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The molecular geometries and the torsional potentials about the inter-ring C-C bond in α-oligothiophenes (α-nTh, n=2-4) have been calculated by means of conventional *ab initio* and density functional theory (DFT) calculations employing the hybrid B3LYP and BH&HLYP functionals. The position and the energetics of the critical points in the potential energy curve generated by rotation about the inter-ring C-C bond are shown to be dependent on the computational method. DFT calculations, in comparison with MP2 calculations, favour conjugative interactions, while steric and coulombic interactions are equally treated by both methods. On oligomerization the electron delocalisation increases slightly, the π-charge being preferentially confined within the rings, although it is sufficient to move the molecular structure towards co-planarization and to increase the barrier through the perpendicular conformation. The IR and Raman spectra on the relevant rotamers of α-2Th have been computed at HF/6-31G* and B3LYP/6-31G* levels. The comparison with the experiment is excellent. It has been found that small twisting from the planar conformation has no apparent effects, while 90° twisting and isomerization to the *syn-gauche* form produce significant frequency and intensity variations which could be useful probes in conformational studies. The simulated IR and Raman spectra of the α-2Th rotamers are consistent with a small π-electron delocalisation between the rings.

Introduction.

Polythiophene and thiophene oligomers are of interest in the area of organic metals [1] and as materials for nonlinear optics [2] and thin-film transistor devices [3]. There are several experimental and theoretical evidences showing that the desired optical and electronic properties of these materials markedly depend on the extension of the π-system, hence on the twisting degree of the backbone [4]. In the solid, polythiophene and thiophene oligomers take a planar or near planar configuration [5]. In solution as well as in the free state significant deviation from planarity can occur owing to a balance between conjugative and steric intramolecular interactions. Evidence of chain flexibility in solution comes from thermochromic and solvatochromic studies [6]. The great plasticity of oligothiophenes indicates that small torsional barriers act along the chain. This is nicely documented by the X-ray structure of 4,4',3",4"'-tetramethyl-2,2':5',2":5",2"'-tetrathiophene which undergoes significant deformations of bond lengths and bond angles in order to reach a planar configuration despite steric interactions [7]. The contribution of the theoretical approach to the conformational problem in oligothiophenes is well documented by several recent research papers [8]. However reliable correlated *ab initio* investigations and detailed description of the torsional potentials are essentially limited to the 2,2'-bithiophene oligomer [8]. In fact, the necessary inclusion of the electron correlation through conventional methods is computationally prohibitive for higher oligomers. Density functional theory (DFT) offers an alternative. The present work aims to investigate on the effects of the chain length on the structure and torsional potentials of α-linked thiophene oligomers α-nTh (n=2-4) by means of Hartree-Fock (HF) and DFT calculations. Infrared and Raman harmonic vibrational frequencies and intensities of the stationary points of α-2Th have also been

calculated in order to gain insight into twisting effects on specific vibrational transitions relevant in describing electronic and conformational effects.

Computational Methods.

HF and DFT calculations were carried out with the 6-31G* basis set. For DFT calculations non-local exchange-correlation functionals were considered. They are combinations of the Lee-Yang-Parr (LYP) [9] gradient-corrected correlation functional with either the Becke's hybrid half-and-half exchange functional (BH&HLYP) [10] or the Becke's three parameters gradient-corrected functional (B3LYP) [11]. So far the BH&HLYP functional has not been extensively employed. However it has been proved to give valuable informations on molecular structures and energetics on a variety of molecular systems [12]. The BH&HLYP functional has the form

$$E_{XC} = 0.5\ E_X(LSD) + 0.5\ E_X(HF) + 0.5\ \Delta E_X(B88) + E_C(LYP)$$

where E_X and E_C are exchange and correlation function, respectively, and B88 refers to the Becke's 1988 exchange function [13]. The molecular geometries were fully optimised. Rigid and relaxed potential energy surfaces (PESs) in the 0°-180° rotation range around the inter-ring C-C bond were obtained in steps of 30° starting from the optimised structure of the planar *anti* conformation ($\phi = 180°$). The relative energies of the rotamers were fitted to a six-term Fourier expansion [14]

$$V(\phi) = \sum_{n=1}^{6} \frac{1}{2} V_n\ [1 - \cos n(180 - \phi)]$$

where V is the relative energy at the torsion angle ϕ. Critical points in the PES were characterised by vibrational analysis and relative energies were corrected for zero point vibrational energy.

