Geometric Structure and Torsional Potential of Biisothianaphthene. A Comparative DFT and ab Initio Study

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Abstract: We present a study of the torsional potential of biisothianaphthene and compare it to that of bithiophene. The calculations are performed at the ab initio and semiempirical Hartree−Fock (HF), ab initio post-Hartree−Fock, and density functional theory (DFT) levels. Our study has two major aims: (i) on the physico-chemical side, to asses the optimal conformation of biisothianaphthene and evaluate the rotational barriers toward coplanar structures and (ii) on the methodological side, to asses the usefulness of DFT approaches. In contrast to previous estimates, the torsional potential of biisothianaphthene is found to differ markedly from that of bithiophene. For biisothianaphthene, strongly rotated *s-cis-* and *s-trans-gauche* minima are predicted as the most stable structures. The structural analysis fully justifies the greater stability of the *s-cis-gauche* conformer, thus explaining the "unexpected" *s-cis*-like structure observed experimentally in the crystal. The attainment of planar conformations is prevented by the high rotational barriers: ∼22 kJ/mol (*s-trans*) and ∼63 kJ/mol (*s-cis*) at the MP2 level. Aromatic polyisothianaphthene chains are therefore predicted to be highly distorted from planarity even in the solid state, which is of importance with regard to their electronic and optical properties. DFT calculations are shown to provide geometries very close to those obtained at the MP2 level, but fail in describing the energetics of the torsional potentials because they overstabilize planar conformers. The results allow us to propose a very efficient computational approach for reliable determinations of conformational potentials in conjugated compounds. The poor quality of the potentials provided by semiempirical HF methods is emphasized.

Introduction

The design of conjugated polymers with a small energetic separation between occupied and unoccupied levels has attracted considerable attention because such materials are expected to present high electrical conductivities, without the need of any external doping, and interesting optical properties.[1−7] One of the most successful approaches to that goal is based on the substitution of the monomer unit in order to modify its electronic structure and, thereby, to modulate the electronic properties of the resulting conjugated polymer. The fusion of a benzene ring upon the thiophene unit leads to polyisothianaphthene (PITN), for which an energy band gap of ∼1 eV has been experimentally measured, compared to the 2 eV band gap reported for the parent thiophene polymer (PT).[1] A large number of theoretical and experimental efforts have been devoted to the determination of the ground-state geometry, aromatic or quinoid, of PITN,[2,3,8−12] which has been the object of controversy since the polymer was synthesized. The more recent works conclude that PITN possesses a quinoid molecular structure in its electronic ground state.[11,12] However, since the two forms are theoretically predicted to be almost isoenergetic,[10,11b] both structures could actually exist depending, for instance, on the polymerization route.

Band-structure calculations on PITN[11b] using the valence effective Hamiltonian (VEH) method[13] indicate that the planar

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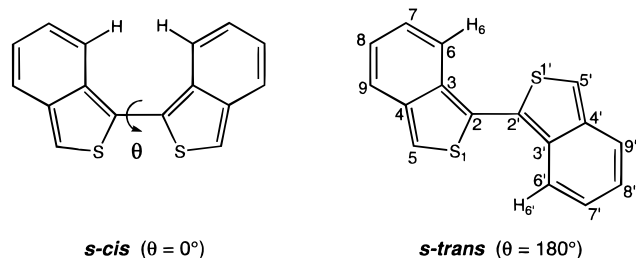
Figure 1. Rotational isomerism and atom numbering[16] of biisothianaphthene. θ denotes the dihedral angle formed by the planes of the isothianaphthene moieties.

aromatic polymer should possess an energy band gap (E_g) even smaller than that of quinoid PITN (0.2 vs 1.2 eV). The E_g value calculated for aromatic PITN strongly depends on the rotational angle between adjacent isothianaphthene units, which governs the intramolecular delocalization of the π electrons along the conjugated chain. The degree of planarity of the chain determines the width of the π bands and, thereby, the electrical and optical properties of the polymer including the optical band gap.

In contrast to polythiophene, for which the internal rotation around interannular bonds has been widely investigated on the basis of calculations on 2,2′-bithiophene and longer oligomers,[14] the conformational behavior of PITN has been scarcely studied. Experimental studies are limited to the very recent X-ray structural determination reported by Quattrocchi et al.[15] for 5,5′-bis(*tert*-butyldimethylsilyl)-2,2′-biisothianaphthene (see Figure 1 and ref 16 for numbering criteria), which possesses an aromatic structure. The molecule shows an *s-cis*-like conformation with a torsional angle θ between the planes of the isothianaphthene (ITN) units of about 50°. This *s-cis* conformation contrasts with the planar *s-trans* form observed for 2,2′-bithiophene in the crystal,[17] and is explained as a consequence of packing effects dominated by the bulky side groups. Longer oligomers up to the tetramer are also synthesized, but attempts to grow single crystals from them were all unsuccessful.[15] The absorption spectra of the oligomers were compared to the results of INDO/SCI calculations, and it was concluded that the molecules adopt strongly nonplanar conformations in solution.

Theoretical studies on the conformational isomerism of PITN have been restricted to calculations performed at the semiempirical level. The MNDO method provides an almost perpendicular conformation with $\theta = 95°$,[3a] but it is well known that this method overstabilizes perpendicular vs planar conformations. The PRDDO approach yields a less twisted structure with a dihedral angle of 121°.[10] More recent AM1 calculations on

both unsubstituted[11b] and disilyl-substituted[15] dimers predict that the most stable conformation corresponds to a rotational angle of about 153° and is separated from the planar *s-trans* form by a barrier of only 1.3 kJ/mol. AM1 results suggest a high flexibility for aromatic PITN chains since the ITN units can easily undergo rotations around inter-ring bonds. These results are in fact very similar to those obtained for 2,2′-bithiophene, for which the AM1 method also provides a rotational angle of about 153° and a barrier of only 0.15 kJ/mol to the planar *s-trans* form.[18] This similarity is however rather surprising since shorter S···H steric contacts take place in the *s-trans* conformer of biisothianaphthene.

The aim of this work is to provide a complete characterization of the internal rotational potential of biisothianaphthene using both ab initio and density functional methods. The conformational behavior of biisothianaphthene is analyzed by comparison with that of 2,2′-bithiophene and can be used as a model to gain information about the conformation of longer PITN chains. The knowledge of the optimal conformations and the potential barriers for internal rotation is of wide interest in order to understand the structural and optical properties observed for aromatic oligoisothianaphthenes,[11,12,15] and to elucidate whether the conformational properties of these oligomers are similar to those of oligothiophenes as suggested.[11b,15]

The torsional potential of biisothianaphthene has been calculated at the ab initio and semiempirical Hartree−Fock (HF) levels and including electron correlation effects by second-order Møller−Plesset (MP2) perturbation theory and density functional methods. Density functional theory (DFT)[19] is increasingly exploited by chemists since it offers a promising tool that may be applied to large systems since it includes correlation effects in a form in which the cost runs with N^3, N being the number of basis functions. This contrasts with conventional ab initio methods such as MP2 or MP4 that scale as N^5 or N^7, respectively.[20] DFT calculations are claimed to provide energetic data closer to MP2 results than HF calculations.[21−23] The comparison of the rotational potentials calculated for biisothianaphthene and 2,2′-bithiophene at the MP2 and DFT levels can serve to test the reliability of the DFT approach. An important aspect of our work of general interest is to propose an efficient computational approach, combining DFT and MP2 calculations, to determine reliable conformational potentials in organic conjugated compounds; the applicability of semiempirical methods is also analyzed and questioned.

