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***Ab Initio* Investigation of the Static Polarizability of Planar and Twisted Infinite Polythiophene Chains**

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Abstract

In this paper we investigate the electronic structure and the static longitudinal polarizability of regular finite and infinite chains of polythiophene at the *ab initio* Hartree-Fock level. The effects of the inclusion of polarization functions in the basis set and the influence of introducing a torsional twist between adjacent rings are considered. © 1994 John Wiley & Sons, Inc.

Introduction

Conjugated polymers have attracted a great deal of theoretical and experimental interest in recent years. These systems possess potential with respect to their interesting conductivity properties and their large nonlinear optical responses [1-3]. In this area, much attention is directed towards polythiophene and its derivatives (for example [4-7]). This is an attractive polymer due to its stability in air and the possibilities of introducing side-chain substituents to enhance its solubility in common organic solvents [8,9]. Materials based upon polythiophene have been synthesized that exhibit high conductivities and large linear and nonlinear responses [10,11].

Large response properties are critically dependent upon the degree of electron delocalization along the polymer backbone [12]. X-ray crystal structures indicate that 2,2'-bithiophene and terthiophene adopt a planar conformation, with the sulfurs in adjacent rings anti to each other [13]. In part of this paper we study the effect of introducing a twist between successive rings in finite and infinite polythiophene chains in order to observe the effect this disruption of conjugation has upon the computed properties. Such distortion from the planar conformation is observed on the introduction of side-chain substituents [14]. Previous studies have studied the variation in the ionization energy, valence band width, and band gap with such twists using parameterized *ab initio* (valence effective Hamiltonian) [15] and MNDO calculations [16].

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In this study, in addition to the energies, band energies and band gap, we present *ab initio* uncoupled and coupled Hartree–Fock predictions of the static longitudinal polarizabilities. Both the uncoupled and coupled schemes were applied to the finite chains, while the treatment of the infinite chains was restricted to the uncoupled Hartree–Fock level. Recently, we have published [17] the results of a comprehensive study of the dipole polarizabilities of oligothiophenes using several basis sets (3-21G, 6-31G**, 6-311G**, and the Sadlej medium-sized polarized basis sets [18]) and the extrapolated values of the longitudinal polarizability per unit cell of polythiophene. This paper is a companion to this in studying the effects of changes in the conformation on the electronic properties of polythiophene.

Methodology

The calculations presented in this paper fall into two categories. Initially, geometry optimizations were performed on *ter*-thiophene at various conformations, using the Gaussian-92 package [19]. The geometries of the central rings were then used as the repeating unit in calculations of the polarizabilities of extended thiophene oligomers, again using Gaussian-92, and of infinite stereoregular polythiophene, using a program developed in our laboratory, PLH-93 [20,21].

The polarizabilities of the oligomers were calculated at the uncoupled and coupled Hartree–Fock levels (from hereon referred to as UCHF and CHF, respectively). The UCHF method, sometimes referred to as the sum over states or SOS method [22], is based upon a perturbation treatment of the Hartree–Fock wavefunction, or the corresponding SCF-MOs. The components of the polarizability can be expressed as

$$\alpha_{uv} = 4 \sum_i \sum_a \frac{\langle \phi_i | \mu_u | \phi_a \rangle \langle \phi_a | \mu_v | \phi_i \rangle}{\epsilon_a - \epsilon_i} \quad (1)$$

where ϕ_i and ϕ_a represent doubly occupied and virtual molecular orbitals, in the absence of an electric field, respectively, and ϵ_a and ϵ_i their corresponding orbital energies. The scheme neglects field-induced reorganizational effects, and is thus described as an uncoupled scheme. In the CHF method [23], the field-induced electron reorganization is included in a way which is fully consistent in terms of adjustments in the average two-electron interactions via analytical differentiation of the field dependent Hartree–Fock equation.

The standard quantum chemical treatment of polymers is based on the periodic model of the polymer chain. In restricted Hartree–Fock theory, the many-electron wave functions of the closed shell periodic systems are approximated by Slater determinants constructed from doubly occupied crystalline orbitals. The LCAO form of such a crystalline orbital is given by

$$\phi_n(k, \mathbf{r}) = N_C^{-1/2} \sum_j \exp[ikja] \sum_p c_{pn}(k) \chi_p(\mathbf{r} - \mathbf{P} - ja\mathbf{e}_z), \quad (2)$$

where n is the band index, k the reciprocal lattice vector in the first Brillouin zone, j represents the cell index, $N_C^{-1/2}$ the normalization factor, $c_{pn}(k)$ the k -dependent

LCAO coefficients, and $\chi_p(\mathbf{r} - \mathbf{P} - j\mathbf{a}\mathbf{e}_z)$, the p th atomic orbital centered in the j th cell. The standard theory of band structure is covered in detail in several reviews (for example, see [24,25]).

In methods for the calculation of the polarizability of polymers serious problems have to be overcome. The most serious of these is that the electric field operator acting on a polymer is unbounded and thus results in destruction of the translational symmetry of the system. Means of overcoming this problem have been proposed and discussed in detail in the literature [26,27].

