A Theoretical Investigation of the Torsional Potential in 3,3′-Dimethyl-2,2′-bithiophene and 3,4′-Dimethyl-2,2′-bithiophene: A Comparison between HF, MP2, and DFT Theory

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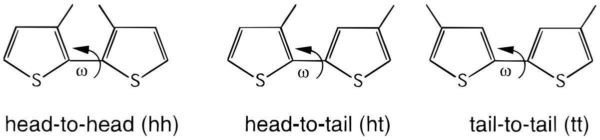
The torsional potential curve of 3,3′-dimethyl-2,2′-bithiophene has been investigated at the MP2 and DFT (B3LYP and BLYP) levels with the 6-31G* basis. The DFT (B3LYP) method has also been used to compute the torsional curve for 3,4′-dimethyl-2,2′-bithiophene. In contrast with previous HF computations, our results indicate for both isomers the existence of a syn-gauche and an anti-gauche conformational minimum. This finding is in agreement with X-ray structural investigations and UV data. Our computations point out the importance of including the correlation energy contributions to study the conformational properties of oligo and polythiophenes and indicate that the DFT approach (in particular the hybrid B3LYP functional) provides a description of these systems which is in satisfactory agreement with the experimental evidence.

Introduction

During the past decade oligo and polythiophenes have become a subject of great interest because of their intrinsic electrical and optical properties:[1] they are characterized by very large optical responses and become good electrical conductors in the oxidized (doped) state. At the molecular level these physical properties are primarily controlled by the energy of the $\pi \rightarrow \pi^*$ interband transition which in turn depends on the overlap between the π orbitals and consequently on the extent of the π conjugation along the polymer chain.[2] This π conjugation is strongly affected by the degree of coplanarity between the polymeric units, and it has been shown that deviation from the coplanarity leads to an increase of ionization potentials and band gap values according to a cosine law.[3] This problem becomes especially important in the case of oligo and polythiophenes which have been functionalized with alkyl groups to obtain more easily processable products. In these compounds the existence of a torsional angle along the polymer chain introduces rotational defects which interrupt and weaken the extent of the π conjugation. If we consider the case of poly(3-methylthiophenes), the simplest model that can be used to study the conformational properties of this compound is represented by the dimer originated by an α−α′ coupling of two 3-methylthiophene units. In this dimer we can recognize three different types of α,α′ junction: a head-to-head (hh), a head-to-tail (ht), and a tail-to-tail (tt) junction corresponding to 3,3′-dimethyl-2,2′-bithiophene, 3,4′-dimethyl-2,2′-bithiophene, and 4,4′-dimethyl-2,2′-bithiophene, respectively (see Scheme 1). In the case of hh junctions, alkyl−alkyl or alkyl−sulfur steric interactions lead to a significant decrease in coplanarity which strongly affects the electronic properties of the polymer.[4−6]

Extensive computational investigations of the rotational features of the possible junctions in the polymer have been recently carried out.[7−11] In these studies 2,2′-bithiophene and 3,3′-, 3,4′-, and 4,4′-dimethyl-2,2′-bithiophene have been assumed as models for polythiophene and for the hh, ht, and tt junctions in the polymer,[7−10] respectively. For the 2,2′-bithiophene HF/3-21G*, HF/6-31G*, and MP2/6-31G* calculations[8−12] predict a torsional profile corresponding to a rotation around the α,α′ junction in agreement with the results obtained for these molecules in gas phase electron diffraction experiments.[12] At the MP2/6-31G* level the torsional curve is characterized by two minima, a syn-gauche and an anti-gauche conformation, corresponding to a value of 43.3° and 142.2° of the torsional angle ω, respectively (the relative orientation of the two rings in Scheme 1 corresponds to $\omega = 0°$): these values are in fairly good agreement with the experimental values of 36° and 148°. A similar profile has been found for 4,4′-dimethyl-2,2′-bithiophene.[8,10] For the 3,4′-dimethyl-2,2′-bithiophene Distefano et al.,[8] in a combined ab initio and ultraviolet photoelectron spectroscopy study, have suggested the existence of two conformational minima (at about 140° and 50°) to explain the observed trend of ionization energies along the series 2,2′-bithiophene, 4,4′, 3,4′, and 3,3′-dimethyl-2,2′-bithiophene. However, these conclusions have not been supported by the results of Hernandez et al.[9] who have found for the 3,4′-dimethyl-2,2′-bithiophene only one minimum at $\omega = 108.6°$ at the Hartree−Fock level with the two 3-21G* and 6-31G* basis sets. Similarly, for the 3,3′ derivative only one minimum at about 90° has been located.[8−10]