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Computational Procedure

The calculations were performed on IBM RS/6000 workstations of the Department of Química Física of the University of València using GAUSSIAN 92/DFT[24] and GAUSSIAN 94[25] programs. To study the internal rotation of biisothianaphthene, at the HF and DFT levels, and that of 2,2′-bithiophene, at the DFT level, the torsional angle θ was scanned in steps of 30° between $\theta = 0°$ (*s-cis* conformer) and $\theta = 180°$ (*s-trans* conformer). The geometries of the resulting conformers and those of the *s-cis*- and *s-trans-gauche* minima were optimized using the 6-31G* (d functions on sulfur and carbon) basis set.[26] Additional calculations were performed at the HF/6-31G* level for biisothianaphthene in the range $\theta = 90-110°$ due to the flatness of the rotational potential in this zone. Conformational relative energies including electron correlation were estimated by recalculating the optimized HF/6-31G* geometries using frozen-core MP2 perturbation theory[27,28] and the 6-31G* basis set. This level of calculations is denoted MP2/6-31G*//HF/6-31G*. In addition, the planar *s-trans* conformer and the *s-cis*- and *s-trans-gauche* minima were optimized at the MP2/6-31G* level.

DFT calculations were carried out using GAUSSIAN 94 and the 6-31G* basis set. Within the local spin density (LSD)[29] approximation, the S-VWN functional, which combines the Slater−Dirac (S) exchange[30] and the Vosko, Wilk, and Nusair (VWN) correlation,[31] was tested. Among the variety of functionals including nonlocal corrections, we used the B-LYP functional, for which gradient corrections are introduced using the Becke (B) exchange[32] and the Lee, Yang, and Parr (LYP) correlation,[33] and Becke's three-parameter hybrid functionals, with the nonlocal correlation provided by the LYP (B3-LYP),[34] Perdew 86 (B3-P86),[35] and Perdew 91 (B3-PW91)[36] functionals. The rotational potentials of biisothianaphthene and bithiophene were studied by mainly using the B3-P86 and B3-PW91 functionals, since functionals that introduce gradient corrections for exchange and correlation reproduce more correctly the energetics of systems where weak nonbonding interactions are present.[22a,37]

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The Berny analytical gradient method[38] was used in all the geometry optimizations. The isothianaphene units in biisothianaphthene and the thiophene rings in 2,2′-bithiophene were assumed to be planar. C_{2v}, C_2, and C_{2h} symmetry restrictions were imposed for planar *s-cis*, twisted, and planar *s-trans* conformations, respectively. The requested HF convergence on the density matrix was 10^{-8}, and the threshold values for the maximum force and the maximum displacement were 0.000 45 and 0.0018 au, respectively.

The energy values computed for the different conformers at the ab initio, MP2, and DFT levels were fitted to the following Fourier expansion:

$$V(\phi) = \sum_{i=1}^{n}(1/2)V_i(1 - \cos i\phi)$$

where V is the relative energy at the rotational angle ϕ. ϕ has to be defined as $180° - \theta$ since the *s-trans* ($\theta = 180°$) conformer was selected as the energy origin. This method of deriving the potential function for the internal rotation has proven to provide an accurate way to obtain the locations and relative energies of the critical points in the torsional potential when these points cannot be determined by direct optimization.[14a]

Results and Discussion

This section is structured as follows. The geometric structures calculated for the thiophene and isothianaphthene monomers are first discussed and compared in order to select the density functionals that are more adequate to deal with the dimers. The geometry of biisothianaphthene and its evolution as a function of the torsional angle are then discussed and compared to theoretical results obtained for 2,2′-bithiophene and experimental X-ray data. Next, a detailed analysis of the torsional potentials (energy minima and barrier heights) calculated for biisothianaphthene and 2,2′-bithiophene is given. The accuracy of the torsional potentials provided by different density functionals is discussed by comparison to MP2 results. Detailed information of the optimized geometries using all methodological approaches is included as Supporting Information, Tables S1−S5.

1. Geometries. A. Thiophene and Isothianaphthene. The molecular geometries calculated for thiophene and isothianaphthene at the HF, MP2, and DFT levels are given in Table 1. In going from thiophene to isothianaphthene, all methods indicate the same trends for the thiophene ring: the S1−C2 bond shortens, the C2−C3 double bonds and the C3−C4 single bond lengthen, and the C5−S1−C2 angle widens. The benzene ring of isothianaphthene presents a carbon−carbon bond-length alternation of 0.05−0.06 Å at the MP2 and DFT levels. This small alternation together with the changes calculated for the thiophene moiety suggest that π-delocalization mainly occurs along the periphery of the isothianaphthene unit.

The reliability of the optimized geometries is analyzed for thiophene by calculating the average difference between the experimental and theoretical values for the bond lengths, $\bar{\delta}(R)$, and the bond angles, $\bar{\delta}(\alpha)$. The HF/6-31G* parameters are the less accurate, $\bar{\delta}(R) = 0.0167$ Å and $\bar{\delta}(\alpha) = 0.45°$, because they provide too short double bonds and too long single bonds. The MP2 results, $\bar{\delta}(R) = 0.0045$ Å and $\bar{\delta}(\alpha) = 0.11°$, are by contrast very close to the experimental values. For the different density functionals used, the accuracy of the results evolves along the series B-LYP < B3-LYP < B3-PW91 ≈ B3-P86 < S-VWN. The geometries calculated for isothianaphthene point to the same trends (see the Supporting Information, Tables S1 and S2). These results indicate that, among the functionals tested, the local S-VWN functional provides the most accurate geometries.

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Table 1. Optimized Geometric Parameters of Thiophene and Isothianaphthene[a]

| parameter[b,c] | thiophene | | | | isothianaphthene | | |
	HF	MP2	B3-PW91	exptl[d]	HF	MP2	B3-PW91
S1−C2	1.7258	1.7178	1.7255	1.7140	1.7092	1.7009	1.7091
C2−C3	1.3451	1.3762	1.3673	1.3696	1.3607	1.3978	1.3856
C3−C4	1.4369	1.4201	1.4258	1.4232	1.4453	1.4427	1.4502
C3−C6					1.4446	1.4232	1.4284
C6−C7					1.3411	1.3760	1.3669
C7−C8					1.4502	1.4252	1.4309
S1−C2−C3	111.84	111.58	111.49	111.47	111.47	111.11	111.27
C2−C3−C4	112.53	112.44	112.63	112.45	112.19	111.93	112.01
C5−S1−C2	91.27	91.97	91.77	92.17	92.69	93.93	93.44
C4−C3−C6					119.11	119.65	119.34
C3−C6−C7					119.41	119.15	119.39
C6−C7−C8					121.48	121.20	121.27
δ̄(R)[e]		0.0167	0.0045	0.0055	0.0216		0.0080
δ̄(α)[e]		0.45	0.11	0.20	0.49		0.23

[a] All the optimizations were carried out using the 6-31G* basis set and assuming C_{2v} symmetry constraints. [b] The atomic numbering corresponds to that displayed in Figure 1. [c] Bond lengths are in angstroms and bond angles in degrees. [d] Microwave data from ref 39. [e] Average deviations calculated for bond lengths, $\bar{\delta}(R)$, and bond angles, $\bar{\delta}(\alpha)$, with respect to experimental values for thiophene and to MP2 values for isothianaphthene.

It is however known that, when dealing with density functional methods, good geometries do not always lead to good relative energies and the introduction of nonlocal corrections is generally required to obtain good energetics.[21,22] This has been recently shown for the rotational barrier of acrolein, for which nonlocal density functionals provide energy differences closer to the MP2 and experimental values than local functionals.[22a] We have thus chosen the B3-P86 and B3-PW91 functionals to investigate the rotational barriers of biisothianaphthene and 2,2′-bithiophene since they are the nonlocal functionals that afford geometries closer to the MP2 results.