In this paper, we apply a scheme for the computation of the uncoupled Hartree-Fock asymptotic longitudinal static polarizability per unit cell of infinite systems developed recently [28,29] based upon the perturbational approach of Genkin and Mednis [30]. The longitudinal polarizability can be expressed as

$$\alpha_{zz} = 4 \sum_i \sum_a \sum_k \frac{|\Omega_{ia}(k)|^2}{\epsilon_a(k) - \epsilon_i(k)}, \quad (3)$$

where the sums over i and a represent sums over occupied and unoccupied bands respectively, $\Omega_{ia}(k)$ are the dipole transition strengths [28,29,31,32]. In order to calculate the polarizability per unit cell, the sum over k is replaced by an integration over the first Brillouin zone, to give

$$\begin{aligned} \frac{\alpha_{zz}}{N_C} &= \frac{2a}{\pi} \sum_i \sum_a \int \frac{|\Omega_{ia}(k)|^2}{\epsilon_a(k) - \epsilon_i(k)} dk \\ &= \sum_i \int \alpha_{zz}(i, k) dk \\ &= \sum_i \alpha_{zz}(i). \end{aligned} \quad (4)$$

This final result illustrates how the polarizability can be decomposed into the contributions made from each of the occupied bands. This can be used to establish relationships between the topology of the bands and the polarizability to provide insight into the nature of bonding and conjugation in the polymer [17,29,33,34]. Coupled schemes to calculate the polarizability have been developed recently [35-37], but their application has been restricted to model systems due to the substantial computational cost involved.

All calculations were performed on IBM RS6000 Model 560 machines of the Namur Scientific Computing Facility.

Results

Geometry Optimizations

All-Anti, Planar Polythiophene. The geometry of the trimer in the all anti conformation was optimized at the Hartree-Fock level with the 3-21G and 3-21G* basis sets. In these geometry optimizations all atoms in the three rings were constrained to be coplanar. The molecule is represented in Figure 1 and the results

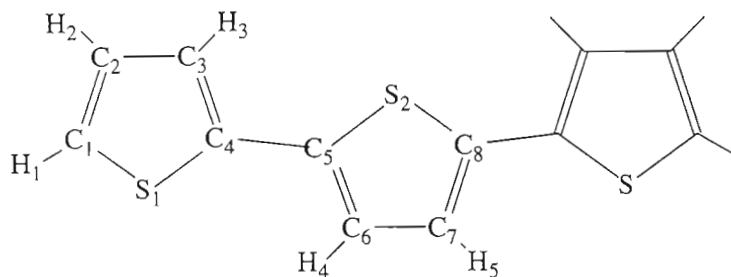


Figure 1. Ter-thiophene with atom labels as referred to in Tables I and II.

listed in Table I. Parameters obtained from an MNDO geometry optimization [4] are also included for comparison. The values of δ given in the final two rows of Table I represent the bond-length alternation, which is the difference between the two adjacent single and double carbon-carbon bond lengths indicated. This alternation gives an indication of the amount electron delocalization along the carbon backbone. The geometrical parameters obtained for the central ring were used in the subsequent polymer calculations. Two such rings constitute the translational unit cell used for the calculations on the infinite chain. It has been noted [7] that using the trimer is sufficient to obtain reliable geometrical parameters for the central ring, with little further change being observed in continuing to higher oligomers.

Twisted Polythiophene. In the idealized conformations considered for twisted polythiophene, equivalence of alternate thiophene rings was imposed. Partial geometry optimizations using the 3-21G basis set were carried out on the three-ring chains for inter-ring twists between 0° and 180° , at 15° intervals. In order to retain the translational periodicity for the polymer calculations, the chains were constrained to be linear (or rodlike) [15], that is, with the interring carbon-carbon bonds lying along the axis of periodicity. In practice, the carbon-sulfur-carbon angle ($C_5-S_2-C_8$) in the central ring and the sulfur-carbon-carbon angle ($S_2-C_5-C_4$) along the backbone were fixed to be 89.77° (the value obtained in the optimization of the planar, anti conformation) and 134.89° , respectively. Additionally, the central ring carbon-sulfur interatomic distances were fixed at 1.809 \AA . All atoms in individual rings were constrained to be coplanar, but all other bond lengths and bond angles were free to vary. The results of the optimizations for the geometrical parameters of the central ring are presented in Table II. An inter-ring twist angle of 180° corresponds to the all-anti conformation. The carbon-hydrogen bond lengths remained nearly constant for all twist angles ($1.069 \pm 0.001 \text{ \AA}$) and, therefore, are not included in the table. The values of δ given in the fifth and sixth columns of Table II give the degree of alternation between adjacent carbon-carbon single and double bonds.

Energy and Polarizability Calculations

All-Anti, Planar Conformation. Using the geometrical parameters given in Table I, molecular calculations were performed for chains containing from one to six

TABLE I. Optimized geometrical parameters of all-anti, planar *ter*-thiophene.^a

	Polythiophene		
	3-21G	3-21G*	MNDO
S ₁ —C ₁	1.795	1.721	
S ₁ —C ₄	1.810	1.738	
C ₁ —C ₂	1.335	1.347	
C ₂ —C ₃	1.442	1.433	
C ₃ —C ₄	1.343	1.355	
C ₁ —H ₁	1.065	1.067	
C ₂ —H ₂	1.070	1.069	
C ₃ —H ₃	1.069	1.069	
<(S ₁ —C ₁ —C ₂)	111.16	111.97	
<(S ₁ —C ₄ —C ₃)	110.59	110.72	
<(C ₁ —C ₂ —C ₃)	113.91	112.50	
<(C ₄ —C ₃ —C ₂)	114.40	113.16	
<(C ₁ —S ₁ —C ₄)	89.45	91.65	
<(S ₁ —C ₄ —C ₃)	120.54	121.40	
<(S ₁ —C ₁ —H ₁)	120.19	120.76	
<(C ₁ —C ₂ —H ₂)	123.47	124.02	
<(C ₄ —C ₃ —H ₃)	122.84	123.59	
S ₂ —C ₅	1.809	1.737	1.704
C ₅ —C ₆	1.342	1.354	1.380
C ₆ —C ₇	1.435	1.427	1.447
C ₄ —C ₅	1.439	1.454	1.444
C ₆ —H ₄	1.069	1.069	1.085
<(S ₂ —C ₅ —C ₄)	120.45	121.29	119.6
<(C ₅ —S ₂ —C ₈)	89.77	92.01	94.6
<(S ₂ —C ₅ —C ₆)	110.49	110.66	110.2
<(C ₅ —C ₆ —C ₇)	114.62	113.34	112.5
<(C ₅ —C ₆ —H ₄)	122.83	123.63	125.7
$\delta_{C_5-C_6-C_7}$	0.093	0.073	0.067
$\delta_{C_4-C_5-C_6}$	0.097	0.100	0.064