SCHEME 1



These computational results must be compared with solution UV data for dimethyl bithiophenes where an ipsochromic effect has been detected on going from the 4,4′ to the 3,4′ and 3,3′ isomer ($\lambda_{max} = 311$, 299 and 268 nm, respectively), which shows a net increase in the torsion of the inter-ring junction on going from tail-to-head substitution[13,14] with a consequent decrease of the π conjugation. The same behavior has been pointed out by gas UPS and ET data[8] on the same isomers.

Similar information has been obtained in a solid state study of the polymer which forms from 3,3′-dimethyl-2,2′-bithiophene.[4] This polymer is characterized by a regular sequence of hh and tt junctions and adsorbs in the visible region with a maximum at 417 nm ($\pi-\pi^*$ transition). On the other hand, poly(3-

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methylthiophene), which can be described as a sequence of ht junctions (3,4′ junctions), has a maximum absorption at 508 nm which is in the range observed for polythiophene (500−550 nm) where no steric defects due to alkyl substituents can be found. Thus, the presence of 3,3′ junctions causes a lower degree of conjugation as found in solution for dimethyl bithiophenes.

Even if this experimental evidence indicates that 3,3′ derivatives must be characterized by the most tilted conformations, they are in contrast with a dihedral angle of 90°, as found at the Hartree−Fock level,[8−10] which would completely cut off conjugation and show more drastic ipsochromic effects on UV spectra. On the other hand, also the only minimum located for the 3,4′-dimethyl-2,2′-bithiophene at the Hartree−Fock level with a nearly orthogonal arrangement of the two rings would predict a too large decrease of the π conjugation in contrast with the experimental evidence which shows only weak effects.[4,8]

The above-discussed experimental data better agree with MM2 calculations,[13,14] which predict a syn-anti conformational equilibrium for all three isomers and inter-ring angles going from 153° to 142° and 134°. In addition, NMR−NOE experiments for 3,4′-dimethyl-2,2′-bithiophene[15] also indicate the existence of a syn conformation in solution, and syn and anti hh junctions have been found in the solid state in methylated tetramers for both hh and ht junctions.[16,17]

In the present paper we examine the torsional curves of 3,3′-dimethyl-2,2′-bithiophene and 3,4′-dimethyl-2,2′-bithiophene using a density functional theory (DFT)[18] approach. For the 3,3′ isomer we use both a pure (BLYP) and a hybrid (B3LYP) functional, and we also compute the curve at the MP2 level. For the 3,4′ isomer we carry out our computations only at the B3LYP level. In both cases we compare our results to the previous Hartree−Fock results.[8−10] The paper has two aims. The first is to shed light on the conformational features of alkylated polythiophenes using accurate quantum mechanical computations. The second is to establish the level of theory which is required to obtain a reliable description of this type of system. This point is particularly important since results obtained with accurate computations on appropriate model systems are used to parametrize force-field methods suitable for describing larger molecules. Also, an accurate analysis of the performance of DFT-based methods is an interesting aspect. The possibility of including electron correlation in the computations of large chemical systems and the discovery of new and more accurate exchange−correlation energy functionals has made DFT more and more popular. Thus, a calibration of DFT methods to establish strengths and weaknesses of each functional has become nowadays a particularly meaningful task.