Results and Discussion.

Molecular Geometry.

The B3LYP/6-31G* and BH&HLYP/6-31G* geometries of α-2Th, together with the gas-phase electron diffraction structure [15] are shown in Figure 1. The theoretical data furnish root mean square deviations (rms) from the experimental ones of 0.017 (B3LYP/6-31G*) and 0.014 Å (BH&HLYP/6-31G*) for bond distances, and 1.4 and 1.2° for the bond angles, respectively. Thus the BH&HLYP functional gives a somewhat better geometry than the B3LYP one. Minimum energy structures of α-3Th and α-4Th are reported in Figures 2 and 3, respectively, together with the corresponding experimental structures in the solid [16-19].
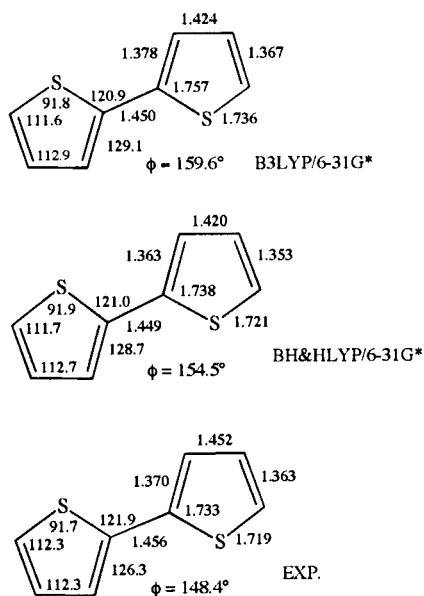

Figure 1. Equilibrium geometry of α-bithiophene where ϕ is the S-C_α-C_α-S dihedral angle. Experimental geometry from reference [15].

Some general considerations can be made: a) the experimental geometrical parameters of the inner ring of α-3Th are well reproduced by DFT calculations with rms values of 0.013 Å and 0.5° (B3LYP/6-31G*) and 0.010 Å and 0.3° (BH&HLYP/6-31G*). For α-4Th the comparison with the experiment is more difficult because the various reported experimental data differ significantly with each other [17-19]. In Figure 3 our theoretical data are compared with the X-ray data of reference [19], producing rms values of 0.03 Å and 1.0° (B3LYP/6-31G*) and 0.02 Å and 0.9° (BH&HLYP/6-31G*), for bond lengths and bond angles, respectively; b) the C-S bond length is better reproduced by the BH&HLYP functional, while the C=C bond length is better reproduced by the B3LYP functional; c) the inter-ring C-C bond length is significantly shorter than a normal single C-C bond (1.51-1.52 Å), indicating partial double bond character and some delocalisation among the rings. The inter-ring C-C bond length is practically equal to that found
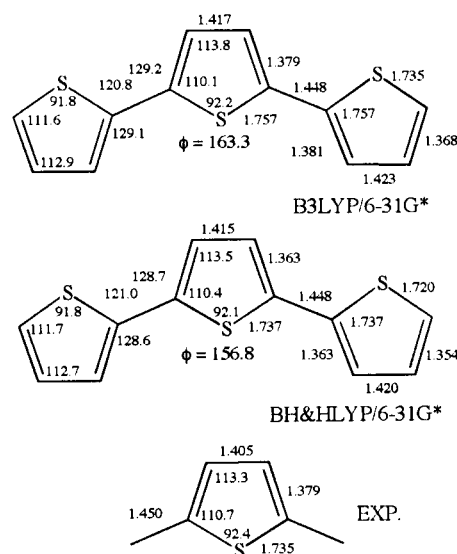

