiazole and 1,2,5-thiadiazole. The N2N3 and C4C5 bonds in the former, the N2C3 in the latter, and SN2 bonds in both molecules exceed the experimental ones by 2.5, 1.4, 1.7, 2.2, and 1.8 pm, respectively. A similar overestimation is observed for SN2 (1.5 pm) and N2C3 (1.4 pm) bonds in 1,2,4-thiadiazole. For bond angles, the average deviation for a single molecule is uniformly good for all the five structures and does not exceed 0.4°, even though a maximum of 1.0° occurs for angle HC5S of 1,2,3-thiadiazole.

There is an electron diffraction (ED) structure of isothiazole[38] that shows an average discrepancy with the calculated one of 1.5 pm in bond lengths and 3.3° in bond angles. This comparison excludes the hydrogen-related parameters for the determination of which the authors reported some difficulties.[38] No better agreement is obtained with the structure calculated using DFT/6-31G** or MCSCF/6-31G** methods.[39] There seems to be still room for significant improvement for the experimental structure of this molecule.

Before this work was completed, El-Azhary published MP2/6-31G** structures for isothiazole,[39] thiazole,[40] 1,2,5-thiadiazole,[41] and 1,3,4-thiadiazole.[42] Our geometries being practically the same, we report only the remaining thiophene derivatives in Table 2. Simandiras et al.[43] optimized the structure of thiophene at the MP2 level using a DZP basis. The geometry agrees well with ours, which is yet in a slightly better agreement with the experimental one. Finally, Shaffer and Wierschke[44] have also reported a MP2/6-31G* structure of thiazole that turns out to be incorrect. The slight difference between our basis sets affects only parameters involving hydrogen and does not explain the large discrepancy between our results and theirs (as large as 3.9 pm for CS2 and 2.2° for C5SC2). In fact, the incorrectness of a similar MP2/6-31G* geometry for oxazole published in the same paper[44] using apparently the same procedure has been already reported.[12]

Dipole Moments

Table 3 lists the dipole moments calculated at different levels of theory using basis sets B1, C1, and C3. Gas-phase experimental values obtained from microwave spectroscopy are

TABLE 2: MP2/6-31G Geometries Compared to Microwave (MW) r_s Structures (Where Available) of Thiophene and Four of Its Aza-Substituted Analogues (Bond Lengths in picometers and Bond Angles in degrees)**

thiophene			1,2,3-thiadiazole			1,2,4-thiadiazole			1,2,3,4-thiatriazole		1,2,3,5-thiatriazole	
	MP2	MW[a]		MP2	MW[b]		MP2	MW[c]		MP2		MP2
S−C2	171.7	171.4	S−N2	171.4	169.2	S−N2	166.4	164.9	S−N2	169.8	S−N2	168.0
C2−C3	137.6	137.0	N2−N3	131.5	129.0	N2−C3	133.1	131.7	N2−N3	131.1	N2−N3	132.7
C3−C4	142.0	142.3	N3−C4	135.9	136.6	C3−N4	136.6	136.6	N3−N4	135.5	N3−C4	135.7
H−C2	107.8	107.8	C4−C5	138.3	136.9	N4−C5	132.2	131.3	N4−C5	132.8	C4−N5	134.3
H−C3	108.0	108.1	C5−S	168.5	168.9	C5−S	171.0	170.7	C5−S	169.1	N5−S	163.1
C5SC2	91.9	92.2	H−C4	107.9	107.8	H−C3	108.0	107.8	H−C5	107.8	H−C4	107.8
SC2C3	111.6	111.5	H−C5	107.7	108.1	H−C5	107.0	107.9	C5SN2	90.2	N5SN2	97.1
C2C3C4	112.4	112.5	C5SN2	93.0	92.9	C5SN2	92.7	92.8	SN2N3	110.3	SN2N3	108.1
HC2S	120.2	119.9	SN2N3	110.4	111.2	SN2C3	106.7	107.1	N2N3N4	116.0	N2N3C4	111.3
HC3C4	124.5	124.3	N2N3C4	113.9	114.0	N2C3N4	120.4	120.1	N3N4C5	110.7	N3C4N5	118.6
			N3C4C5	114.5	114.2	C3N4C5	107.5	107.7	N4C5S	114.0	C4N5S	105.0
			C4C5S	108.2	107.8	N4C5S	112.8	112.3	HC5S	124.8	HC4N5	120.8
			HC4N3	119.4	119.2	HC3N4	120.4	119.9				
			HC5S	123.9	122.9	HC5S	123.4	123.9				

[a] Reference 32. [b] Reference 34. [c] Reference 36.