Computational Details

All of the ab initio and DFT molecular computations reported here were performed with the *Gaussian 94*[19] series of programs using the 6-31G*[20] basis set. At both MP2 and DFT levels we computed the total energy at frozen values of the inter-ring torsional angle ω (see Scheme 1). At each point we fully optimized all of the remaining geometrical parameters with the gradient method available in *Gaussian 94* without imposing any additional constraint during the optimization process. A full geometry optimization without any constraint on the angle ω was carried out to locate the minima of the torsional potential surface. The nature of each minimum was characterized at the DFT level by computing the harmonic vibrational frequencies. For the DFT computations we have used the pure (BLYP)[21] and the hybrid (B3LYP)[22] functional as implemented in *Gaussian 94*.

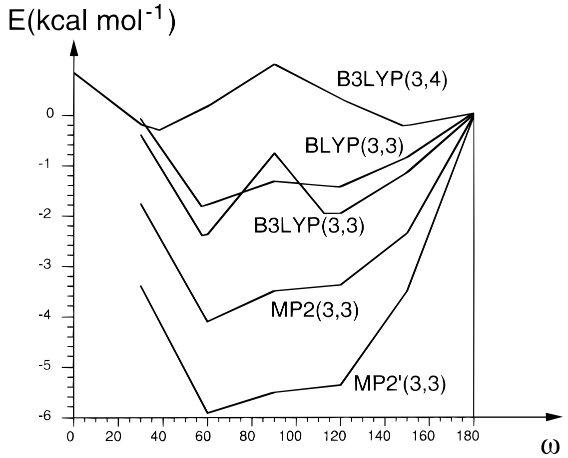

Figure 1. Diagrams of the potential energy versus the inter-ring torsional angle ω obtained for the 3,3′-dimethyl-2,2′-bithiophene (MP2(3,3), MP2′(3,3), B3LYP(3,3), and BLYP(3,3)) and the 3,4′-dimethyl-2,2′-bithiophene (B3LYP(3,4)). MP2′(3,3) computed with the G-31+G* basis.

TABLE 1: Relative Energies (E, kcal mol^{-1})[a] Computed for Different Values of the Torsional Angle ω of the 3,3′-Dimethyl-2,2′-bithiophene and 3,4′-Dimethyl-2,2′-bithiophene

	3,3′ isomer				3,4′ isomer
ω[b]	MP2	MP2′	B3LYP	BLYP	B3LYP
180.0	0.00	0.00	0.00	0.00	0.00
150.0	−2.36	−3.52	−1.17	−0.89	−0.25
120.0	−3.41	−5.38	−1.98	−1.47	0.28
90	−3.52	−5.50	−0.78	−1.38	0.97
60		−5.93	−2.41	−1.85	0.14
30	−1.80	−3.39	−0.43	−0.12	−0.24
0					0.80
anti-gauche[c]			−1.98	−1.47	−0.25
syn-gauche[d]	−4.12		−2.42	−1.86	−0.34

[a] The absolute energies (hartree) at ω = 180° are: 3,3′-dimethyl-2,2′-bithiophene −1181.04304 (MP2), −1181.06915 (MP2′), −1183.44715 (B3LYP), −1183.22011 (BLYP); 3,4′-dimethyl-2,2′-bithiophene −1183.45186 (B3LYP). [b] Degree. [c] For the 3,3′ isomer ω is 112.6° (B3LYP), 118.2° (BLYP); for the 3,4′ isomer ω is 148.2° (B3LYP). [d] For the 3,3′ isomer ω is 60.1° (MP2), 58.1° (B3LYP), 57.4° (BLYP); for the 3,4′ isomer ω is 38.6° (B3LYP).

Results and Discussion

In the present section we discuss the potential energy curves obtained for the 3,3′-dimethyl-2,2′-bithiophene and the 3,4′-dimethyl-2,2′-bithiophene as a function of the torsional angle ω. The torsional curves computed at different levels of theory (MP2, BLYP, and B3LYP for the 3,3′ isomer and B3LYP for the 3,4′ isomer) are represented in Figure 1 while the corresponding energies are reported in Table 1.