^a Geometry of central rings used in calculations on the extended oligomers and infinite chains. The MNDO parameters are listed for comparison. All bond lengths are given in angstroms. The atom labels correspond to Figure 1.

thiophene rings with the 3-21G and 3-21G* basis sets. The larger chains were constructed using the geometries obtained for the terminal rings in the trimer optimizations, and repeating the central unit. The evolution of the UCHF and CHF static longitudinal polarizability per thiophene ring [calculated by $\alpha_{zz}(N) - \alpha_{zz}(N-1)$] with an increasing number of thiophene rings for both basis sets at the two optimized geometries is represented graphically in Figures 2 and 3.

Calculations on infinite chains with two thiophene rings per unit cell were also carried out using the 3-21G and 3-21G* basis sets using the optimized geometries in both cases. The short and intermediate ranges of interaction were set to ± 3 and

TABLE II. 3-21G geometrical parameters of the central ring resulting from the restricted optimization of *ter*-thiophene at various twist angles.

	C ₄ —C ₅	C ₅ —C ₆	C ₆ —C ₇	$\delta_{C_{4-5},C_{5-6}}$	$\delta_{C_{5-6},C_{6-7}}$	$\angle(S_2-C_5-C_6)$	$\angle(C_5-C_6-C_7)$	$\angle(C_5-C_6-H_4)$
180.0	1.454	1.347	1.401	0.107	0.054	109.81	115.31	121.83
165.0	1.455	1.347	1.402	0.108	0.055	109.82	115.30	121.78
150.0	1.458	1.347	1.404	0.111	0.057	109.86	115.26	121.67
135.0	1.463	1.345	1.407	0.118	0.062	109.90	115.22	121.59
120.0	1.467	1.343	1.410	0.124	0.067	109.94	115.18	121.56
105.0	1.471	1.342	1.413	0.129	0.071	109.97	115.14	121.59
90.0	1.472	1.341	1.415	0.131	0.074	110.0	115.12	121.64
75.0	1.463	1.344	1.408	0.119	0.064	109.91	115.21	121.74
60.0	1.464	1.345	1.408	0.119	0.063	109.91	115.21	121.77
45.0	1.467	1.345	1.406	0.122	0.061	109.87	115.25	122.00
30.0	1.474	1.343	1.402	0.131	0.059	109.75	115.36	122.64
15.0	1.482	1.341	1.400	0.141	0.059	109.60	115.51	122.51
0.0	1.487	1.340	1.396	0.147	0.056	109.54	115.57	123.94

± 6 unit cells about the reference cell respectively. The total energies, energy of the highest occupied crystalline orbital (HOCO), valence band-gap (E_{gap}), and UCHF polarizabilities per unit cell and length are presented in Table III.

Twisted Conformations. The 3-21G basis set was used for all oligomeric and polymeric calculations on the twisted conformations of thiophene chains. This choice is justified due to the increased computational cost and relatively small effect of the inclusion polarization functions on the sulfur atom. Using the optimized geometries described in the previous subsection and listed in Table II for each twist angle, the UCHF and CHF static polarizabilities were calculated for the three-, five-, and seven-ring oligomer chains. The evolution of the CHF polarizability per pair of thiophene rings with an increasing number of rings for each twist angle is illustrated in Figure 4.

Polymeric calculations for the infinite chains were performed for each twist angle at the optimized geometry obtained in each case. The short and intermediate ranges of interaction were again set to ± 3 and ± 6 translational cells. The effect of the twist angle on the electronic properties is detailed in Table IV and the behavior of the band gap and UCHF static polarizability per unit cell are illustrated in Figures 5 and 6, respectively.

Discussion

Effect of Polarization Functions on the Sulfur Atom

The inclusion of polarization functions on the sulfur atom in the 3-21G* basis set generally has a more marked effect on the results of the geometry optimizations of the all-anti trimer than on the subsequent energy and polarizability calculations.