Figure 2. Equilibrium geometry of α-terthiophene, where ϕ is the dihedral angle resulting from the disrotatory rotation of the two outer rings. Experimental geometry from reference [16].
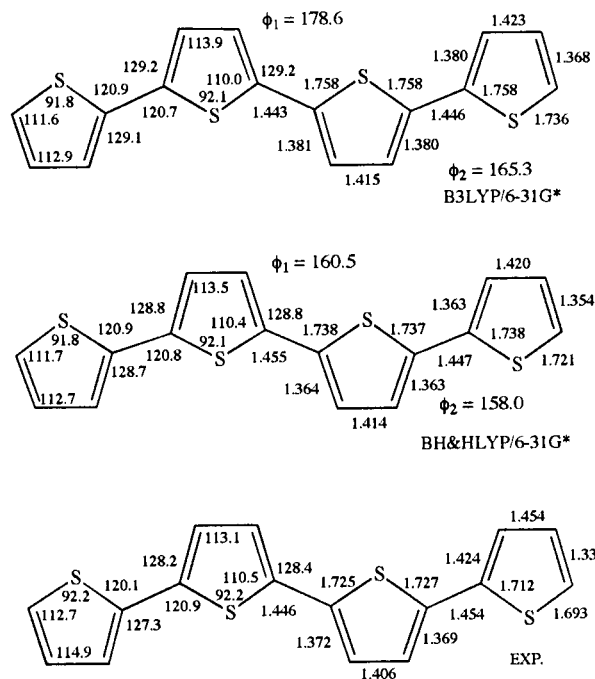

Figure 3. Equilibrium geometry of α-quaterthiophene, where ϕ_I is the dihedral angle between the plane of the two outer rings. Experimental geometry from reference [19].

in the corresponding pyrrole oligomers [20], thus establishing an analogy between the two systems. On passing from the dimer to the trimer and tetramer the C-C inter-ring bond length and the bond length alternation within the ring decrease, the first one by a very modest amount. This behaviour indicates that in α-oligothiophenes the π charge tends to be confined within the aromatic rings, delocalisation

along the chain being damped in agreement with the results obtained from vibrational frequency dispersion measurements [4a].

Molecular Conformation and Torsional Potential.

Bithiophene is planar-*anti* in the solid [21]. Some studies [21b] suggest that ca. 15% of the molecules are in the planar-*syn* form. In the vapour [15] two minimum energy conformations are found with dihedral angle ϕ between the planes of the rings of $148\pm3°$ and $36\pm5°$ for the *anti-gauche* and *syn-gauche* forms, respectively, the first one being more stable by 0.18 kcalmol^{-1} at $100°C$. This energy difference was estimated to be 1.16 ± 0.13 kcalmol^{-1} from the temperature dependence of the relative weights of the two conformations in the fluorescence spectra [22]. Fluorescence-excitation, hole-burning and dispersed-fluorescence spectra of α-2Th in a supersonic jet suggested [23] a double-minimum torsional potential around $\phi=0°$, whose equilibrium structures are twisted by about $21°$ from the planar-*anti* conformation, with an interconnecting barrier of ca. 25 cm^{-1} (0.072 kcalmol^{-1}). This work also gives an estimate of the $90°$ barrier in the range of 3.7-4.3 kcalmol^{-1}. The experimental conformations in the vapour of α-3Th and α-4Th are not known. In the solid both compounds are planar or near planar with twisting angle within $10°$[16-19].