A. 3,3′-Dimethyl-2,2′-bithiophene. The rotational profiles obtained at the MP2 and BLYP levels are similar, and both show the existence of a syn-gauche conformer corresponding to a value of ω close to 60° (60.1° and 57.4° at the MP2 and BLYP levels, respectively). The region corresponding to an anti-gauche conformer is very flat in both cases; however, while the BLYP curve is characterized by a very shallow minimum at ω = 118.2°, at the MP2 level this minimum disappears. Furthermore, while at both computational levels the difference between the syn-gauche and the anti-gauche region is about 0.5 kcal mol^{-1}, the rotational barrier computed with respect to the anti planar structure ($\omega = 180°$) significantly varies being 4.12 and 1.85 kcal mol^{-1} at the MP2 and BLYP levels, respectively. The most significant difference found with the hybrid B3LYP functional is the presence of a well characterized minimum also in the anti-gauche region corresponding to $\omega = 112.6°$ and a sharp maximum at $\omega = 90°$. The syn-gauche conformer ($\omega = 58.1°$) is more stable than the anti-gauche conformer by about 0.5 kcal mol^{-1}, and the rotational barrier connecting the syn to the anti region is 1.20 kcal mol^{-1}.

To assess the importance of the basis set in determining the different description provided by the MP2 approach when compared to the DFT approach (missing minimum in the anti-gauche region at the MP2 level), we have carried out single point MP2 computations with the more accurate 6-31+G* basis[23] at the MP2/6-31G* optimized geometries. The 6-31+G* basis includes additional diffuse functions on the carbon and sulfur atoms and, in principle, can improve the description of the ring π system and especially of the sulfur lone-pairs. The corresponding potential energy curve is also reported in Figure 1 (MP2′(3,3) curve). The shape of this curve is almost identical to that found with the less accurate 6-31G* basis: no anti-gauche minimum appears, and the energy difference between the syn-gauche and the anti-gauche region remains about 0.5 kcal mol^{-1}. This finding indicates that the lack of the anti-gauche minimum is not determined by the use of the less accurate 6-31G* basis which can be considered to be suitable for describing the topology of the potential surface.

The ω values determined at the various computational levels for the syn-gauche conformer are in good agreement with that found in the X-ray structures of tetra-methyl α-conjugated quaterthiophenes where the external hh junctions are characterized by a noncoplanar syn conformation with a dihedral angle ω of 54.2°.[17] It is interesting to point out that the existence of a second minimum (anti-gauche), which has been clearly located at the B3LYP level ($\omega = 112.6°$), is in agreement with the structural features of the inner hh junctions in tetra-methyl α-conjugated quaterthiophenes which experimentally have been found to be either anti-planar[16] or anti-gauche.[17] Furthermore, a tilted conformation with a dihedral angle significantly smaller or higher than 90° also agrees with the magnitude of the ipsochromic effect found in 3,3′-dimethyl-2,2′-bithiophene when compared to 4,4′ and 3,4′-dimethyl-2,2′-bithiophene. All of these results suggest that the DFT approach, in particular the B3LYP functional, can provide a description which better agrees with the experiment than that obtained with the MP2 method.

A schematic representation of the syn-gauche conformer is given in Figure 2a, while the values of the most important geometrical parameters for both the syn-gauche and anti-gauche structures are collected in Table 2 (in Figure 2, ω is defined as the dihedral angle between the two planes **er** and **ra′**). The most relevant change observed in the comparison between the MP2 and DFT results is a lengthening of the C−S bond lengths (**e** and **d** parameters) at both B3LYP and BLYP levels. At all computational levels (MP2, B3LYP, and BLYP) the inter-ring C−C bond (**r** parameter) is found to be in the range 1.45−1.47 Å: this value is in good agreement with the experimental value found in X-ray diffraction studies for 2,2′-bithiophene, i.e., 1.456 Å.

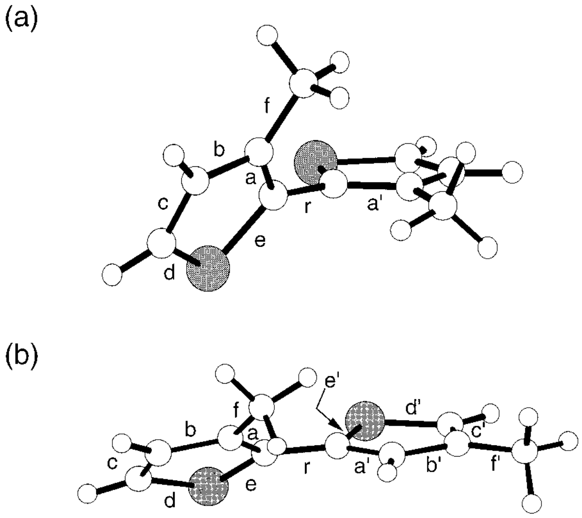

Figure 2. Schematic representation of the syn-gauche conformer for (a) the 3,3′-dimethyl-2,2′-bithiophene and (b) the 3,4′-dimethyl-2,2′-bithiophene.