B. Biisothianaphthene. The geometries of the θ = 0°, 30°, 60°, 90°, 120°, 150°, and 180° conformers of biisothianaphthene were optimized at the HF/6-31G*, B3-P86/6-31G*, and B3-PW91/6-31G* levels. For 2,2′-bithiophene, HF/6-31G* and MP2/6-31G* geometries have been reported previously[14a] and optimizations were performed only at the B3-P86/6-31G* and B3-PW91/6-31G* levels. Two additional geometry optimizations including the relaxation of the torsional angle θ were performed in order to localize *s-cis-* and *s-trans-gauche* minima. The planar *s-trans* and the *s-cis-* and *s-trans-gauche* conformers of biisothianaphthene were also optimized at the MP2/6-31G* level. To simplify the notation, the basis set used in the calculations will be hereafter omitted.

Table 2 summarizes the MP2- and B3-PW91-optimized geometries for the planar *s-trans* conformers of 2,2′-bithiophene and biisothianaphthene (HF and B3-P86 geometries are given as Supporting Information, Tables S3 and S4). For both molecules, B3-P86 and B3-PW91 calculations provide bond lengths and bond angles very close to the MP2 values, while HF results yield more localized structures. The following discussion focuses on the MP2 results.

Starting with 2,2′-bithiophene, the geometric parameters undergoing the most significant changes with respect to the thiophene monomer are the S1−C2 and C2−C3 bonds which lengthen by 0.02 and 0.01 Å, respectively. These changes originate in the conjugation between the π-electronic clouds of both rings and in the steric interactions that take place between them. The existence of a strong delocalization between the two rings is evidenced by the length of 1.450 Å predicted for the interannular C2−C2′ single bond. This length is significantly shorter than that reported for a biaryl system like biphenyl (1.496

Table 2. Optimized Geometric Parameters for the Planar *s-trans* Conformers of Bithiophene and Biisothianaphthene[a]

| parameter[b,c] | bithiophene | | biisothianaphthene | |
	MP2[d]	B3-PW91	MP2	B3-PW91
C2−C2′	1.450	1.448	1.446	1.446
S1−C2	1.736	1.746	1.732	1.740
C2−C3	1.386	1.378	1.428	1.416
C3−C4	1.415	1.420	1.444	1.450
C4−C5	1.376	1.367	1.395	1.383
C5−S1	1.719	1.726	1.694	1.700
C3−C6			1.422	1.427
C6−C7			1.381	1.371
C7−C8			1.418	1.424
C8−C9			1.376	1.366
C9−C4			1.420	1.426
C2′−C2−C3	128.7	129.1	130.7	131.0
S1−C2−C3	110.3	110.1	108.8	108.7
C2−C3−C4	113.2	113.5	112.3	112.6
C3−C4−C5	112.6	112.8	112.7	112.7
C4−C5−S1	111.7	111.6	111.2	111.3
C5−S1−C2	92.2	92.1	95.0	94.6
C4−C3−C6			117.6	117.4
C3−C6−C7			120.1	120.4
C6−C7−C8			121.7	121.6
C7−C8−C9			120.2	120.3
C8−C9−C4			119.4	119.7
C9−C4−C3			121.0	120.6
S1···H3′	2.93	2.94		
S1···H6′			2.47	2.45

[a] All the optimizations were carried out using the 6-31G* basis set and assuming C_{2h} symmetry constraints. [b] The atomic numbering corresponds to that used in Figure 1. [c] Bond lengths are in angstroms and bond angles in degrees. [d] Data from ref 14a.

Å, X-ray data)[40] and comparable to that observed for the central bond of a polyenic system like 1,3,5,7-octatetraene (1.451 Å, X-ray data).[41] The steric interaction between both rings is mainly due to the S1···H3′ (S1′···H3) and S1−C3′ (S1′···C3) contacts which take place at shorter distances (2.93 and 3.21 Å, respectively) than the sum of the van der Waals radii (3.05 and 3.50 Å, respectively).

The geometric parameters calculated for biisothianaphthene undergo more important changes with respect to the geometry of the monomer than those obtained for bithiophene. Now, both the S1−C2 and C2−C3 bonds lengthen by 0.03 Å. This lengthening is accompanied by a narrowing of the S1−C2−C3 and C4−C3−C6 angles of ∼2.2° and a broadening of the C5−S1−C2 (1.0°) and C3−C6−H6 (1.8°) angles. All these changes tend to alleviate the high steric hindrance present in the interannular region of biisothianaphthene, where two S1···H6′ contacts occur at only 2.47 Å and the S1···C3′ and S1···C6′ distances are 3.28 and 3.19 Å, respectively. Despite these nonbonding interactions, the inter-ring C2-C2′ bond is predicted to have a length of 1.446 Å slightly shorter than in bithiophene (1.450 Å). This result suggests that an important π conjugation, even stronger than in bithiophene, takes place between the two isothianaphthene moieties. The biisothianaphthene molecule offers in fact the possibility of delocalizing the π electrons along the long polyenic chain defined by the periphery of the two isothianaphthene units, i.e., a hexadecaoctaene chain, which is 2 times longer than the octatetraene chain present in bithiophene.

Figures 2 and 3 sketch the variation with the torsional angle θ of those bond lengths and bond angles in the interannular region of biisothianaphthene which undergo the most important changes with internal rotation. The variations presented are based on B3-PW91 calculations since MP2 optimizations were

(40) Charbonneau, G.; Delugeard, V. *Acta Crystallogr., B* **1976**, *32*, 1420.
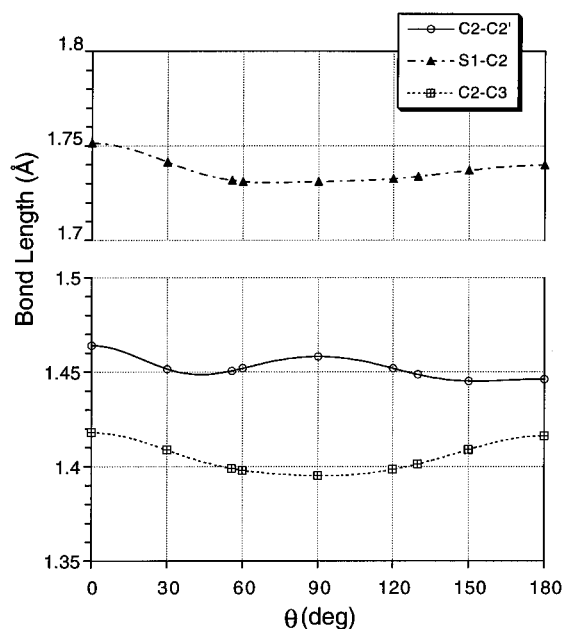(41) Baughman, R. H.; Kohler, B. E.; Levy, I. J.; Spangler C. *Synth. Met.* **1985**, *11*, 37.