As concerns α-3Th, IR and Raman spectra [24,25], UV absorption and fluorescence spectra in solution [26], as well as NMR spectra in liquid crystalline solution [27], gave evidence of the presence of more than one conformer. Fluorescence spectra in *n*-decane matrix at 77 K suggested that α-3Th adopts a planar ground-state conformation [6c].
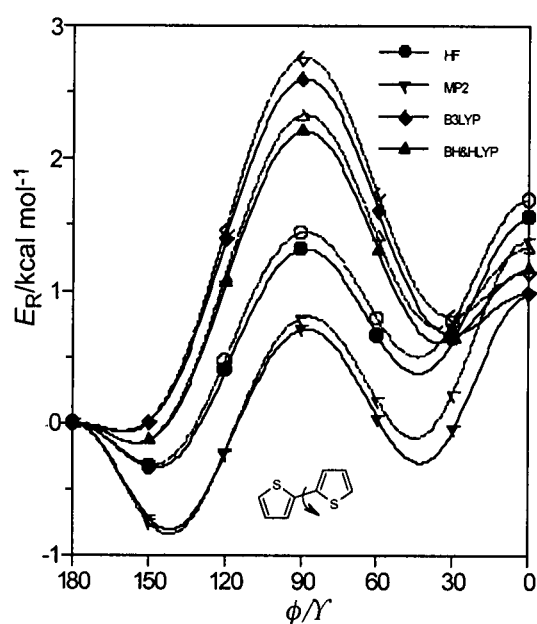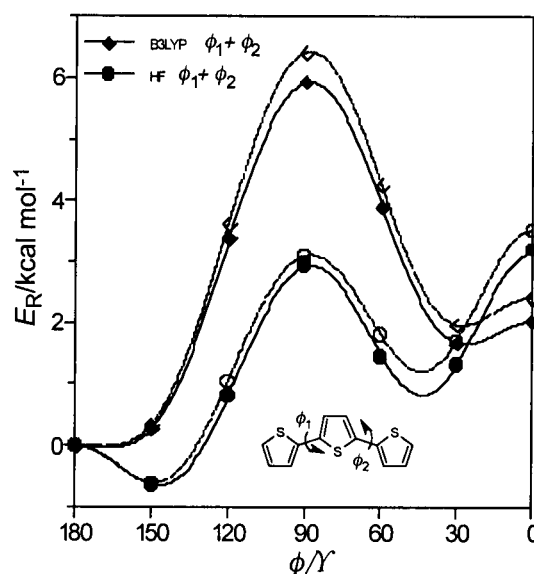

Figure 5. Torsional potentials for the disrotatory rotation ($\phi_1 = \phi_2$) of the two outer rings of α-terthiophene. Open marks and dashed lines refer to rigid rotor approximation results.

On the theoretical side, the HF/MIDI-4 [28], HF/3-21G* [29,30] and QCFF/PI+CISD [30] molecular geometries of the planar all-*anti* form of α-3Th were reported. Recently the conformational behaviour of α-3Th was studied by HF/6-31G* [31] and HF/3-21G* [32] calculations. Theoretical studies on α-4Th are more limited. We know only the HF/3-21G*, HF/6-31G*, BLYP/6-31G* and B3LYP/6-31G* geometries of the *gauche* structures [33] and the QCFF/PI+CISD of the all-*trans* planar structure [30]. Our calculated values of the rotation angles and the

Figure 4. Torsional potentials of α-bithiophene. Open marks and dashed lines refer to rigid rotor approximation results.
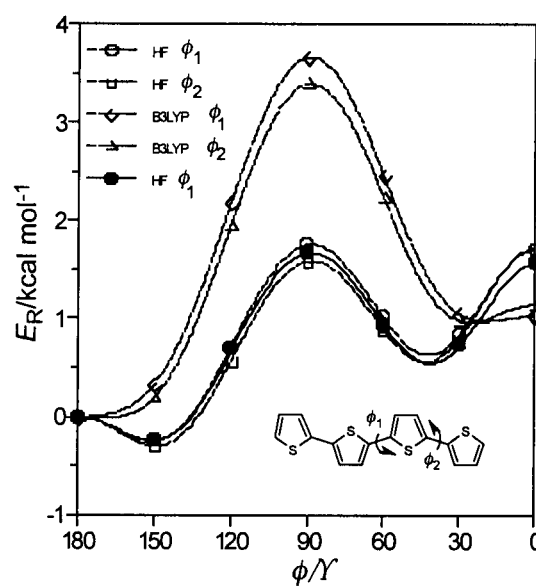

Figure 6. Torsional potentials of α-quaterthiophene. Open marks and dashed lines refer to rigid rotor approximation results.

Table 1

Dihedral Angles ϕ (degrees) and Relative Energies E_R (kcalmol^{-1}) of Thiophene Oligomers
Obtained by Direct Optimisation of the Stationary Points in Figures 4-6 [a]