TABLE 2: Values of the Most Relevant Geometrical Parameters[a] Computed for the Syn and Anti Conformers of 3,3′-Dimethyl-2,2′-bithiophene at the MP2 and DFT (B3LYP and BLYP) Levels with the 6-31G* Basis Set

	MP2	B3LYP	BLYP
syn-gauche			
a	1.390	1.381	1.395
b	1.421	1.433	1.439
c	1.376	1.365	1.376
d	1.716	1.731	1.749
e	1.736	1.760	1.784
f	1.501	1.506	1.516
r	1.455	1.461	1.464
∠ab	111.7	112.1	112.4
∠bc	113.4	113.8	114.0
∠cd	111.5	111.6	111.6
∠de	92.0	91.6	91.5
∠ar	127.7	128.9	129.4
∠af	124.2	124.8	124.6
ω	60.1	58.1	57.4
anti-gauche			
a		1.380	1.394
b		1.433	1.441
c		1.366	1.376
d		1.731	1.748
e		1.760	1.784
f		1.506	1.515
r		1.466	1.469
∠ab		112.2	112.4
∠bc		113.7	114.0
∠cd		111.5	111.5
∠de		91.7	91.6
∠ar		129.2	129.7
∠af		124.9	124.8
ω		112.6	118.2

[a] Bond lengths are in Ångstrom and angles in degree.

These results are significantly different from those obtained with the same basis set at the Hartree−Fock level where only one minimum at about 90° was found[9] and point out the importance of using a computational method which correctly describes the dynamic correlation energy contributions in the investigation of this class of systems. It is interesting to point out that, in contrast to the results obtained here for the 3,3′-dimethyl-2,2′-bithiophene, it has been shown that for the nonalkylated system 2,2′-bithiophene the HF, MP2,[10,11] and DFT (B3LYP)[24] methods provide the same description, and at all levels of theory two different conformers, a syn-gauche and an anti-gauche, are located. This result can be explained as follows. In the absence of alkyl substituents as in 2,2′-bithiophene, the contribution of energy correlation can be considered almost constant along the rotational profile. Thus, neglecting this contribution does not change significantly the shape of the curve. This is much more unlikely to occur in the 3,3′-dimethyl-2,2′-

bithiophene because of methyl−methyl and sulfur−methyl interactions which vary significantly when we rotate around **r**. In this case, to leave out the correlation corrections or to provide a nonbalanced description of these contributions, can affect significantly the rotational profile.

B. 3,4′-Dimethyl-2,2′-bithiophene. Since the B3LYP functional seems to provide the best agreement with the experiment in the case of the 3,3′ isomer, we have used this computational level to investigate the torsional curve for the 3,4′-dimethyl-2,2′-bithiophene. The rotational profile that we have obtained (see Figure 1) shows the existence of three maxima at $\omega = 0°$, 90°, and 180° and two almost degenerate minima corresponding to a syn-gauche ($\omega = 38.6°$) and an anti-gauche conformer ($\omega = 148.2°$). The syn-gauche → anti-gauche rotational barrier is 1.2 kcal mol^{-1} which is almost identical to that determined at the same computational level for the 3,3′-dimethyl-2,2′-bithiophene.