TABLE 3: Dipole Moment Magnitudes μ (in debye) and Orientation Angles (in degrees) with Respect to the Inertial A-Axes; All Calculated Values Are at the MP2/6-31G Geometry**

		SCF			MP2			MP4	
molecule		B1	C1	C3	B1	C1	C3	C1	expt
thiophene	μ	0.57	0.65	0.71	0.26	0.37	0.45		0.55 ± 0.01[a]
isothiazole	μ	2.73	2.87	2.87	2.31	2.45	2.45	2.52	2.46 ± 0.13[b]
	Θ	28.0	59.5	59.2	20.5	65.8	64.9	63.8	63.4 ± 3.2[b]
thiazole	μ	1.73	1.71	1.65	1.93	1.90	1.83		1.61 ± 0.03[c]
	Θ	31.0	31.2	32.5	33.0	34.3	35.9		36.9 ± 1.0[c]
1,2,3-thiadiazole	μ	3.83	3.98	3.83	3.68	3.87	3.68	3.77	3.59 ± 0.13[d]
	Θ	17.0	74.6	73.0	20.0	72.3	70.0	72.7	73.2 ± 2.0[d]
1,2,5-thiadiazole	μ	1.77	2.00	1.98	1.18	1.43	1.44	1.60	1.57 ± 0.02[e]
1,3,4-thiadiazole	μ	3.82	3.97	3.82	3.67	3.78	3.62		3.28 ± 0.03[f]
1,2,4-thiadiazole	μ	1.74	1.77	1.73	1.64	1.62	1.56		1.49[g]
	Θ	25.8	67.8	68.6	43.4	51.4	52.2		
1,2,3,4-thiatriazole	μ	4.24	4.40	4.30	4.01	4.20	4.08	4.16	
	Θ	39.5	40.4	41.0	35.8	37.4	38.0	38.4	
1,2,3,5-thiatriazole	μ	1.38	1.43	1.39	1.66	1.71	1.66		
	Θ	27.3	68.1	68.4	35.7	60.7	61.5		

[a] Reference 45. [b] Reference 46. [c] Reference 47. [d] Reference 34. [e] Reference 48. [f] Reference 49. [g] Reference 50.

also given whenever available. For the C_s molecules we specify the orientation of the dipole moment by giving the acute angle Θ with respect to the inertial A-axis, whereas its orientation is dictated by the C_{2v} symmetry for the rest of them ($\Theta = 0°$). Note that the magnitude and the angle thus given do not uniquely specify the dipole moment vector within the molecule. The same magnitude and angle could be represented by four (in the case of C_s symmetry) and two (in the case of C_{2v} symmetry) possible vectors. The two given parameters could be used as polar coordinates, and thus specify a unique vector, if the sense of each in-plane inertial axis is chosen and given. However, it is rather easier to refer to Figure 1 to remove this ambiguity.

Basis set effects are relatively small in keeping with the azoles[11] and oxazoles.[12] From B1 to C1, the changes average 0.12 D and 2.9° with a maximum of 0.25 D and 6.4° for 1,2,5-thiadiazole and 1,2,3,5-thiatriazole. As the basis set is enlarged from C1 to C3, however, the changes average 0.04 D and 0.6°, reaching a maximum of 0.13 D and 3.1° for 1,2,3-thiadiazole. Correlation effects are much larger. At the MP2 level, correlation effects average 0.27 D and 6.6° and reach a maximum of 0.59 D in basis B1 for 1,2,5-thiadiazole and 17.6° in the same basis for 1,2,4-thiadiazole. In basis C1, the ratio of the MP4(SDQ) (fourth-order Møller−Plesset (MP) perturbation theory including single, double, and quadruple excitations) correlation change, in magnitude and orientation, to the MP2 one is below 0.33 for all the four molecules, except for the magnitude μ of the 1,2,3-thiadiazole dipole moment (about 0.91).