Method	anti	anti-gauche		syn-gauchesyn		perpendicular		
	E_R	ϕ	E_R	ϕ	E_R	E_R	ϕ	E_R
bithiophene								
HF/6-31G*	0.00	147.7	-0.34(-0.29)[a]	44.7	0.31(0.36)	1.56(1.50)	88.6	1.32(1.35)
MP2/6-31G*	0.00	141.5	-0.86	43.2	-0.28	0.98	88.3	0.72
B3LYP/6-31G*	0.00	159.6	-0.05(-0.01)	30.0	0.67(0.70)	1.00(0.95)	89.1	2.61(2.64)
BH&HLYP/6-31G*	0.00	154.5	-0.14	35.0	0.62	1.17	88.9	2.22
terthiophene								
HF/6-31G* (ϕ_1)	0.00	149.5	-0.28	43.0	0.45	1.62	88.5	1.49
HF/6-31G* ($\phi_1 + \phi_2$)	0.00	148.7	-0.62	43.9	0.80	3.20	88.0	2.96
B3LYP/6-31G* ($\phi_1 + \phi_2$)	0.00	163.3	-0.03	26.7	1.66	2.04	88.7	5.95
BH&HLYP/6-31G* ($\phi_1 + \phi_2$)	0.00	156.8	-0.20					
quaterthiophene								
HF/6-31G* (ϕ_1)	0.00	151.0	-0.23	41.8	0.56	1.57	88.8	1.68

[a] Values in parentheses are corrected for zero point vibrational energy. For the definition of ϕ see Figures 5 and 6.

Table 2

Torsional Potentials of Thiophene Oligomers (kcal mol^{-1})

Method	V_1	V_2	V_3	V_4	V_5	V_6
bithiophene						
HF/6-31G*	1.166	0.615	0.346	-0.942	0.046	-0.072
MP2/6-31G*	0.801	0.344	0.154	-1.112	0.022	-0.120
B3LYP/6-31G*	0.786	2.183	0.193	-0.838	0.018	-0.073
BH&HLYP/6-31G*	0.916	1.706	0.230	-0.900	0.023	-0.076
terthiophene [a]						
HF/6-31G* (ϕ_1)	1.182	0.764	0.372	-0.958	0.066	-0.083
HF/6-31G* ($\phi_1 + \phi_2$)	2.395	1.420	0.648	-2.047	0.157	-0.071
B3LYP/6-31G*($\phi_1 + \phi_2$)	1.658	5.066	0.332	-1.552	0.047	-0.134
quaterthiophene [a]						
HF/6-31G* (ϕ_1)	1.167	0.969	0.358	-0.932	0.047	-0.075
HF/6-31G* (ϕ_1) [b]	1.295	0.979	0.365	-0.972	0.047	-0.077
HF/6-31G* (ϕ_2) [b]	1.313	0.804	0.355	-0.978	0.047	-0.076
B3LYP/6-31G*(ϕ_1) [b]	0.850	3.184	0.164	-0.777	0.017	-0.039
B3LYP/6-31G*(ϕ_2) [b]	0.929	2.887	0.197	-0.856	0.019	-0.068

[a] For the definition of ϕ see Figures. 5 and 6. [b] Rigid rotation.

relative energies of the critical points in the PES of α-nTh (Figures 4-6), obtained by direct optimisation, are reported in Table 1. The torsional potentials are given in Table 2. Some few observations can be made: Bithiophene: a) MP2 and B3LYP results agree with those previously obtained at the same level of theory [8]. We add zero-point vibrational energy correction, which indeed results to be of negligible importance; b) the rigid rotor approximation introduces some error (0.2-0.3 kcalmol^{-1}) only in the syn region, indicating that the PES of this system can be adequately accounted for by the rigid rotor approximation; c) BH&HLYP/6-31G* calculations, which are unprecedented, furnish results similar to the B3LYP/6-31G* ones,

the 90° barrier and the dihedral angle of the anti-gauche form, being only decreased by 0.4 kcalmol^{-1} and 5°, respectively. Both these functionals give conformational parameters somewhat different from those obtained by MP2/6-31G* calculations, which predict flatter PES, deeper anti-gauche and syn-gauche minima, the syn form as the global maximum, and rotation angles biased towards the twisted conformation. Torsional potential values (Table 2) indicate that steric and/or electrostatic interactions, expressed by the V_1 term, are of comparable entity in both MP2 and DFT calculations. By contrast the two methods assign different weight to the conjugative effects, expressed by the V_2 term, DFT approximation predicting much higher V_2 values. As a result, while both methods give similar energy differences between the syn and anti forms (ca. 1 kcalmol^{-1}) and between the syn-gauche and anti-gauche forms (ca. 0.7 kcalmol^{-1}), DFT calculations give a lower 0° barrier (0.05-0.15 versus 0.86 kcalmol^{-1}), a higher 90° barrier (2.22-2.61 versus 0.72 kcalmol^{-1}), and smaller anti-gauche (160-155 versus 141°) and syn-gauche (30-35 versus 43°) rotation angles. Indeed the DFT conformational parameters are much closer than the MP2 ones to those obtained by fluorescence spectroscopy [23]. Thus the asserted shortcomings of DFT calculations in describing the energetics of the conformational isomerism in bithiophene and related compounds [8c], merit to be reconsidered and further investigated.