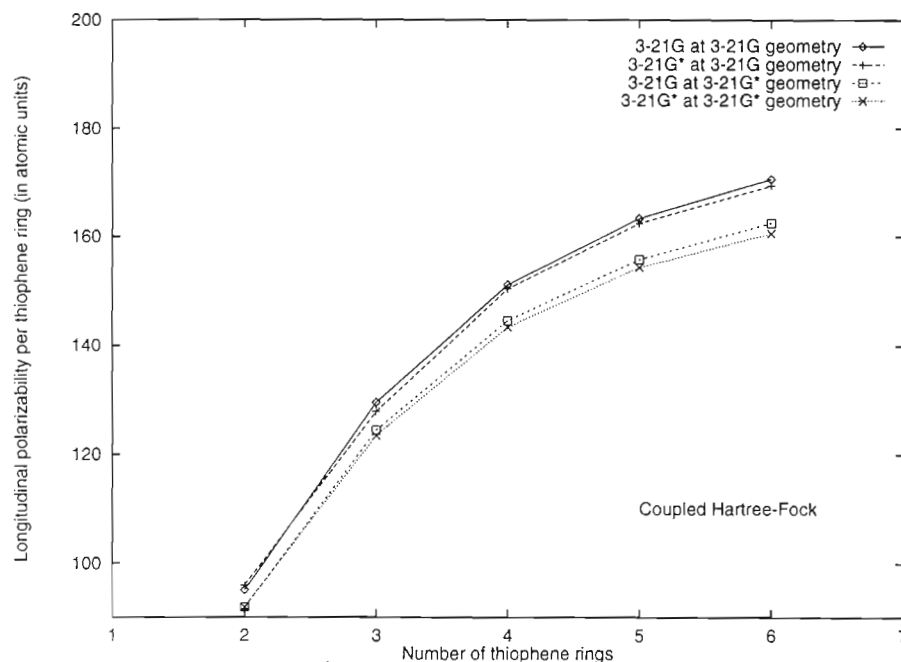


Figure 2. Evolution of the CPHF longitudinal polarizability per thiophene ring with an increasing number of thiophene rings with the 3-21G and 3-21G* basis sets at the geometries indicated.

The calculated carbon-sulfur bond length using the 3-21G* basis set is substantially shorter (0.072 \AA) compared to that obtained using the basis set without the polarization functions. The carbon-sulfur-carbon angle is correspondingly wider (2.2°) in the former case. Further investigation [38] indicates that any role for the d-orbitals in the bonding orbitals is small, and that this observation can be attributed, at least in part, to the paucity of the 3-21G basis set in the core region.

For the carbon-carbon bonds, the polarized basis set results in a lengthening of the carbon-carbon double bond (0.012 \AA) and a lengthening and shortening of the interrings and intraring carbon bonds ($+0.015$ and -0.008 \AA) respectively, compared to the 3-21G basis set. Due to these contrary effects, it is difficult to make any overall remarks regarding the bond length alternation with the two basis sets used. The overestimation of bond length alternancy using *ab initio* Hartree-Fock methods is well known and can be attributed largely to the absence of electron correlation effects. The MNDO method is regarded as quite capable of yielding acceptable geometrical parameters for conjugated systems at low computational cost.

Comparison of the electronic properties of the valence region of infinite planar polythiophene obtained using the two basis sets listed in Table III indicate a minor role for the polarization functions located on the sulfur atom. At the two fixed geometries, the difference between the energy gaps obtained using the 3-21G and

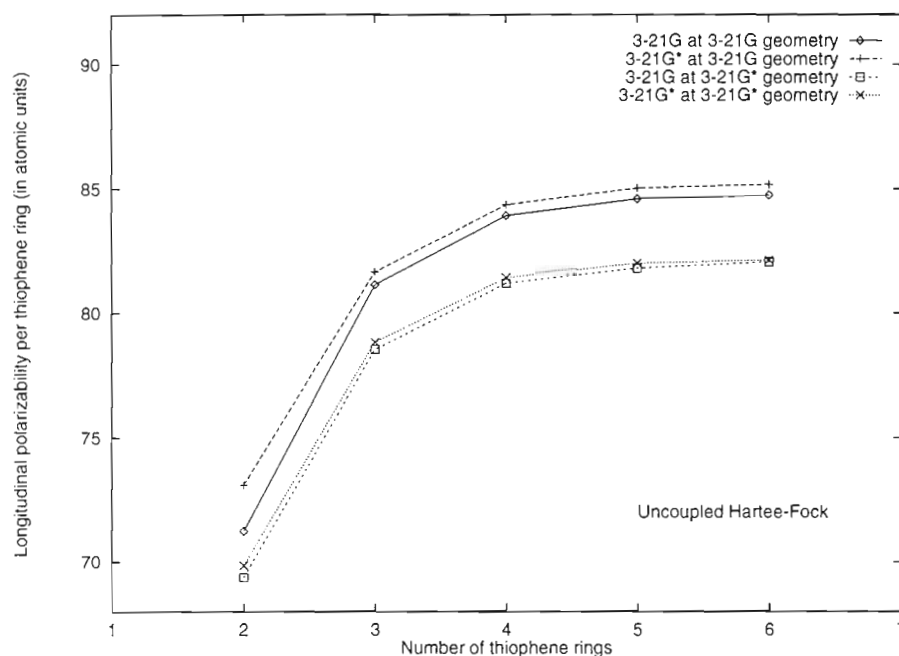


Figure 3. Evolution of the UCHF longitudinal polarizability per thiophene ring with an increasing number of thiophene rings with the 3-21G and 3-21G* basis sets at the geometries indicated.

3-21G* basis sets is small (≤ 0.02 eV). The difference between the gaps predicted at the two optimized geometries is more marked, with the predicted gap being in the region of 0.1 eV larger with the 3-21G* basis set.

The CHF and UCHF polarizabilities per thiophene ring in the extended oligomeric calculations illustrated in Figures 2 and 3 show similar behavior. The difference

TABLE III. Electron properties of infinite polythiophene using 3-21G and 3-21G* basis sets at two different geometries. All values in atomic units (except where marked).