The MP2/C3 orientations of the dipole moments agree remarkably well with the experimental determinations, deviating by about 3° at most and by 2° on average. This gives a reassuring indication about our basis set balance, to which the dipole moment is quite sensitive. The MP2/C3 values of μ differ on average by 0.1 D from their experimental counterparts, reaching a maximum deviation of 0.3 D for 1,3,4-thiadiazole. The discrepancy between our best results (MP2/C3) and experiment seems to be primarily due to the effects of molecular vibration and secondarily to residual effects of electronic correlation.

Polarizability

We choose as coordinate systems the ones that diagonalize the polarizability tensor for the four thiophene derivatives with C_{2v} symmetry. Figure 1 shows the principal 3-axis of polarizability associated with the highest eigenvalue for all molecules. In case of C_s symmetry, this axis is obtained through diagonalizing the 2 × 2 in-plane polarizability submatrix. Thus, Table 4 lists three polarizability invariants. One is the mean polarizability given by the trace

$$\bar{\alpha} = {}^{1}/_{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = {}^{1}/_{3}(\alpha_1 + \alpha_2 + \alpha_3) \qquad (1)$$

We denote by $\alpha_1 \leq \alpha_2 \leq \alpha_3$ the eigenvalues or principal values of the polarizability tensor. One measure of the polarizability

TABLE 4: Coupled Hartree−Fock (CHF), Finite-Field MP2, and Some MP4(SDQ)/C1 Polarizabilities

		CHF			MP2			MP4
molecule		B1	C1	C3	B1	C1	C3	C1
thiophene	$\bar{\alpha}$	60.4	62.5	63.0	61.5	63.8	64.5	
	$\Delta_1\alpha$	28.6	27.7	27.9	29.3	28.5	28.9	
	$\Delta_2\alpha$	29.0	28.4	28.6	29.4	28.9	29.3	
isothiazole	$\bar{\alpha}$	54.6	56.8	57.4	55.7	58.6	59.4	57.9
	$\Delta_1\alpha$	26.5	26.2	26.3	27.8	27.7	27.8	27.4
	$\Delta_2\alpha$	27.8	27.9	27.9	28.5	28.6	28.7	28.7
thiazole	$\bar{\alpha}$	54.6	56.4	57.0	55.9	58.3	59.2	
	$\Delta_1\alpha$	25.9	25.1	25.7	27.5	26.9	27.5	
	$\Delta_2\alpha$	26.1	25.5	26.1	27.6	27.2	27.7	
1,2,3-thiadiazole	$\bar{\alpha}$	50.1	52.6	53.2	51.1	54.5	55.3	54.1
	$\Delta_1\alpha$	24.4	24.6	25.1	25.9	26.6	26.9	26.4
	$\Delta_2\alpha$	25.3	25.6	26.0	26.8	27.5	27.8	27.4
1,2,4-thiadiazole	$\bar{\alpha}$	49.5	50.5	51.2	50.4	53.1	54.0	
	$\Delta_1\alpha$	25.0	23.0	23.6	25.8	25.3	25.9	
	$\Delta_2\alpha$	27.9	24.0	24.6	27.1	26.1	26.5	
1,2,5-thiadiazole	$\bar{\alpha}$	49.0	51.9	52.4	50.7	53.4	54.1	53.1
	$\Delta_1\alpha$	23.0	25.1	25.5	24.8	26.2	26.5	25.2
	$\Delta_2\alpha$	23.0	28.4	28.8	24.8	27.7	28.1	28.4
1,3,4-thiadiazole	$\bar{\alpha}$	48.6	51.0	51.5	50.3	53.4	54.1	
	$\Delta_1\alpha$	23.4	22.7	23.6	25.3	24.9	25.7	
	$\Delta_2\alpha$	24.2	22.9	23.8	26.0	25.1	25.9	
1,2,3,4-thiatriazole	$\bar{\alpha}$	44.5	46.9	47.4	46.1	49.6	50.3	49.1
	$\Delta_1\alpha$	21.0	21.7	22.2	22.7	24.3	24.6	23.9
	$\Delta_2\alpha$	21.4	22.3	22.8	23.2	24.9	25.2	24.7
1,2,3,5-thiatriazole	$\bar{\alpha}$	44.6	47.1	47.6	45.8	49.3	49.7	
	$\Delta_1\alpha$	21.9	22.4	22.9	23.0	24.2	24.5	
	$\Delta_2\alpha$	24.1	24.6	25.1	24.5	25.6	25.9	