Figure 2. Variation as a function of the torsional angle θ of the interannular C2—C2′, S1—C2, and C2—C3 bond lengths calculated for biisothianaphthene at the B3-PW91/6-31G* DFT level.
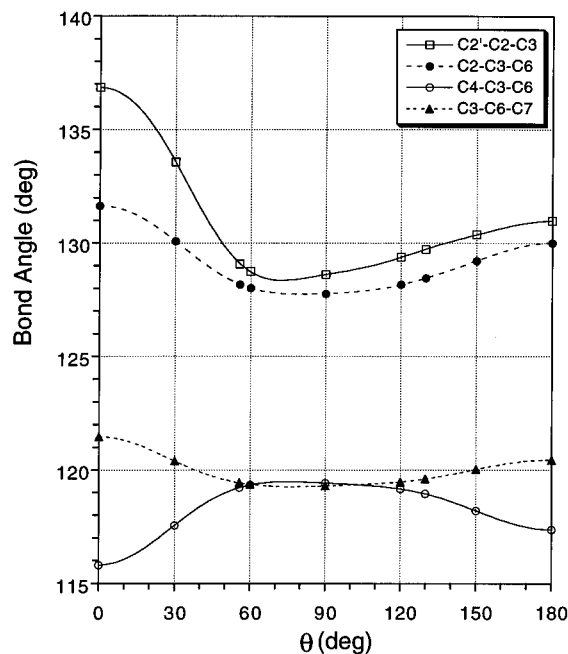

Figure 3. Variation as a function of the torsional angle θ of the C2′—C2—C3, C2—C3—C6, C4—C3—C6, and C3—C6—C7 bond angles calculated for biisothianaphthene at the B3-PW91/6-31G* DFT level.

only performed for the *s-cis-* and *s-trans-gauche* conformers. The MP2- and B3-PW91-optimized geometries of these conformers are listed in Table 3 (HF- and B3-P86-optimized geometries are given as Supporting Information, Table S5). The changes shown in Figures 2 and 3 are mostly due to the decrease of the steric interactions in passing from the highly hindered planar conformers to the less crowded twisted structures. In this way, the minimum lengths of the S1—C2 and C2—C3 bonds appear for the perpendicular conformation (1.731 and 1.395 Å), and the maximum lengths for the planar *s-trans* (1.740 and 1.416 Å) and *s-cis* (1.751 and 1.418 Å) conformers. The longer bonds obtained for the *s-cis* conformer are due to the short steric contacts that take place in the interannular region for this conformer. The H6 and H6′ atoms are separated by only 1.58 Å and the two sulfur atoms by 2.94 Å. These distances are

Table 3. Optimized Geometric Parameters for the *s-cis-* and *s-trans-gauche* Conformers of Biisothianaphthene[a]

parameter[b,c]	*s-cis*-gauche			*s-trans*-gauche	
	MP2	B3-PW91	exptl[d]	MP2	B3-PW91
θ^e	56.7	55.6	~50	126.5	129.9
C2—C2′	1.445	1.451	1.471	1.444	1.449
S1—C2	1.721	1.732	1.718	1.723	1.734
C2—C3	1.411	1.399	1.393	1.412	1.401
C3—C4	1.439	1.447	1.445	1.440	1.448
C4—C5	1.400	1.386	1.414	1.399	1.386
C5—S1	1.701	1.705	1.718	1.700	1.705
C3—C6	1.420	1.426	1.426	1.420	1.426
C6—C7	1.379	1.369	1.353	1.379	1.369
C7—C8	1.423	1.429	1.425	1.422	1.428
C8—C9	1.377	1.367	1.364	1.377	1.367
C9—C4	1.422	1.428	1.428	1.421	1.427
C2′—C2—C3	127.7	129.1		128.8	129.7
S1—C2—C3	110.0	109.9		109.9	109.8
C2—C3—C4	112.4	112.6		112.4	112.6
C3—C4—C5	112.1	112.2		112.2	112.3
C4—C5—S1	111.3	111.5		111.3	111.5
C5—S1—C2	94.1	93.8		94.2	93.9
C4—C3—C6	119.9	119.2		119.6	118.9
C3—C6—C7	118.9	119.4		119.1	119.6
C6—C7—C8	121.3	121.3		121.3	121.4
C7—C8—C9	121.2	121.1		121.0	121.0
C8—C9—C4	119.1	119.4		119.1	119.4
C9—C4—C3	119.7	119.5		119.8	119.7

[a] All the optimizations were carried out using the 6-31G* basis set and assuming C_2 symmetry constraints. [b] The atomic numbering is given in Figure 1. [c] Bond lengths are in angstroms and bond angles in degrees. [d] Average C_2 solid state X-ray data for 5,5′-bis(*tert*-butyldimethylsilyl)-2,2′-biisothianaphthene from ref 15. [e] Torsional angle defined by the planes of the two isothianaphthene units. Values of 64.9° and 103.8° at the HF level and of 53.8° and 132.9° at the B3-P86 level are obtained for *s-cis* and *s-trans-gauche* conformers, respectively.

very much shorter than the sum of the van der Waals radii (2.40 and 3.70 Å, respectively) and also than the distances calculated at the B3-PW91 level for the H3···H3′ (2.43 Å) and S1···S1′ contacts (3.31 Å) in the *s-cis* conformer of 2,2′-bithiophene.

The evolution of the C2—C2′ bond length with θ is determined by both conjugative and steric effects. For the less hindered bithiophene molecule, the loss of the π-conjugation present in the planar forms prevails; the length of the C2—C2′ bond has a similar value for the *s-cis* and *s-trans* planar conformers and increases in going from planar to perpendicular forms.[14a] This is not the case for biisothianaphthene, for which the strong steric interactions occurring in the planar conformers determine a decrease of the C2—C2′ bond length in going from planar to twisted structures, especially for the *s-cis* conformers, despite the loss of π-conjugation. The largest value (1.464 Å) calculated at the B3-PW91 level for this bond length indeed corresponds to the planar *s-cis* conformer. This value is ~0.02 Å larger than for the *s-trans* conformer, thus showing that the *s-cis* form is significantly more hindered than the *s-trans* form.

Steric interactions lead also to large variations of the interannular bond angles with the torsional angle θ (see Figure 3). The C2′—C2—C3 angle decreases from 131.0° for the *s-trans* conformer to 128.6° for the perpendicular form and again increases up to 136.9° for the *s-cis* conformer. A similar, but less marked evolution is found for the C2—C3—C6 angle which varies from 130.0° ($\theta = 180°$) to 127.8° ($\theta = 90°$) and to 131.7° ($\theta = 0°$). This evolution is complemented by the narrowing of the C4—C3—C6 angle in passing from perpendicular (119.4°) to planar *s-cis* (115.8°) and *s-trans* (117.4°) structures. All these trends tend to alleviate the steric interactions, especially for the *s-cis* conformer.

It is worth noting that, although the planar *s-cis* conformer is more crowded than the planar *s-trans* conformer, the bond

Table 4. Relative Energies ($E_\theta - E_{trans}$, kJ/mol) Calculated for Biisothianaphthene at Different Torsional Angles (θ)[a]

conformation θ (deg)	HF[b]	MP2//HF[c]	MP2//B3-PW91[c]	MP2[b]	B3-P86[b]	B3-PW91[b]
0 (*s-cis*)	39.14	38.29	39.23		34.73	34.33
30	−2.03	−3.20	−2.65		2.85	2.30
50	−26.70	−23.53				
s-cis-gauche[d]	−29.95	−23.38	−23.93	−24.75	−11.96	−13.72
60	−29.70	−24.25	−23.71		−11.43	−13.47
75	−29.42					
90	−28.54	−19.22	−18.75		6.66	−9.43
95	−28.43					
100	−28.41					
110	−28.36					
120	−27.65	−21.64	−21.18		−10.28	−12.36
s-trans-gauche[e]	−28.41	−19.73	−21.54	−22.06	−11.50	−13.01
150	−14.60	−15.73	−15.69		−8.69	−9.28
180 (*s-trans*)	0.0	0.0	0.0	0.0	0.0	0.0

[a] All the calculations were performed using the 6-31G* basis set. [b] Geometries were optimized fixing θ and keeping planar the isothianaphthene units. θ was also optimized for the *s-cis-* and *s-trans-gauche* minima. [c] Single-point calculations. [d] The optimized values of θ for the *s-cis-gauche* minimum are 64.9°, 56.7°, 53.8°, and 55.6° at the HF, MP2, B3-P86, and B3-PW91 levels, respectively. [e] The optimized values of θ for the *s-trans-gauche* minimum are 103.8°, 126.5°, 132.9°, and 129.9° at the HF, MP2, B3-P86, and B3-PW91 levels, respectively.

lengths and bond angles reported in Table 3 for the *gauche* minima suggest that the *s-cis-gauche* conformer is less hindered than the *s-trans-gauche* conformer. For instance, for the *s-cis-gauche* conformer, the S1−C2 and C2−C3 bonds are slightly shorter, the C2′−C2−C3 angle is ∼1° smaller, and the C4−C3−C6 angle is ∼0.3° larger. That suggestion is also supported by the distances calculated for steric contacts. At the MP2 level, the *s-cis-gauche* conformer only shows a single S1···S1′ contact (3.56 Å) below the respective van der Waals distance (3.70 Å), since the H6 and H6′ atoms are now separated by a distance of 2.66 Å. For the *s-trans-gauche* minimum, two S1···H6 contacts are found (2.92 Å) below the van der Waals distance (3.05 Å), and four S1···C3′ and S1···C6′ contacts are calculated at distances of 3.44 and 3.51 Å, which are on the order of the van der Waals distance (3.50 Å).