	3-21G optimized geometry		3-21G* optimized geometry	
	3-21G	3-21G*	3-21G	3-21G*
Total energy	-1094.662095	-1094.87989241	-1094.65346482	-1094.88779487
HOCO	-0.254888	-0.251336	-0.250778	-0.247438
E_{gap}	0.2668 (7.26 eV)	0.2660 (7.24 eV)	0.2704 (7.36 eV)	0.2702 (7.35 eV)
$\alpha_{zz}/\text{unit cell}$	169.58	170.53	163.77	164.16
$\alpha_{zz}/\text{thiophene ring}$	84.79	85.26	81.89	82.08
$\alpha_{zz}/\text{unit length}$	11.369	11.432	11.095	11.121

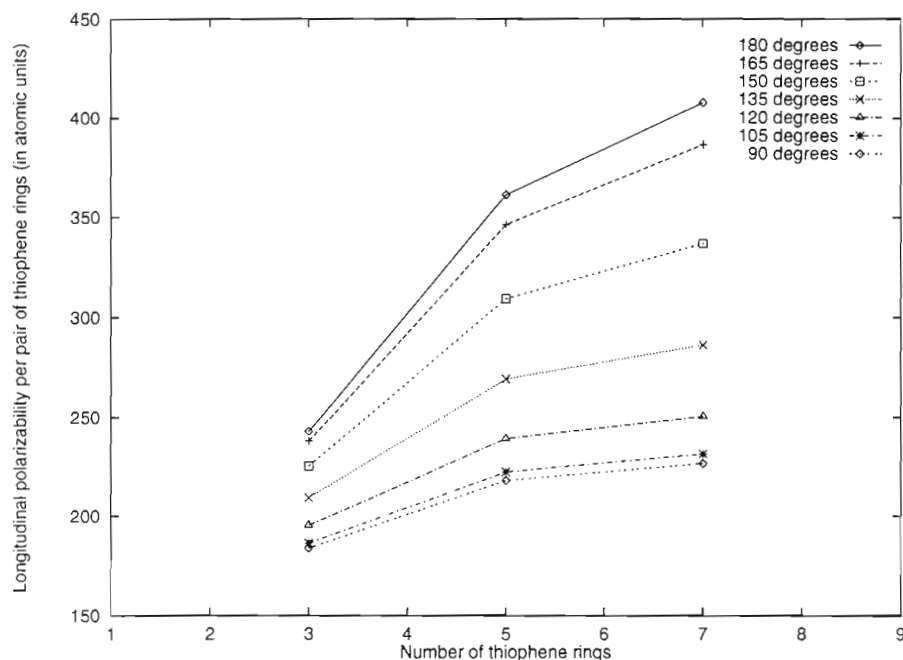


Figure 4. Evolution of the 3-21G Coupled Hartree-Fock longitudinal polarizability per pair of thiophene rings with increasing chain length at different torsion angles between adjacent rings.

between the polarizabilities obtained at the two optimized geometries using the two basis sets is small. Taking the example of the six-ring chain, at the 3-21G optimized geometry, the coupled value per thiophene ring using the 3-21G basis set (170.6 a.u.) slightly exceeds that obtained using the 3-21G* basis (169.4 a.u.). At the same geometry, the ordering of the uncoupled polarizabilities is reversed, with that obtained using the 3-21G* basis (85.18 a.u.) greater than that found with the unpolarized basis (84.75 a.u.). These features are replicated at the 3-21G* optimized geometry. The coupled and uncoupled polarizability per ring for the hexamer obtained, with the 3-21G and 3-21G* basis sets, respectively, are 162.5 and 160.6 a.u. and 82.05 and 82.13 a.u. For chains containing four and more thiophene rings, the uncoupled polarizability per ring is very close to saturation. However, the coupled value has still not reached saturation for the six-ring chain, the longest chain considered in this part of the work.

The uncoupled polarizabilities per thiophene ring obtained on the infinite polythiophene chains are detailed in Table III. At the 3-21G optimized geometry, the computed polarizabilities per thiophene ring are 84.79 and 85.26 a.u. with the 3-21G and 3-21G* basis sets, respectively, while, at the 3-21G* optimized geometry, the values are 81.89 and 82.08 a.u. These are all in very close concordance with the values obtained from the extended oligomer calculations. This confirms that

TABLE IV. 3-21G electronic properties of infinite polythiophene for various twist angles between successive rings.^a

	Total energy	HOCO	E_{gap}	α_{zz}/N	α_{zz}/L
180°	-1094.61007260	-0.2384	0.2508 (6.82 eV)	190.47	12.58
165°	-1094.61001614	-0.2416	0.2578 (7.01 eV)	184.01	12.15
150°	-1094.60995122	-0.2514	0.2780 (7.57 eV)	168.39	11.11
135°	-1094.60999025	-0.2682	0.3109 (8.46 eV)	150.37	9.91
120°	-1094.61039159	-0.2894	0.3504 (9.54 eV)	137.16	9.03
105°	-1094.61170400	-0.3137	0.3933 (10.70 eV)	129.83	8.54
90°	-1094.61397675	-0.3398	0.4171 (11.35 eV)	127.85	8.40
75°	-1094.61647400	-0.3148	0.3764 (10.24 eV)	132.56	8.73
60°	-1094.61803623	-0.2923	0.3393 (9.23 eV)	141.06	9.29
45°	-1094.61559726	-0.2724	0.3061 (8.33 eV)	153.11	10.08
30°	-1094.60669924	-0.2570	0.2803 (7.63 eV)	165.61	10.88
15°	-1094.59456895	-0.2469	0.2642 (7.19 eV)	175.34	11.50
0°	-1094.58876100	-0.2435	0.2591 (7.05 eV)	178.68	11.71