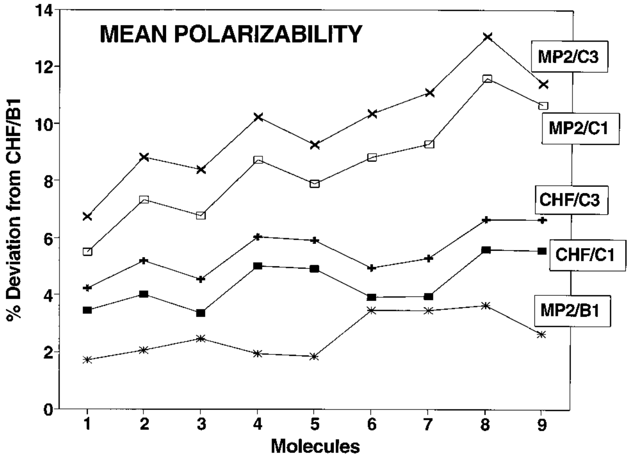

Figure 2. Percentage differences between the mean polarizability computed by various methods and its counterpart calculated at the CHF level in basis B1. The molecules are represented by their numbers according to Figure 1.

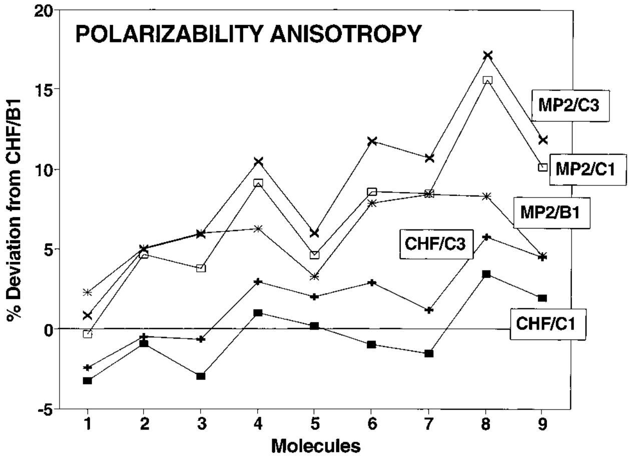

Figure 3. Percentage differences between the polarizability anisotropy $\Delta_1\alpha$ computed by various methods and its counterpart calculated at the CHF level in basis B1. The molecules are represented by their numbers according to Figure 1.

anisotropy is the difference between the mean in-plane and out-of-plane components given in our coordinate system by

$$\Delta_1\alpha = \alpha_{\parallel} - \alpha_{\perp} = {}^1/_2(\alpha_{yy} + \alpha_{zz}) - \alpha_{xx} = {}^1/_2(\alpha_2 + \alpha_3) - \alpha_1 \quad (2)$$

Another invariant, related to the Kerr effect and often used in the literature, is given by

$$\Delta_2\alpha = \left[\frac{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2}{2}\right]^{1/2} \quad (3)$$

Table 4 lists the polarizability mean and anisotropy for all molecules. Figure 2 shows the deviations in percentage of various computed mean polarizabilities from their CHF/B1 counterparts. In keeping with azoles[11] and oxazoles,[12] there is a consistent increase of the polarizability average upon extending the basis set and including electron correlation at MP2 level. An important point arises here as to whether this increase at the SCF level is an improvement in virtue of the Hylleraas variational principle.[23,51] This point seems to have received little attention in the literature, even though the principle has been quite often used, both implicitly and explicitly, as a criterion to optimize basis sets.[52,53] We think therefore that it, despite its subtlety, warrants a discussion. The principle predicts that the exact (in our case the Hartree−Fock limit) polarizability is approached by lower values when the zero-order problem (in this case the unperturbed Hartree−Fock equation) is exactly solved. When it is not, it can be readily shown that the principle remains formally the same except that one approaches by lower values a reference polarizability shifted from its true Hartree−Fock limit.[54] This shift indeed undermines the use of the principle, since it is theoretically unpredictable whether it is a negative (reference below the true value) or a positive one. Empirical observation shows, however, that within the unavoidable limitations on the basis set size the inexactness of the zero-order problem results in such an underestimation of the true Hartree−Fock limit polarizability that one still approaches it by lower values regardless of the shift. Thus it appears that, in most cases, this shift is either very small, which is likely for basis sets of reasonable size, or negative, in which case the increase in polarizability is certainly an improvement. We think it is this empirical fact that justifies the usage of the approximate variational principle as an optimizational tool for the one-particle polarizability basis set.