The only experimental information about the structure and conformation of biisothianaphthene is the single-crystal X-ray diffraction determination of the structure of 5,5′-bis(*tert*-butyldimethylsilyl)-2,2′-biisothianaphthene.[15] The dimer is reported to show a *s-cis-gauche* conformation with the two isothianaphthene moieties pointing in the same direction and forming an angle of ∼50°. The average (C_2 symmetry) bond lengths measured for that compound are given in Table 3 and should be compared with those calculated for the *s-cis-gauche* minimum, for which torsional angles of 56.7°, 53.8°, and 55.6° are predicted at MP2, B3-P86, and B3-PW91 levels, in good agreement with the experimental value. HF calculations afford too strongly a twisted structure with a torsional angle of 64.9°. The largest deviation between the MP2 and experimental bond lengths is found for the inter-ring C2−C2′ distance, which has a calculated value of 1.445 Å and an X-ray value of 1.471 Å. We believe, however, that the experimental estimate might be too long, since recent X-ray studies of 2,2′-bithiophene all report inter-ring distances of 1.444−1.448 Å[17b,c] in very good accord with the distance calculated at the MP2 level (1.450 Å). As a whole, the optimized geometries are in good accord with the experimental data.

2. Torsional Potentials. A. Biisothianaphthene. Table 4 collects the relative energies obtained for different conformations of biisothianaphthene from HF/6-31G*, MP2/6-31G*, B3-P86/6-31G*, and B3-PW91/6-31G* calculations including geometry optimization and from MP2/6-31G*//HF/6-31G* and
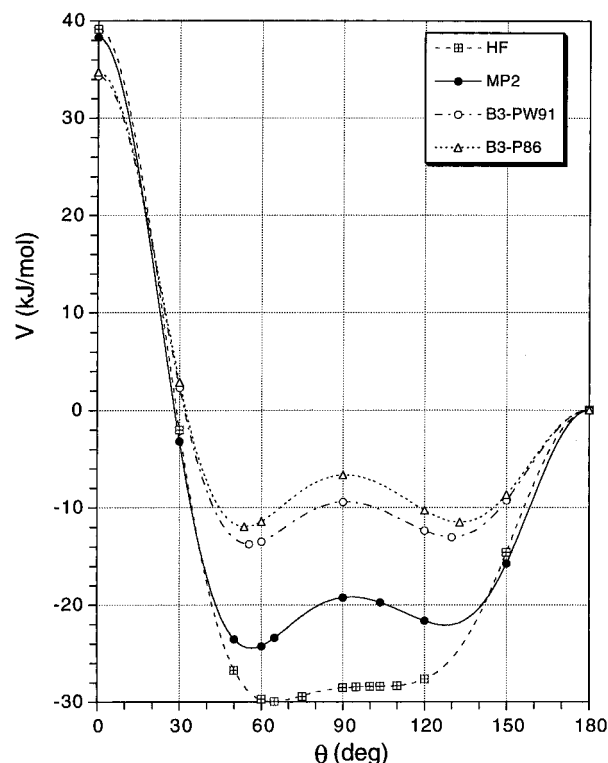

Figure 4. Fourier-fitted HF/6-31G*, MP2/6-31G*//HF/6-31G*, B3-P86/6-31G*, and B3-PW91/6-31G* torsional potentials V calculated for biisothianaphthene as a function of the dihedral angle θ. The *s-trans* planar conformer ($\theta = 180°$) is taken as the energy origin.

Table 5. Fourier-Fitted Torsional Potentials of Biisothianaphthene[a]

parameter[b,c]	MP2//HF	MP2//B3-PW91	parameter[b,c]	MP2//HF	MP2//B3-PW91
V_1	19.14	19.76	V_5	4.41	4.55
V_2	−34.56	−34.43	V_6	−3.81	−3.94
V_3	14.48	14.77	V_7	0.26	0.30
V_4	−21.32	−21.32	V_8	−0.22	−0.34
θ_{CG}	56.3	56.3	θ_{TG}	127.8	127.9
ΔE_{CG}	−24.45	−23.94	ΔE_{TG}	−22.09	−21.57

[a] All the calculations were performed using the 6-31G* basis set. [b] V_i (kJ/mol) are the coefficients of the eight-term Fourier expansion. [c] θ and ΔE refer respectively to the torsional angle (deg) and the relative energy ($E_\theta - E_{trans}$, kJ/mol) calculated from the fitted potential for the *s-cis-gauche* (CG) and *s-trans-gauche* (TG) minima.

MP2/6-31G*//B3-PW91/6-31G* single-point calculations. The *s-trans* planar conformer is always taken as the energy origin. (The basis set will be hereafter omitted in the notation.) Figure 4 plots the potential energy curves for the internal rotation of biisothianaphthene as a function of the dihedral angle θ. The MP2//B3-PW91 potential is not displayed because it is almost fully superimposed on the MP2//HF potential. The potential curves were obtained by fitting the relative energy values given in Table 4 to an eight-term Fourier expansion as explained above. The use of six-term Fourier expansions provides slightly less accurate potential curves and is not adequate to describe the bottom of the HF curve. The values calculated for the coefficients V_i of the eight-term expansions are given in Table 5 for the MP2//HF and MP2//B3-PW91 potentials.

The HF results predict a steep torsional potential with high energy maxima for the planar conformers and a wide, deep energy well around the perpendicular conformation. The torsional potential is very flat in the $\theta = 60-120°$ zone, where a *s-cis-gauche* minimum appears at $\theta = 64.9°$ and a very shallow *s-trans-gauche* minimum is localized at $\theta = 103.8°$. The *s-cis-gauche* minimum is separated from the *s-trans* and

s-cis planar conformers by barriers of 29.95 and 69.09 kJ/mol, respectively. These high energy barriers are due to the strong nonbonding interactions that take place for planar conformations, as the analysis of the geometric structure has revealed. Those interactions largely destabilize the planar structures and, in particular, the *s-cis* conformer, for which very short H···H and S···S contacts occur.

The introduction of electron correlation effects at the MP2 level very significantly changes the shape of the torsional potential (see Figure 4). The major effect is the stabilization of the planar conformations with respect to twisted structures, thus reducing the depth of the potential wells, and especially with respect to the perpendicular conformer, which now clearly corresponds to a maximum. As a consequence, well-defined *s-cis-* and *s-trans-gauche* minima are obtained from MP2 calculations in contrast to the flat potential yielded by HF calculations in the $\theta = 60-120°$ range.