^a All values in atomic units (except where marked).

the uncoupled static polarizability per ring in the larger oligomers is very close to its saturation value, as discussed above. The smaller polarizability at the 3-21G* optimized geometry indicates less delocalization along the polymer backbone at this geometry. This is supported by the slight increase in interranging bond length alternation compared to the 3-21G optimized geometry and the increase in band gap. The HOCO, which makes the largest contribution to the polarizability, is of π -symmetry [17], composed of contributions from the carbon atoms along the backbone, thus resembling segments of all-*trans* and *trans-cisoid* polyacetylene. For this reason, it is not surprising that the addition of d-orbitals on the sulfur atom in the 3-21G* basis set has only a small effect on the computed polarizability. The influence of the bond length alternation on the computed polarizability is critical. Using the less alternating MNDO optimized geometry, the longitudinal polarizability per unit cell of infinite polythiophene has been calculated to be 86.02 a.u. using the 3-21G basis set [17], slightly larger than the values obtained here.

Influence of Torsional Twist between Adjacent Rings

Generally speaking, the effect of introducing a torsional twist between adjacent thiophene rings, thus disrupting the conjugation, is seen to be large. From the values listed in Table II, it can be seen that the intraring bond length alternation is at a minimum at the all-anti conformation, indicating a larger degree of electron delocalization. The alternation then increases to a maximum for the case in which the planes containing adjacent rings are perpendicular to each other, pointing to a reduction in conjugation, before decreasing for twist angles between 90° and 0°. The interranging carbon-carbon bond length alternation shows similar behavior for twist angles between 180° (all anti-) and 60°. For smaller angles, the length of the

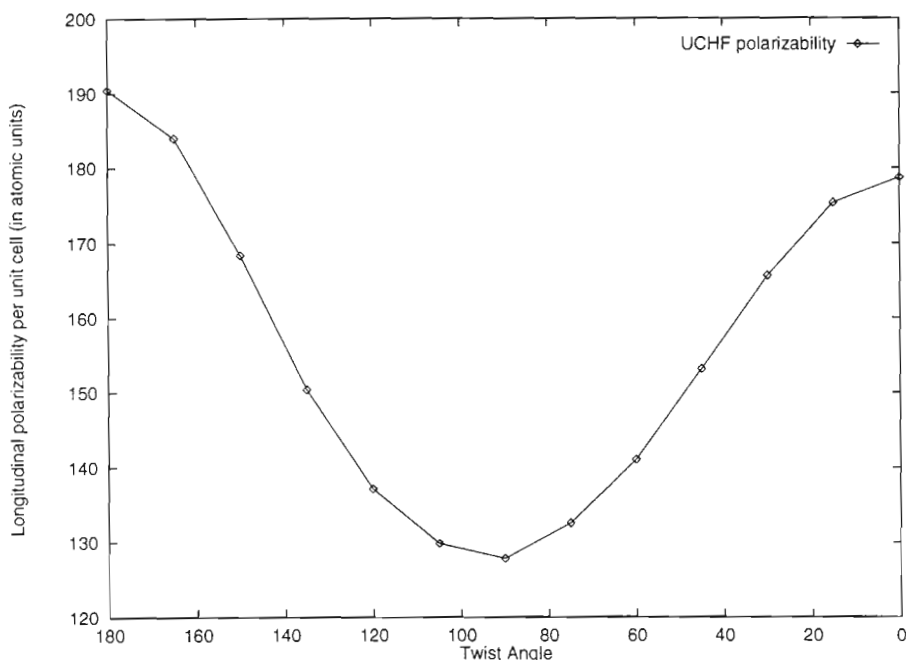


Figure 5. Evolution of the 3-21G uncoupled longitudinal polarizability per unit cell of infinite polythiophene with the torsion angle between adjacent rings.

interring carbon-carbon increases, increasing the bond length alternation. This effect is most likely due to steric effects and inherent strain as a result of the restricted optimization.

For the polymer calculations, the variation in the total energies calculated (see Table IV) are generally small. As the twist angles decrease towards 0° , the increase is notable, but this is primarily a result of the imposed, idealized geometry of the chain.

For the oligomer calculations, the values of the CHF polarizability per pair of thiophene rings for the heptamer in the most conjugated case (all-anti, 180° degree twist between adjacent rings) and the case in which adjacent rings are perpendicular to each other are 407.7 and 226.5 a.u., respectively, representing a decrease of over 40% between the two extremes. The difference is slightly less marked for the UCHF polarizability calculations, with the values at the all-anti and perpendicular conformations 190.3 and 127.9 a.u., respectively. The ratio of the CHF and UCHF polarizabilities for the most conjugated case is 2.12, while for the least conjugated case it is somewhat smaller at 1.79.

Two important features of Figure 4 showing the CHF polarizability per unit cell with increasing chain length for twist angles between 180° and 90° should be emphasized. First, it is evident that, in the less conjugated cases, the saturated value of the polarizability is attained more rapidly than for the more conjugated chains.