As apparent in Figure 2, the major basis effect on the mean polarizability occurs when enlarging the basis set from B1 to C1. The increase averages 4.4% and 5.8% at the SCF and MP2 levels, respectively, and ranges from 3.4% (thiazole at the CHF level) to 7.8% (1,2,3,5-thiatriazole at the MP2 level). Further enlargement of the basis set from C1 to C3 increases the mean by an average of only 1.0% and 1.4% at the CHF and MP2 levels, respectively.

MP2 correlation increases the mean polarizability by an average of 2.6%, 3.9%, 3.9%, and 4.2% in basis B1, C1, C2, and C3, respectively. MP4(SDQ)/C1 correlation reduces the MP2/C1 values by about 1% for the four molecules as shown in Table 4.

Figure 3 shows that, in contrast to the mean polarizability, the correlation effects are more important for the anisotropy

TABLE 5: Comparison of Polarizabilities (in au) for Thiophene

	$\bar{\alpha}$	$\Delta_1\alpha$	$\Delta_2\alpha$
CHF/4-31G+(dp)[a]	55.9		29.1
CHF/6-31+G(d,p)[b]	57.0	26.7	27.8
CHF/6-31+G(3d,3p)[b]	61.1	26.6	27.8
CHF/6-31G+(sp+sd)[c]	61.6	30.3	30.9
CHF/Sadlej[d]	63.1	27.8	28.5
CHF/C3[e]	63.0	27.9	28.6
MP2/6-31+G(d,p)[b]	58.2	27.8	28.5
MP2/6-31G+(sp+sd)[c]	63.6	31.0	31.4
MP2/C3[e]	64.5	28.9	29.3
Lefevre et al.[f]	60.6	23.1	23.1
Dennis et al.[g]	65.2 ± 2.1	19.9 ± 4.1	21.6 ± 3.4
Zhao et al.[h]	66.1		
Coonan et al.[i]	64.9 ± 0.6	31.1 ± 8.2	31.9 ± 7.9

[a] At the SCF/4-31G* geometry.[18] [b] At the SCF/6-31G** geometry.[19] [c] At the experimental MW geometry and a wavelength λ of 632.8 nm.[16] [d] At a MNDO-based geometry.[17] [e] At the MP2/6-31G** geometry (this work). [f] At $\lambda = 589.3$ nm in carbon tetrachloride solvent.[20] [g] At $\lambda = 632.8$ nm in cyclohexane solvent.[21] [h] At $\lambda = 589.8$ nm in tetrahydrofuran solvent.[22] [i] At $\lambda = 632.8$ nm.[16]

TABLE 6: MP2/C3 Polarizabilities (in au) for Thiophene and Its Aza-Substituted Analogues at MP2/6-31G Geometries[a]**

molecule	α_1	α_2	α_3	ϕ_3	$\bar{\alpha}$	$\Delta_1\alpha$	$\Delta_2\alpha$
thiophene	45.3	71.3	77.0	90.0	64.5	28.9	29.3
isothiazole	40.9	72.8	64.5	86.7	59.4	27.8	28.7
thiazole	40.9	70.5	66.1	96.2	59.2	27.5	27.7
1,2,3-thiadiazole	37.3	60.4	68.1	83.5	55.3	26.9	27.8
1,2,5-thiadiazole	36.4	57.5	68.4	90.0	54.1	26.5	28.1
1,3,4-thiadiazole	37.0	64.4	61.0	90.0	54.1	25.7	25.9
1,2,4-thiadiazole	36.8	59.2	66.0	84.9	54.0	25.9	26.5
1,2,3,4-thiatriazole	33.9	61.7	55.2	80.0	50.3	24.6	25.2
1,2,3,5-thiatriazole	33.3	62.7	53.0	90.4	49.7	24.5	25.9