Terthiophene and Quaterthiophene.

The conformational data on α-3Th and α-4Th are shown in Tables 1 and 2, and in Figures 5 and 6. The energetics and the conformational properties of these compounds closely resemble those of α-2Th. On passing from the dimer to the trimer and tetramer, following the rotation of

one external ring, the relative energy of the *anti-gauche* form gradually increases and the corresponding torsion angle moves towards the planar structure, in agreement with the experimental results in the solid [16-19] and in *n*-decane solutions [6c]. Thus on oligomerization the π delocalisation, although small, has appreciable effects on the molecular conformation. Accordingly the V_2 torsional potential and the perpendicular barrier steadily increase, while non-bonding interactions remain constant.

Conrotatory and disrotatory rotation of the two outer rings in α-3Th produce stationary states resulting from all the possible combinations of the dihedral angles in the dimer, as described by Ciofalo and La Manna [31]. The relative energies of these forms are obtainable additively from the energetics of the PES of the dimer indicating little variation in the conjugative interaction among the rings. We report in Tables 1 and 2 the results relative to the relaxed disrotatory rotation which generates the minimum energy conformations reported in Figure 5. The obtained S-C_α-$C_{\alpha'}$-S dihedral angle may be compared with the reported HF/3-21G* and HF/6-31G* values of 147.2 [32] and 148.2 [31], respectively. In α-4Th both the rotations around the outer or the internal C-C inter-ring bonds produce identical torsional potentials, indicating an uniform conformational flexibility along the chain. The differences between rigid and relaxed torsional potentials are here further reduced. The absolute minimum energy structure of α-4Th shows a dihedral angle significantly higher than in the dimer, while the 90° barrier is increased relative to bithiophene owing to some π-energy gain. This tendency to co-planarization is particularly evident in the B3LYP/6-31G* results, which show almost co-planar internal rings (Figure 6). The above results are similar to those found in the analogues α-selenophene oligomers [34]. Substitution of Se for S produces somewhat higher steric and somewhat smaller π-electron interactions.

Vibrational Spectra of α-2Th.