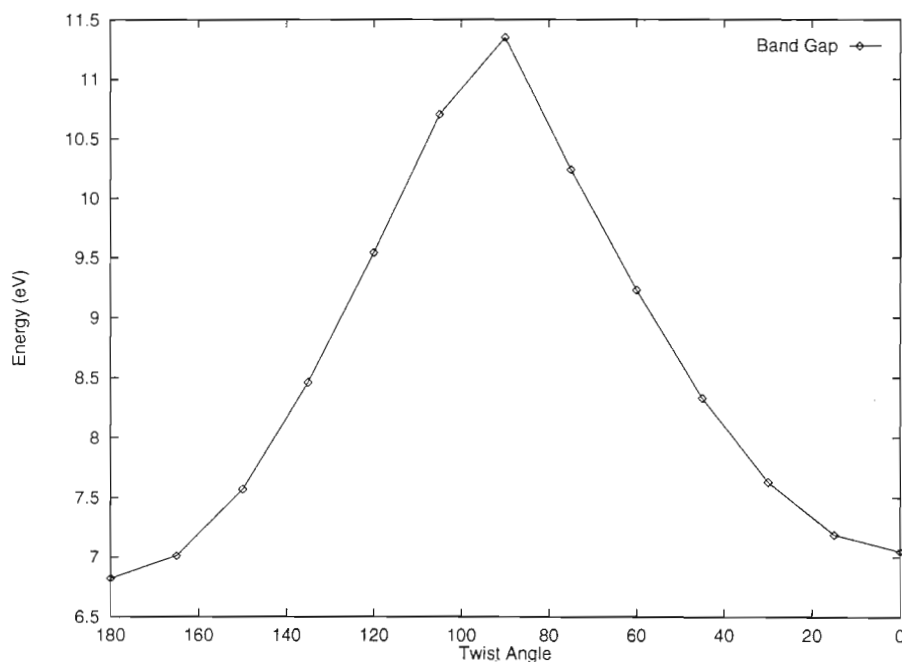


Figure 6. Evolution of the 3-21G band gap of infinite polythiophene with the torsion angle between adjacent rings.

This demonstrates the appeal of polymer calculations able to provide the asymptotic value directly. Second, the evolution of the polarizability per unit cell with twist angle does not evolve linearly. Small deviations in the twist angles, at either the more or less conjugated extremes, provoke only small changes in the computed values. More substantial twists induce more substantial changes.

This behavior is seen again in the smooth cosinelike curve for the variation of the uncoupled polarizability per unit cell with twist angle for infinite polythiophene chains in Figure 5. In Figure 6, in which the variation of the band gap with twist angle is illustrated, the overall form of the curve is repeated (although inverted, as would be expected, with the band gap increasing as the conjugation is reduced), but with a less smooth variation for twist angles around 90° . The ionization energies given in Table IV ($-E_{\text{HOCO}}$) also show this behavior, with the ionization energy being highest when two adjacent rings are perpendicular to each other. The overestimation of the band gap by Hartree-Fock calculations due to the neglect of electron correlation is well known. As can be seen from Eq. (3), the prediction of the UCHF polarizability is critically dependent on the size of the band gap. The excessively large band gap will result in an underestimation of the polarizability. UCHF polarizabilities can only, at best, give a qualitative indication, but are sufficient to reproduce trends. Accurate predictions of polarizabilities require coupled schemes and consideration of electron correlation.

This cosinelike form has been observed previously in studies of the electronic properties of polythiophene using the valence effective Hamiltonian method [15]. However, there the authors suggest torsions of up to 40° fail to induce any significant modifications of the electronic properties. While this may be the case for the computed ionization energies and band gaps, such a twist has substantial impact on the electron delocalization along the chain, evidenced by the substantial reduction of polarizability. Our observation is that small distortions from planarity (0 – 15°) will have only a small detrimental effect on the conjugation and computed properties, while larger twists result in considerable changes.

Figure 7 shows the valence band structures at two adjacent-ring twist angles (180° and 90°). There are strong similarities between the band structures for the anti (180°) and syn (0°) conformations (not shown), while that for the perpendicular case shows some strikingly different features. Perhaps the most obvious is the narrowness of the upper-valence bands. This supports the idea that the π -electronic distribution is significantly more localized in this case.

The bands making significant contributions to the UCHF longitudinal polarizability per unit cell for adjacent ring twist angles of 180° , 90° , and 0° are given in Table V. Distinction between bands of π - and σ -symmetry enables some conclusions to be drawn regarding the nature of the conjugation and its disruption as adjacent rings are twisted with respect to each other. For the anti and syn conformers, in which all atoms are coplanar, the π -bands are composed entirely of $2p_y$ (C,S) and $3p_y$ (S only) atomic orbitals perpendicular to the plane of the chain, and the π -electrons are delocalized over the whole system. For the conformer with a 90° torsion angle the situation is different, with the π -structure being defined by p_x and p_y orbitals alternately. This leads to the observed localization of the states (the top four bands, 39–42). However, it is also important to note that there is also a weak interaction of the sulfur $3p_z$ orbital with the π -subsystem on the adjacent ring. The overall picture is more complicated and assignment to π and σ contributions more difficult.

The approximate summed π and σ contributions to the polarizability for each conformer are given at the foot of Table V. A twist of 90° results in a sharp reduction of the π and slight reduction of the σ contributions. Additionally, the different π contributions distinguish between the syn and anti forms. The bands which contribute most to the polarizability of the anti conformer have the same form as the HOCO of alternate all *trans* and *trans-cisoid* segments of polyacetylene, while for the syn conformer, they correspond to the HOCO of *trans-cisoid* polyacetylene. The sulfur p_y orbitals do not contribute in either case. The larger polarizability of the anti conformer can be explained bearing in mind that *trans-transoid* (all *trans*) polyacetylene is more polarizable than the *trans-cisoid* form [34].