[a] α_1, α_2, and α_3 are eigenvalues of the polarizability tensor; the 1-axis is perpendicular to the molecular plane, and the counterclockwise rotation by ϕ_3 degrees brings the 3−4 bond into coincidence with the 3-axis.

than the basis set ones. For example, it seems premature to include correlation effects for the mean in a small basis such as B1 (Figure 2), whereas including them is definitely worthwhile for the anisotropy (Figure 3). As the basis set is enlarged progressively from B1 to C3, the basis set effects at CHF and MP2 levels average 2.1% from B1 to C1, 0.6% from C1 to C2, and 2.3% from C2 to C3. MP2 correlation increases the anisotropy by an average of 6.9%. The highest (7.5%) and the lowest (5.8%) averages are obtained in basis C1 and B1, respectively. The increase obtained in basis C1 and C2 is, however, very similar. The little effect obtained on polarizability from basis C1 to C2 suggests that the d-shell is almost saturated. Thus, including polarization functions of higher angular momentum is appropriate. MP4(SDQ)/C1 correlation decreases the MP2/C1 values by 0.9% for isothiazole and 1,2,3-thiadiazole, 3.8% for 1,2,5-thiadiazole, and 1.5% for 1,2,3,4-thiatriazole.

The increase in polarizability due to the addition of f-type functions is rather small. Although it seems relatively more significant for the anisotropy (2.3% on average) than for the mean (0.7% on average), this rather reflects the difference in magnitude between the two quantities. Both of them seem to be consistently decreased, on the other hand, by MP4(SDQ) correlation effects (see Table 4). This trend was noticed in the azoles as well.[11] A partial cancellation between the effects of basis set extension and inclusion of higher correlation effects seems to be plausible. This perhaps is a contributing factor to the well-known effectiveness of MP2 level calculations of polarizability.

In Table 5, we list various computed and experimental polarizabilities for thiophene. First, we compare the CHF calculations. Our CHF/C3 values agree quite well with Champagne et al.'s.[17] The Sadlej medium size basis used in this calculation is of the same quality as our C1 basis. The difference in geometry, which must be considerable, does not seem to affect the polarizability of this molecule to any great extent. The largest discrepancies for the zero-frequency values occur with the average polarizability of Keshari et al.[18] and the $\Delta_1\alpha$ anisotropy of Hinchliffe and Soscun.[19] The former and the latter values are 11.3% and 4.8% lower than our CHF/C3 counterparts, respectively. The CHF/6-31G(3d,3p) mean polarizability due to the last two authors[19] is in reasonable agreement with ours, but their CHF/6-31G(d,p) is 9.6% lower. The difference between our geometries of thiophene can hardly explain such a discrepancy. The same remark applies to Keshari et al.'s value[18] (11.3% lower than CHF/C3) computed at SCF/4-31G* geometry. The discrepancy is rather due to the polarizability basis sets. A variational argument would suggest that the basis C3 provides a significantly better underestimation of the true CHF limit polarizability. In fact, the 6-31G(d,p)[19] basis shows a similar performance in the case of furan as was pointed out earlier.[12] The MP2/6-31G(d,p) is even lower than the CHF/6-31G(3d,3p)[19] for both furan and thiophene molecules. A direct comparison with Coonan et al.'s[16] values is not possible, since they pertain to 623.8 nm, but one should note that they are expected to be lower still at zero frequency.

Experimental polarizability determinations at finite wavelengths are available for the thiophene. Le Fèvre et al.[20] reported their values at 589.3 nm based on depolarization ratios, refraction, and dielectric polarization in a carbon tetrachloride solvent. Dennis et al.[21] determined them at 632.8 nm using experimental values of the molar refraction, molar Kerr and Cotton−Mouton constants, dipole moment, and magnetizability in cyclohexane solvent. Zhao et al.[22] obtained their values from refractive index measurements in tetrahydrofuran solution at 589.9 nm. Finally, Coonan et al.[16] reported polarizabilities at 632.8 nm that were obtained from experimental values of the refractive index, Rayleigh depolarization ratio, and the temperature dependence of the vapor-phase molar Cotton−Mouton constant, dipole moment, and anisotropic magnetizability. It is obviously pointless to attempt a narrowly quantitative comparison of these values with the computed ones. Dispersion and vibrational effects, in addition to solvent effects when measurements are done in solution, preclude such a comparison. Bearing that in mind, one may simply note that the computed MP2/C3 values and experimental ones are fairly corroborative.