The Fourier-fitted MP2 torsional potentials given in Table 5 can be used to calculate the position and relative energy of the minima. At the MP2//HF level, the *s-cis-* and *s-trans-gauche* minima are located at $\theta = 56.3°$ and $127.8°$, respectively, and are predicted to be 24.45 and 22.09 kJ/mol lower in energy than the planar *s-trans* conformer. The use of a six-term Fourier expansion gives a similar description of the *s-cis-gauche* ($\theta = 55.6°$, $\Delta E = -24.57$ kJ/mol) and *s-trans-gauche* ($\theta = 128.4°$, $\Delta E = -22.05$ kJ/mol) minima. The *s-cis-gauche* minimum is therefore predicted as the most stable conformation by an energy difference of 2.36 kJ/mol. It is separated from the *s-trans-gauche* minimum by a barrier of only 5.28 kJ/mol through the perpendicular ($\theta = 93.0°$) transition state, and by a high barrier of 62.74 kJ/mol through the planar *s-cis* form. The energy difference between the planar forms (38.29 kJ/mol) is almost identical to that calculated at the HF level (39.14 kJ/mol). Nearly identical relative conformational energies and torsional angles are obtained at the MP2//B3-PW91 level (see Tables 4 and 5).

The geometries of the *s-cis-* and *s-trans-gauche* minima and that of the *s-trans* planar conformer were also optimized at the MP2 level. The minima were localized at $\theta = 56.7°$ and $126.5°$ and lie at energies of 24.75 and 22.06 kJ/mol below the *s-trans*-conformer, respectively. The Fourier-fitted torsional potentials based on single-point MP2//HF and MP2//B3-PW91 calculations therefore allow one to predict the torsional angles and relative energies of the *gauche* minima with an accuracy of ~1° and ~1 kJ/mol, respectively. This clearly establishes the validity of using HF- or DFT-optimized geometries.

The MP2 results thus show that the most stable conformation of biisothianaphthene corresponds to a *s-cis-gauche* disposition of the isothianaphthene units. This result is fully consistent with the *s-cis* conformation ($\theta \approx 50°$) observed for single crystals of 5,5′-bis(*tert*-butyldimethylsilyl)-2,2′-biisothianaphthene.[15] In ref 15, that conformation was thought to be "unexpected" because the planar *s-cis* conformer is much more hindered than the planar *s-trans* conformer, as the structural and energetic results discussed above demonstrate for biisothianaphthene, and because it contrasts with what is found for thiophene oligomers, which generally adopt *s-trans*-like orientations in the crystal.[17,42] The authors of ref 15 tentatively explained the appearance of

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such a conformation as a consequence of packing effects which were associated with the bulky side groups. The theoretical calculations presented here show that this is not actually the case, since the conformational behavior of biisothianaphthene is very different from that found for 2,2′-bithiophene. While 2,2′-bithiophene presents a very flat torsional potential with maximum energy differences of 7.4 kJ/mol and where *s-trans* conformations are preferred,[14] biisothianaphthene shows a very steep potential where the absolute minimum lies on a *s-cis-gauche* conformation. The fact that the *s-cis-gauche* conformer is more stable than the *s-trans-gauche* conformer agrees with the structural analysis performed above, which indicates that steric interactions are weaker for the former.

The small energy difference between the two minima (2.74 kJ/mol at the MP2 level) suggests the coexistence of both *gauche* conformers in solution, where the *s-cis-gauche* would be more abundant, and does not exclude the possibility of finding the *s-trans-gauche* disposition in the solid state. Recent studies on tetrathiophenes and longer thiophene oligomers have shown that, although the *s-trans* orientations are more stable by about 2−4 kJ/mol,[14] *s-cis* conformations are also found in the solid state.[42f,g] The low barriers of ~5.2 and ~2.9 kJ/mol that separate both *gauche* minima suggest a rapid interconversion between them in solution. In contrast, the large energy difference (22−25 kJ/mol) between the minima and the *s-trans* planar form would make it difficult to attain fully planar conformations even in the solid state. These results show that the optical properties observed in solution for aromatic isothianaphthene oligomers up to the tetramer are due to molecules adopting strongly nonplanar conformations, as previous INDO/SCI calculations of the electronic spectra suggested.[15] However, the reason for those conformations is not the high chain flexibility, which allows isothianaphthene units to easily undergo rotations around the inter-ring bond, as previously argued[15] but, on the contrary, the high energy of the planar conformations that restricts internal rotation to the neighborhood of the perpendicular structure. The adoption of strongly twisted conformations dramatically reduces the π conjugation between adjacent isothianaphthene units, and thus limits the optical and semiconductivity properties of *aromatic* isothianaphthene chains. The energy band gap extrapolated for nonplanar aromatic PITN from the optical data recorded for aromatic oligomers in solution is 1.94 eV.[15] This value is much higher than the energy gap predicted for planar aromatic PITN from INDO/SCI (0.63 eV)[15] or VEH (0.21 eV)[11b] calculations.

We now focus on the description that DFT calculations provide of the conformational isomerism of biisothianaphthene. As can be seen from Table 4 and Figure 4, both B3-P86 and B3-PW91 calculations yield 4-fold torsional potentials with well-defined *s-cis-* and *s-trans-gauche* minima. The major difference between DFT and MP2 results is that the energy differences between twisted and planar conformations are reduced by ~10 kJ/mol, i.e., by about a factor of 2. It seems like DFT calculations underestimate the steric interactions that take place for planar conformers, thus leading to a stabilization of these conformers with respect to twisted structures. This shortcoming is more pronounced for the B3-P86 functional, for which the twisted structures are shifted up in energy by 2−3 kJ/mol with respect to the B3-PW91 torsional potential.

The relative stabilization of the planar conformers provided by DFT calculations has two main effects on the *s-cis-* and *s-trans-gauche* minima: (i) they appear at less twisted angles (B3-P86, 53.8° and 132.9°; B3-PW91, 55.6° and 129.9°) than the minima calculated at the MP2 level (56.7° and 126.5°) and (ii) the energy difference between them almost vanishes (B3-

P86, 0.46 kJ/mol; B3-PW91, 0.71 kJ/mol). The energy barriers separating both *gauche* minima through the perpendicular conformation have values of 3.5−5.5 kJ/mol and are on the same order as those obtained at the MP2 level. The energy difference between the *s-cis* and *s-trans* planar conformers is calculated to be ∼34 kJ/mol by both functionals, underestimating the MP2//B3-PW91 value by only 5 kJ/mol.

The fact that DFT calculations using the B3-P86 and B3-PW91 functionals underestimate by 45−65% the MP2 $E_\theta - E_{trans}$ relative energies calculated for twisted conformations in the $\theta = 45-135°$ range while they underestimate by only 10% the $E_{cis} - E_{trans}$ energy difference suggests that, in addition to an underestimation of the steric interactions, there are other factors that determine the destabilization of the twisted structures relative to planar conformers at the DFT level. The overestimation of the π conjugative effects present in the planar conformers and the underestimation of the $\sigma - \pi$ hyperconjugative effects occurring in the perpendicular conformers are two factors that would, for instance, contribute to the relative destabilization of the twisted conformations.

To test the importance of including gradient corrections in the functional used in the DFT calculations, the geometries of the planar and perpendicular conformers and of the *s-cis*- and *s-trans-gauche* minima of biisothianaphthene were optimized using the local S-VWN functional. The *gauche* minima now appear at torsional angles of 47.2° and 146.8° and lie below the *s-trans* planar conformer by only 2.76 and 5.09 kJ/mol. The *s-trans-gauche* conformer is therefore predicted to be more stable by 2.33 kJ/mol. It is separated by a barrier of 14.63 kJ/mol from the *s-cis-gauche* minimum since the perpendicular form is now calculated to be 9.54 kJ/mol above the planar *s-trans* conformer. In contrast, the $E_{cis} - E_{trans}$ energy difference has a value of 32.25 kJ/mol similar to those obtained with the B3-P86 and B3-PW91 functionals. These results indicate that the local S-VWN functional energetically favors the planar conformers to a higher degree than the B3-P86 and B3-PW91 functionals. The shortcomings of DFT calculations in describing the energetics of the conformational isomerism of biisothianaphthene are therefore accentuated if a local functional is used.