The vibrational properties of α-2Th have been investigated by IR, Raman and inelastic neutron scattering experiments [24,25,33,35,36]. Theoretical data on planar α-2Th obtained at *ab initio* [28,30,33,37] and semiempirical [25,30,38] levels have also been reported. We have calculated the harmonic IR frequencies and intensities of all the stationary states of α-2Th at B3LYP/6-31G* level in order to reveal conformational effects related to the twisting of the rings. It is expected that C_2 structures show up vibrational transitions originally inactive in the C_{2h} form. The simulated B3LYP/6-31G* IR spectra of the most relevant rotamers are shown in Figure 7 together with the experimental spectrum built from the data of reference [33]. The planar *anti*, the planar *syn* and the perpendicular forms are transition states in the PES, showing one imaginary frequency each at 27, 38 and 27 cm⁻¹, respectively. It can be seen that the experimental spectrum is nicely reproduced without the
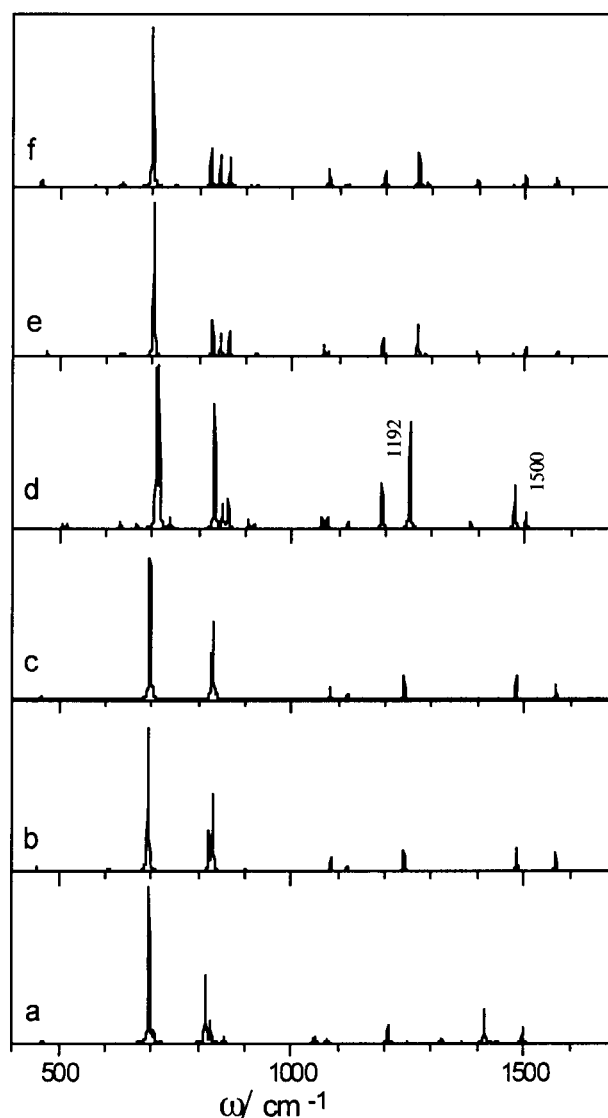

Figure 7. Calculated B3LYP/6-31G* vibrational spectra of α-bithiophene conformers: (a) Experimental spectrum from reference [33]. (b) *anti*; (c) *anti-gauche*; (d) perpendicular; (e) *syn-gauche*; (f) *syn*.

recourse to any scale factor, although the use in the 1000-1600 cm⁻¹ region of a scale factor of about 0.96 [39] could give a better agreement with the experiment. We did not attempt an assignment of the vibrational transitions, this being already been made in the cited works. The spectra of the *anti* and *anti-gauche* forms appear to be identical as are those of the *syn* and *syn-gauche* forms. Thus evidences of slightly twisted structures can hardly be obtained by IR spectroscopy. On 90° rotation the simulated IR spectrum shows some interesting features, the most clear of them are related to: (i) A 14 cm⁻¹ blue-shift of the A_g mode at 1610 cm⁻¹ in the planar *anti* form, although this transition remains very weak also in the perpendicular form. (ii) The appearance of an intense transition at 1192 cm⁻¹ which correlates