Our best results are given in Table 6 with more details concerning the polarizability tensor. The in-plane polarizability axes, which can be rapidly grasped from Figure 1, are numerically specified by giving the angle ϕ_3 that brings the bond between atoms 3 and 4 into coincidence with the in-plane 3-axis of polarizability.

Summary

This work has provided a consistent computational investigation of the structures, dipole moments, and dipole polarizabilities for the thiophene molecule and its aza-substituted derivatives. Our structures and dipole moments are in good agreement with accurate experimental microwave determinations where available. In particular, the dipole moment orientations are remarkably good. Based on our systematic examination of basis sets that were extended to include f-type functions and of correlation

effects up to the MP4(SDQ) level, our polarizabilities are expected to be reliable within 5%. This work will be an important addition to the polarizability data reported earlier on the same line. Such consistent data would be useful in investigating chemically interesting issues such as aromaticity.

Acknowledgment. The authors thank Dr. Ajit J. Thakkar at the University of New Brunswick where this work was initiated and Dr. Anthony Hess at the Pacific Northwest National Laboratory where all relevant computations were performed using the Gaussian 94 package.[26]

References and Notes

(1) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107.
(2) Miller, T. M.; Bederson, B. *Adv. At. Mol. Phys.* **1977**, *13*, 1.
(3) Miller, T. M.; Bederson, B. *Adv. At. Mol. Phys.* **1988**, *25*, 37.
(4) Hasanein, A. A. *Adv. Chem. Phys.* **1993**, *85*, 415.
(5) Bulgarevich, S. B.; Yusman, T. A.; Osipov, O. A. *J. Gen. Chem. USSR* **1984**, *54*, 1427.
(6) Lazzeretti, P.; Tossell, J. A. *J. Mol. Struct.* **1991**, *236*, 403.
(7) Archibong, E. F.; Thakkar, A. J. *Mol. Phys.* **1994**, *81*, 557.
(8) Hohm, U. *J. Chem. Phys.* **1994**, *101*, 6362.
(9) Nilar, S. H.; Pluta, T. S. *J. Am. Chem. Soc.* **1995**, *117*, 12603.
(10) Katritzky, A. R. *Handbook of Heterocyclic Chemistry*; Pergamon: New York, 1985.
(11) El-Bakali Kassimi, N.; Doerksen, R. J.; Thakkar, A. J. *J. Phys. Chem.* **1995**, *99*, 12790.
(12) El-Bakali Kassimi, N.; Doerksen, R. J.; Thakkar, A. J. *J. Phys. Chem.* **1996**, *100*, 8752.
(13) Wong, K. Y.; Alex K. Y.; Rao, V. P. J. *Phys. Rev.* **1994**, *49*, 3077.
(14) Karna, S. P.; Keshari, V.; Prasad, P. N. *Chem. Phys. Lett.* **1995**, *234*, 390. Verbandt, Y.; Thienpont, H.; Veretennicoff, I.; Geerlings, P.; Rikken, G. L. J. A. *Chem. Phys. Lett.* **1997**, *270*, 471.
(15) Bhavsar, S. B.; Shinde, D. B.; Shingare M. S. *Indian J. Chem B* **1995**, *34*, 70.
(16) Coonan, M. H.; Craven, I. E.; Hesling, M. R.; Ritchie, G. L. D.; Spackman, M. A. *J. Phys. Chem.* **1992**, *96*, 7301.
(17) Champagne, B.; Mosley, D. H.; André J.-M. *J. Chem Phys.* **1995**, *100*, 2034.
(18) Keshari, V.; Wijekoon, W. M. K. P.; Prasad, P. N.; Karna, S. P. *J. Phys. Chem.* **1995**, *99*, 9045.
(19) Hinchliffe, A.; Soscún M. H. J. *J. Mol. Struct. (THEOCHEM)* **1995**, *331*, 109.
(20) Le Fèvre, C. G.; Le Fèvre, R. J. W.; Rao, B. P.; Smith, M. R. *J. Chem. Soc.* **1959**, 1188.