As a conclusion, we suggest that a very efficient computational methodology would be to perform single-point MP2 calculations on DFT-optimized geometries as it constitutes a low-cost approach that provides a good description of the conformational behavior. The use of DFT geometries, even calculated with local functionals like the S-VWN functional, guarantees an accurate description of the molecular structure. An MP2 calculation on the basis of these geometries ensures good energetics for the rotational potential.

B. Bithiophene. In order to gain a deeper understanding of the applicability and shortcomings of DFT calculations, the torsional potential of the closely related 2,2′-bithiophene was calculated at the DFT level. Steric interactions in bithiophene are less strong than in biisothianaphthene, but large enough to cause the appearance of *gauche* minima, as gas-phase electron-diffraction experimental data have recently shown.[43] The results of previous MP2/6-31G* calculations[14a] are summarized in Table 6 together with those obtained here from B3-P86/6-31G* and B3-PW91/6-31G* calculations. Figure 5 plots the torsional potentials obtained for 2,2′-bithiophene by fitting the relative energies listed in Table 6 to a six-term Fourier expansion.

MP2 calculations provide a very flat 4-fold potential in which the energy difference between the most stable *s-trans-gauche* minimum and the absolute maximum (*s-cis* planar conformer)

Table 6. Relative Energies ($E_\theta - E_{trans}$, kJ/mol) Calculated for 2,2′-Bithiophene at Different Torsional Angles (θ)[a]

conformation θ (deg)	MP2[b,c]	B3-P86[c]	B3-PW91[c]
0 (*s-cis*)	4.09	4.04	4.04
30	−0.17	2.74	2.55
s-cis-gauche[d]	−1.19	2.73	2.55
60	0.17	6.75	6.16
90	2.99	10.98	10.16
120	−0.90	5.87	5.27
s-trans-gauche[e]	−3.32	−0.26	−0.35
150	−2.99	−0.02	−0.19
180 (*s-trans*)	0.0	0.0	0.0

[a] All calculations were performed using the 6-31G* basis set. [b] Data from ref 14a. [c] Geometries were optimized fixing θ and keeping planar the thiophene rings. θ was also optimized for the *s-cis*- ans *s-trans-gauche* minima. [d] The optimized values of θ for the *s-cis-gauche* minimum are 43.3°, 29.3°, and 30.8° at the MP2, B3-P86, and B3-PW91 levels, respectively. [e] The optimized values of θ for the *s-trans-gauche* minimum are 142.2°, 159.0°, and 157.4° at the MP2, B3-P86, and B3-PW91 levels, respectively.
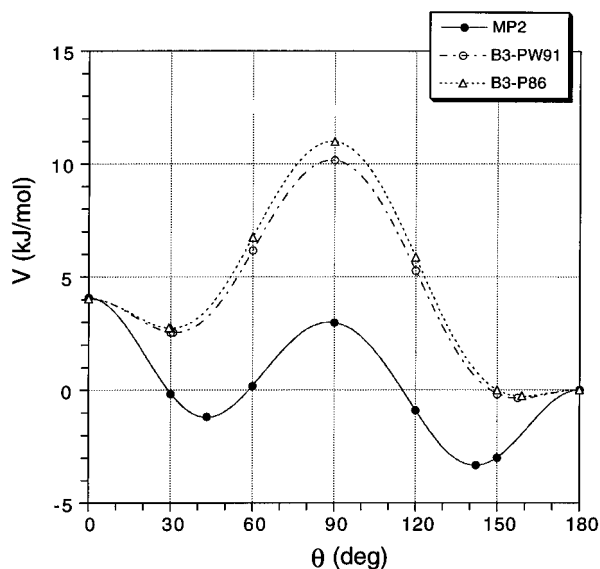

Figure 5. Fourier-fitted MP2/6-31G*, B3-P86/6-31G*, and B3-PW91/6-31G* torsional potentials V calculated for 2,2′-bithiophene as a function of the dihedral angle θ. The *s-trans* planar conformer ($\theta = 180°$) is taken as the energy origin.

is only 7.41 kJ/mol. The *s-cis*- and *s-trans-gauche* minima appear at $\theta = 43.3°$ and 142.2°, respectively, and are separated by barriers of 3.3 kJ/mol (*s-trans-gauche* → *s-trans*) to 6.3 kJ/mol (*s-trans-gauche* → perpendicular). These theoretical results explain the coexistence of *s-cis*- and *s-trans*-like conformations in solution[44] and in the gas phase[43] and justify the planar *s-trans* structures observed in the solid state.[17,42] Moreover, the flatness of the torsional potential is the key to understanding the optical properties (intensity and broadness of the absorption bands, shift of the absorption maxima with the aggregation state, etc.) of bithiophene and longer oligothiophenes.[45]

As can be seen from Figure 5, the description obtained for the conformational isomerism of 2,2′-bithiophene from DFT calculations is markedly different from that calculated at the MP2 level. B3-P86 and B3-PW91 functionals provide nearly identical torsional potentials where the *s-trans* conformations continue to be the most stable structures; however, the *s-trans-*

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gauche minimum has almost vanished and appears at $\theta \approx 160°$ as a very shallow minimum ~ 0.3 kJ/mol below the *s-trans* planar conformer. The *s-cis-gauche* minimum appears at $\theta \approx 30°$ and lies $1.3-1.5$ kJ/mol below the *s-cis* planar form, thus being very shallow compared with MP2 results (5.28 kJ/mol). The interconversion between both *gauche* minima through the perpendicular conformation is restricted by barriers of about 8 kJ/mol (*s-cis* → *s-trans*) and 11 kJ/mol (*s-trans* → *s-cis*) which are twice as high as the barriers obtained at the MP2 level.

The shallowness of the *gauche* minima and the higher rotational barriers obtained for 2,2′-bithiophene confirm that, as discussed above for biisothianaphthene, DFT calculations favor planar vs perpendicular conformers. The relative stabilization of the planar forms could be ascribed to the underestimation of the steric interactions. However, the energy difference between the *s-cis* and *s-trans* planar forms (4.04 kJ/mol), which is due to the difference in steric hindrance, is well reproduced with respect to MP2 calculations (4.09 kJ/mol). Other factors like those invoked for biisothianaphthene, i.e., overestimation of π conjugative effects in planar conformers and/or underestimation of $\sigma-\pi$ hyperconjugative effects in the perpendicular conformer, should therefore be considered as responsible for the relative stabilization of planar vs twisted structures at the DFT level. We have also verified for 2,2′-bithiophene that the shortcomings of DFT calculations in describing the torsional potential increase when the local S-VWN functional is used. At this level, the *gauche* minima disappear and the rotational barrier for the *s-trans* → *s-cis* interconversion increases to 16.83 kJ/mol.

We complete our discussion by briefly considering the applicability of semiempirical methods of the NDDO type: MNDO,[46] AM1,[47] and PM3,[48] since these methods are often used in the field of conducting polymers to study the conformation of polyarylenes. The MNDO method fails in describing the rotational isomerism of conjugated systems because it strongly favors perpendicular vs planar forms. This shortcoming has been corroborated for bithiophene[49] and biisothianaphthene,[3a] for which the rotational energy curves provided by the MNDO method present no *gauche* minimum and localize the preferred conformation in the neighborhood of the perpendicular structure.