Conclusions

In this paper we have shown the attractiveness of polymeric methods to compute the asymptotic polarizability per unit cell directly and their ability to yield useful scientific insight into an interesting problem. Unfortunately, the polymeric calcu-

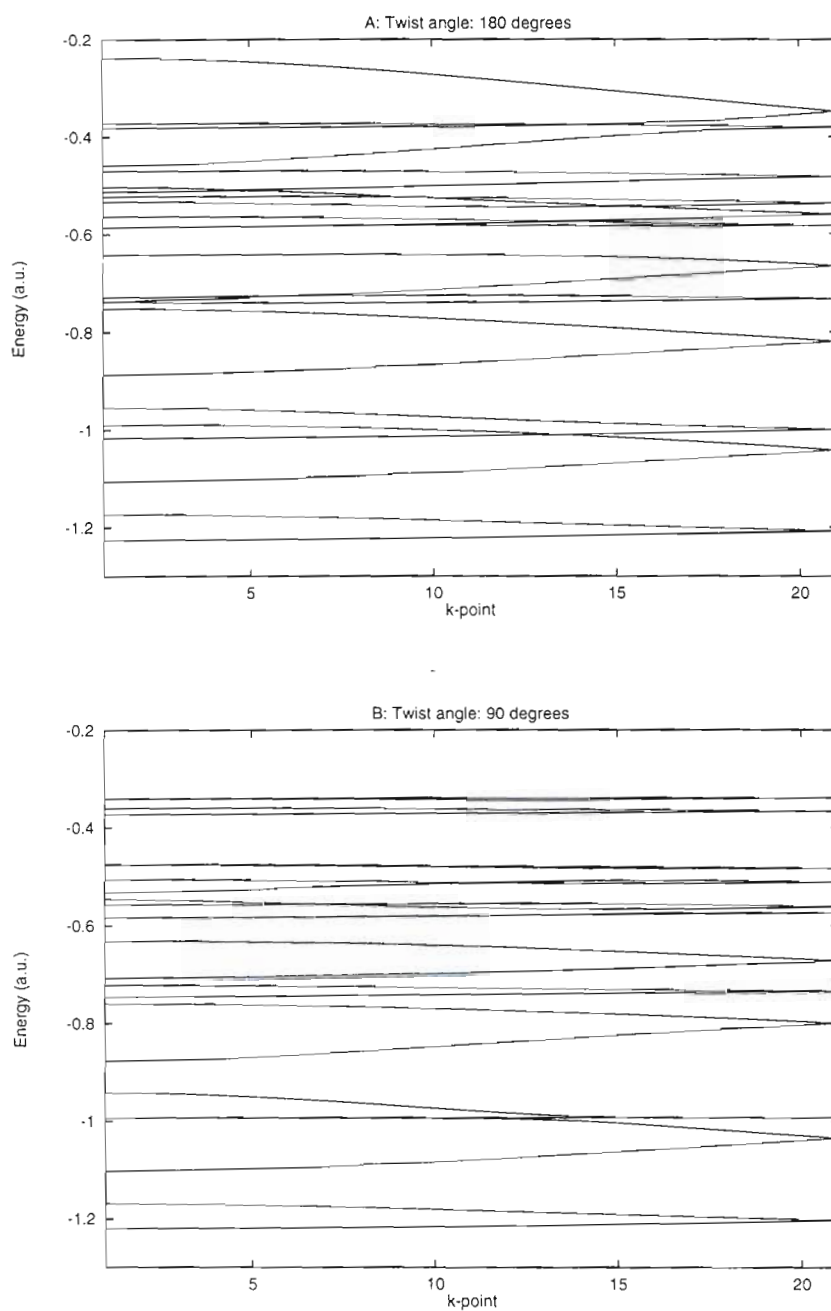


Figure 7. 3-21G valence band structures of polythiophene at two different interring twist angles: A: 180°, and B: 90°.

TABLE V. 3-21G valence band contributions to the longitudinal polarizability per unit cell at inter-ring twist angles of 180°, 90°, and 0°. ^a

Band	180°	90°	0°
19	0.07	0.07	0.06
20	0.08	0.08	0.08
21	0.18	0.18	0.16
22	0.12	0.20	0.14
23	0.22	0.17	0.19
24	0.31	0.29	0.31
25	0.57	0.67	0.60
26	0.54	0.69	0.46
27	0.73	0.57	0.70
28	2.64	0.85	0.54
29	1.12	2.61	2.33
30	5.09	4.59	3.30
31	0.03	3.43	5.38
32	10.29	8.00	0.02
33	4.42	5.87	5.54
34	11.08	5.79	16.13
35	8.83	6.28	12.86
36	9.21	3.70	0.08
37	0.09	7.06	8.03
38	14.05	7.74	11.58
39	1.59	3.03	1.68
40	1.82	5.57	3.64
41	5.86	31.60	4.59
42	111.47	28.76	100.24
α_{zz}/N	190.47	127.85	178.68
Approx. total π	120.8	69.0	110.1
Approx. total σ	69.7	58.8	68.6

^a The final four bands are of π -character.

lations of the polarizability are limited to an uncoupled scheme. A coupled scheme for polymers has been developed, but due to the substantial computational cost involved its implementation has been restricted to model cases [35,36]. For accurate polarizabilities, the corrections brought about by including electron correlation, vibrational contributions, and the frequency dependent character of the polarizability should also be considered [37].

There is much scope for further work, considering the effects of ring substituents on the polarizability, and also the *ab initio* study of the electronic properties and polarizabilities of polythiophene chains in helical coil conformations. The energetics of such systems have already been studied at the MNDO level [16].

The potential of polythiophene and its derivatives offers an incentive to understand fully the effect of substituents on the structure, electronic properties and linear and nonlinear response.

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