with the A_g mode at 1244 cm^{-1} in the *anti* form, describing a deformation mode of the $C_\beta=C_\alpha-C_{\alpha'}=C_{\beta'}$ fragment. This transition is also active in the spectra of the *syn* and *syn-gauche* forms. Thus charge redistribution and dipole moment variation on 90° twisting produce a consistent red-shift and intensity enhancement of this mode which could be a useful probe for twisting. (iii) The 863 cm^{-1} (A_g) vibrational transition in the planar *anti* form has a corresponding intense transition at 862 cm^{-1} in the 90° structure, which takes place, together with the transitions at 833 cm^{-1} (γ C-H, ν C-S) and at 850 cm^{-1} (γ C-H), to a characteristic vibrational pattern (Figure 7) also present in the spectra of the *syn-gauche* and *syn* forms. A close comparison of this feature with the corresponding IR spectrum in the solid (see also Figure. 5 of reference [36]) seems to indicate the presence of *syn*-like structures in the solid, in agreement with the results of X-ray analysis [21b]. (iv) The most intense transition in the IR spectrum of α-2Th is found near 700 cm^{-1} and originates from out-of-plane C-H deformation modes. Experimentally this band is observed in solution as a strong and sharp peak at 688 cm^{-1} [25]. It is accurately reproduced by the B3LYP/6-31G* calculations as the most intense A_u transition at 693 cm^{-1} (I = 113 km mol^{-1}) in the planar *anti* structure. This transition is almost isoenergetic with the IR active B_g transition at 698 cm^{-1}. The A_u mode transforms as A and A_2 under C_2 and C_{2v} symmetry, respectively. It progressively looses intensity, being silent in the *syn* form. The B_g mode concomitantly transforms as B and B_1, gradually acquiring intensity (110 km mol^{-1} in the *syn* form). As a consequence the IR spectrum of the 90° structure shows a doublet assigned to two equally intense transitions of A (714 cm^{-1}, I = 58 km mol^{-1}) and B (708 cm^{-1}, I = 53 km mol^{-1}) symmetry. Thus the A/B intensity is indicative of the *anti-syn* equilibrium position around the perpendicular conformation. Indeed the experimental transition at 688 cm^{-1} is temperature dependent, at room temperature becoming a
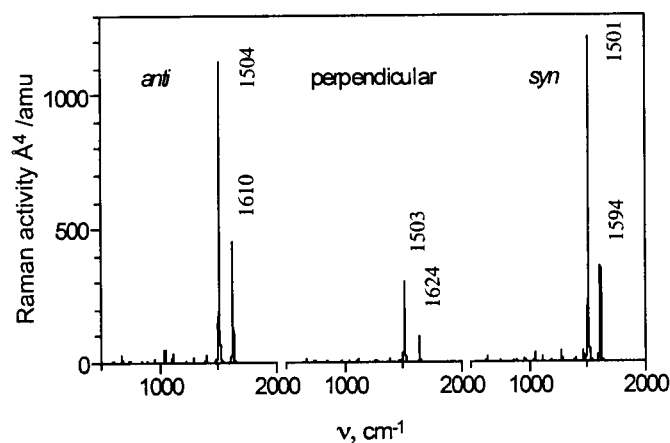
shoulder near 693 cm^{-1} of a strong peak at 703 cm^{-1}, which in its turn becomes stronger and sharper at 0°C [25].

The HF/6-31G* Raman spectra of the *anti*, perpendicular and *syn* forms of the α-2Th are shown in Figure 8, where the frequencies have been scaled to those of the B3LYP/6-31G* ones. The Raman spectra are very simple, being dominated by two intense transitions at 1610 and 1504 cm^{-1} in the *anti* form. The first one describes the antisymmetric C=C stretching mode in the ring, while equivalent C=C bonds in the two rings vibrate in-phase, Figure 9. This frequency is red-shifted at 1594 cm^{-1} in the *syn* form and blue-shifted at 1624 cm^{-1} in the perpendicular form, where its intensity decreases by 4.7 times with respect to the planar *anti* configuration, indicating some delocalisation of π electrons between the rings. In the oligothiophenes this transition shows frequency and relative intensity softening as the chain length increases [40]. The transition at 1504 cm^{-1} is a collective totally symmetric vibration, Figure 9.
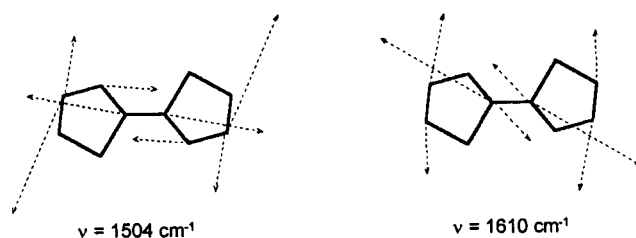

Figure 9. Calculated displacements of the normal modes of the two intense vibrational transitions in the Raman spectra of *anti* α-bithiophene.

This mode does not show appreciable frequency variation on 90° twisting of the rings as it does not show frequency softening on chain lengthening [40]. Its intensity decreases by 3.8 times in the 90° form and increases superlinearly with the chain length in planar oligothiophenes [40]. This mode gives a large contribution to the so called effective conjugation coordinate in linear polyconjugated oligomers as described by Zerbi *et al.* [4a].

In conclusion, on ring rotation, appreciable variations in the Raman vibrational properties of bithiophenes, and very probably oligothiophenes, are evidenced only by intensity variations.

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Figure 8. HF/6-31G* Raman spectra of planar and perpendicular forms of α-bithiophene. Frequencies are scaled to the B3LYP/6-31G* values.

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