(21) Dennis, G. R.; Gentle, I. R.; Ritchie, G. L. D.; Andrieu, C. G. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 539.
(22) Zhao, M. T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988**, *89*, 5535.
(23) Epstein, S. T. *The Variation Method in Quantum Chemistry*; Academic Press: New York, 1974.
(24) Cohen, H. D.; Roothaan, C. C. J. *J. Chem. Phys.* **1965**, *43*, S34.
(25) Dykstra, C. E. *Ab Initio Calculation of the Structures and Properties of Molecules*; Elsevier: Amsterdam, 1988.
(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrezewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Gioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, Y.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian, Revision E.1*; Gaussian, Inc.: Pittsburgh, PA, 1995.
(27) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
(28) Sadlej, A. J. *Collect. Czech. Chem. Commun.* **1988**, *53*, 1995.
(29) El-Bakali Kassimi, N.; Tadjeddine, M.; Flament, J. P.; Berthier, G.; Gervais, H. P. *J. Mol. Struct. (THEOCHEM)* **1992**, *254*, 177.
(30) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
(31) Mulliken, R. S. *J. Chem. Phys.* **1962**, *36*, 3428.
(32) Bak, B.; Christensen, D.; Hansen-Nygaard, L.; Rastrup-Anderson, J. *J. Mol. Spectrosc.* **1961**, *7*, 58
(33) Nygaard, L.; Asmussen, E.; Hog, J. H.; Rastrup-Anderson, J.; Sorsensen, G. O. *J. Mol. Struct.* **1971**, *8*, 225.
(34) Stiefvater, O. L. *Chem. Phys.* **1976**, *13*, 73.
(35) Nygaard, R.; Hansen, L.; Sorensen, G. O. *J. Mol. Struct.* **1971**, *9*, 163.
(36) Stievater, O. L. *Z. Naturforsch.* **1976**, *31A*, 1681.
(37) Stievater, O. L. *Z. Naturforsch.* **1978**, *33A*, 1511.
(38) Shultz, G.; Hargittai, I.; Friedman, P. *J. Mol. Struct.* **1988**, *176*, 61.
(39) El-Azhary, A. A.; Suter, H. U. *J. Phys. Chem.* **1995**, *99*, 12751.
(40) El-Azhary, A. A. *J. Chem. Res.* **1995**, *174*, 1149.
(41) El-Azhary, A. A. *Acta Chem. Scand.* **1995**, *94*, 11.
(42) El-Azhary, A. A. *Acta Spectrochim. Acta* **1995**, *51A*, 995.
(43) Simandiras, E. D.; Handy, N. C.; Amos, R. D. *J. Phys. Chem.* **1988**, *92*, 1739.
(44) Shaffer, A. A.; Wierschke, S. G. *J. Comput. Chem.* **1993**, *14*, 75.
(45) Ogata, T.; Kozima, K. *J. Mol. Spectrosc.* **1972**, *42*, 38.
(46) Griffits, J. H.; Wardley, A.; Williams, V. E.; Owen, N. L.; Sheridan, J. *Nature* **1972**, *216*, 1301.
(47) Bak, B.; Christensen, D.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Mol. Spectrosc.* **1962**, *9*, 222.
(48) Dobyns, V.; Pierce, L. *J. Am. Chem. Soc.* **1963**, *85*, 3553.
(49) Bak, B.; Christensen, D.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Mol. Spectrosc.* **1962**, *9*, 225.
(50) Katritzky, A. R. *Physical Methods in Heterocyclic Chemistry*; Academic Press: New York, 1974; Vol. VI.
(51) Hyllerass, E. A. *Z. Phys.* **1930**, *54*, 347. (b) Atanassof *Phys. Rev.* **1930**, *36*, 1232.
(52) Werner, H. J.; Meyer, W. *Mol. Phys.* **1976**, *31*, 855.
(53) Spackman, M. A. *J. Phys. Chem.* **1989**, *93*, 7594.
(54) El-Bakali Kassimi, N. Application du principe variationnel au calcul des polarizabilites et des hyperpolarizabilites. Ph.D. Thesis, Paris VI, 1992.