Figure 6 shows the torsional potentials calculated at the AM1 and PM3 levels for bithiophene and biisothianaphthene. The AM1 method reproduces correctly the torsional profile of bithiophene showing *s-cis-gauche* ($\theta = 34.5°$) and *s-trans-gauche* ($\theta = 152.6°$) minima.[18,49b] The torsional potential is, however, calculated to be very flat, the maximum energy difference (*s-trans-gauche* → *perpendicular*) being only 1.79 kJ/mol. The PM3 method also predicts a very flat torsional where *gauche* minima practically do not exist and the minimum energy conformation wrongly corresponds to *s-cis* structures. For biisothianaphthene, both the AM1 and the PM3 methods provide inaccurate torsional potentials. The AM1 potential is very steep between 0 and 45°, completely flat between 60° and 120°, and shows a shallow minimum at $\theta = 153.7°$ lying 1.32 kJ/mol below the *s-trans* planar conformer. The PM3 potential presents a unique minimum at $\theta \approx 60°$, from which the energy rises smoothly until reaching the energy maximum at $\theta = 180°$. None of the three semiempirical methods MNDO, AM1, and PM3 thus provide realistic descriptions of the conformational behavior of bithiophene and biisothianaphthene. All of them
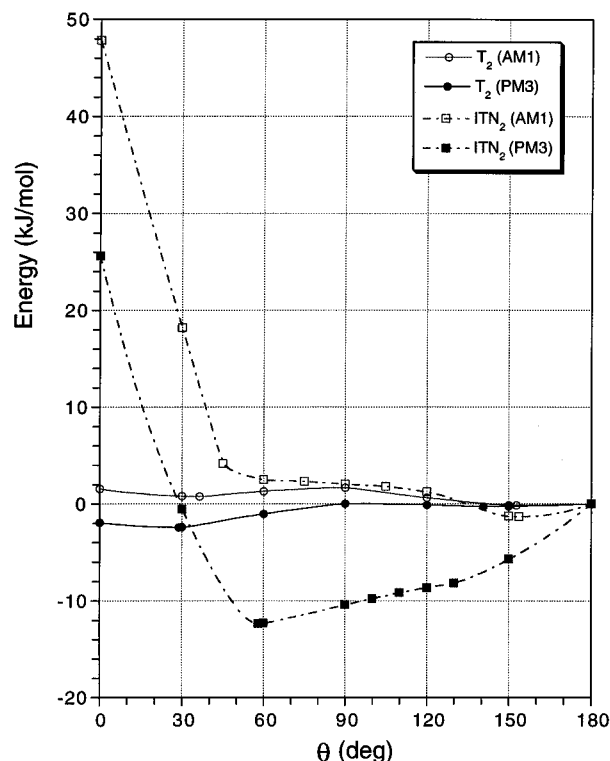

Figure 6. AM1 and PM3 torsional potentials calculated for 2,2′-bithiophene (T_2) and biisothianaphthene (ITN_2) as a function of the dihedral angle θ. The *s-trans* planar conformer ($\theta = 180°$) is taken as the energy origin.

uncorrectly describe the steric interactions that provoke the appearance of *gauche* conformations and overstabilize perpendicular conformations. Their use to investigate the conformational behavior of polyarylenes should therefore be restricted to cases for which their applicability has been previously tested against more accurate methods.

Synopsis

The conformational isomerism of biisothianaphthene has been theoretically investigated at the HF, MP2, and DFT levels in order to gain some insight into the conformational properties of longer isothianaphthene oligomers and aromatic PITN. MP2 calculations provide a 4-fold potential for the internal rotation around the inter-ring bond, where minimum energy conformations correspond to strongly twisted structures and high energy maxima to the *s-cis* and *s-trans* planar structures. The *s-cis-gauche* minimum ($\theta = 56.7°$) lies 2.74 kJ/mol below the *s-trans-gauche* minimum ($\theta = 126.5°$) and is predicted to be the most stable conformer. This result explains the *s-cis*-like conformation ($\theta \approx 50°$) observed for disilyl-substituted biisothianaphthene in the crystal.[15] The analysis of the molecular structure shows that, although the planar *s-cis* conformer is more hindered than the planar *s-trans* conformer, the steric interactions are more readily alleviated for *s-cis* twisted structures, thus justifying the higher stability of the *s-cis-gauche* mimimum. The small energy difference between the two minima further suggests the coexistence of both conformers in solution and makes feasible the appearance of the *s-trans-gauche* conformer in the solid state.

Interconversion between the two *gauche* minima through the perpendicular conformation is made possible by low barriers of $3-5$ kJ/mol. On the contrary, interconversion through the planar conformers, which are destabilized by the short steric contacts that take place in the interannular region, is prevented by high barriers of ~ 22 kJ/mol (*s-trans*) and ~ 63 kJ/mol (*s-*

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cis). These high barriers restrict the internal rotation of biisothianaphthene and make it difficult to attain planar conformations even in the solid state. The conformational behavior of polyisothianaphthene chains is therefore predicted to be markedly different from that observed for polythiophene chains; in the latter, the torsional potential is very flat and (nearly) planar structures are the preferred conformations in the solid state. An important result of the present work is that the preference for twisted conformations drastically reduces the π conjugation in native nonsubstituted aromatic isothianaphthene chains, thus limiting their optical and semiconductivity properties.

The optimized geometries provided by DFT calculations using both the local S-VWN and the gradient-corrected B3-P86 and B3-PW91 functionals are very close to the MP2 geometries. DFT calculations however fail in describing the energetics of the internal rotation even when gradient-corrected functionals are used. For biisothianaphthene, the B3-P86 and B3-PW91 functionals overstabilize the planar conformers with respect to twisted structures, thus reducing the *gauche* → planar barrier heights. These trends are confirmed for 2,2′-bithiophene, for which the *gauche* minima almost disappear and the barrier height through the perpendicular conformation is doubled with respect to MP2 results. The overstabilization of the planar structures is more pronounced when the local S-VWN functional is used. This functional does not lead to any *gauche* minima for bithiophene, wrongly predicts the *s-trans-gauche* minimum to be more stable than the *s-cis-gauche* minimum for biisothianaphthene (both minima being very shallow), and increases the barriers through the perpendicular conformation by a factor of 3 with respect to MP2 results. Gradient-corrected functionals are therefore needed to obtain a qualitatively correct description of the torsional potential, even though they do not provide very accurate conformational energies.

HF ab initio calculations correctly predict the greater stability of the *s-cis-gauche* conformer for biisothianaphthene but provide too flat a potential in the neighborhood of the perpendicular conformation. The semiempirical AM1 and PM3 NDDO-type methods have been shown to be inadequate to describe the conformational behavior of biisothianaphthene and bithiophene; for instance, the popular AM1 method provides a qualitatively correct torsional profile for bithiophene but completely fails in describing the torsional potential of biisothianaphthene.

A very useful methodological aspect of our work of general interest is to propose a novel efficient computational approach to describe conjugated compounds: we suggest to have geometries optimized at the DFT level (even simply using local functionals) and conformational energies evaluated via single-point MP2 calculations. The fitting of the MP2//DFT energies to truncated Fourier expansions allows one to predict the torsional angles and the relative energies of the critical points of the conformational potential with an accuracy similar to that afforded by MP2 calculations including full geometry optimization.

Supporting Information Available: Tables S1 and S2, fully detailed HF/6-31G*-, MP2/6-31G*-, S-VWN/6-31G*-, B-LYP/6-31G*-, B3-LYP/6-31G*-, B3-P86/6-31G*-, and B3-PW91/6-31G*-optimized geometries for thiophene and isothianaphthene; Tables S3 and S4, fully detailed HF/6-31G*-, MP2/6-31G*-, B3-P86/6-31G*-, and B3-PW91/6-31G*-optimized geometries for 2,2′-bithiophene and biisothianaphthene; and Table S5, HF/6-31G*- and B3-P86/6-31G*-optimized geometries for the *s-cis-* and *s-trans-gauche* conformers of biisothianaphthene (5 pages). See any current masthead page for ordering and Internet access instructions.

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