Also, in this case the results provided by the B3LYP approach are significantly different from those obtained at the Hartree−Fock level with the same basis set, i.e., only one minimum at $\omega = 108.6°$,[9] and point out once again the need of including the correlation energy contributions. It is important to outline that the B3LYP results are in fairly good agreement with the experimental evidence. In particular, the decrease of the rotational distortion on passing from the 3,3′ to the 3,4′ isomer (ω varies from 58.1° to 38.6° for the syn-gauche conformer and from 112.6° to 148.2° for the anti-gauche conformer) explains very well the ipsochromic effect experimentally observed for dimethyl bithiophenes in liquid phase[13,14] and for the polymer which forms from 3,3′-dimethyl-2,2′-bithiophene[4] in solid phase.

We have schematically represented the syn-gauche conformer in Figure 2b and we have reported the values of the most important geometrical parameters for both conformers in Table 3. It is evident that the two rings are almost identical and a comparison with the data reported in Table 2 shows that the change of geometrical parameters is negligible on passing from the 3,3′ to the 3,4′ isomer. The only significant change is a shortening of the inter-ring distance *r* in the 3,4 isomer which is probably due to the increase of conjugation associated with the higher degree of coplanarity of the two rings.

Conclusion

In this paper we have discussed the torsional potential curves obtained at the MP2 and DFT (B3LYP and BLYP) levels for 3,3′-dimethyl-2,2′-bithiophene and at the DFT (B3LYP) level for 3,4′-dimethyl-2,2′-bithiophene. In both cases the results are significantly different from those previously found with the HF method which pointed out for both isomers the existence of only one conformational minimum where the two rings are in a nearly orthogonal orientation. Here, for the 3,3′ isomer all three computational levels indicate that the most stable conformational arrangement corresponds to a syn-gauche orientation of the two rings; the inter-ring dihedral angle ω has been found to be almost independent of the level of theory being 60.1°, 58.1°, and 57.4° at the MP2, B3LYP, and BLYP levels, respectively. This value is in good agreement with that found in the X-ray structures of tetra-methyl α-conjugated quaterthiophenes where the external hh junctions are characterized by a noncoplanar syn conformation with a dihedral angle ω of 54.2°.[17] Furthermore, the existence of a second anti-gauche minimum, which has been clearly located at the B3LYP level ($\omega = 112.6°$), agrees with the structural features of the inner hh junctions in tetra-methyl α-conjugated quaterthiophenes which can be either anti-planar[16] or anti-gauche.[17]

TABLE 3: Values of the Most Relevant Geometrical Parameters[a] Computed for the Syn and Anti Conformers of 3,4′-Dimethyl-2,2′-bithiophene at the DFT (B3LYP) Level with the 6-31G* Basis Set

	B3LYP		B3LYP
syn-gauche			
a	1.384	a′	1.376
b	1.432	b′	1.432
c	1.365	c′	1.370
d	1.731	d′	1.735
e	1.759	e′	1.759
f	1.506	*f*′	1.506
r	1.455	∠a′b′	114.4
∠ab	112.0	∠b′c′	111.6
∠bc	113.9	∠c′d′	112.5
∠cd	111.5	∠d′e′	91.6
∠de	91.7	∠a′r	128.9
∠ar	128.9	∠b′f′	123.8
∠af	125.3	ω	38.6
anti-gauche			
a	1.384	a′	1.377
b	1.432	b′	1.430
c	1.365	c′	1.370
d	1.731	d′	1.735
e	1.760	e′	1.758
f	1.508	*f*′	1.506
r	1.455	∠a′b′	114.5
∠ab	112.0	∠b′c′	111.6
∠bc	114.0	∠c′d′	112.4
∠cd	111.3	∠d′e′	91.7
∠de	91.8	∠a′r	127.8
∠ar	131.0	∠b′f′	123.8
∠af	125.7	ω	148.2

[a] Bond lengths are in Ångstrom and angles in degree.

The B3LYP torsional curve obtained for the 3,4′ isomer is characterized by two almost degenerate conformational minima corresponding to a syn-gauche ($\omega = 38.6°$) and to an anti-gauche ($\omega = 148.2°$) conformer. Also, this finding is significantly different from the description provided by the Hartree−Fock method, i.e., only one minimum at $\omega = 108.6°$, and better agrees with the conclusions reached by Distefano et al.[8] who invoked the existence of a syn-gauche and an anti-gauche conformer to explain the experimental trend of ionization energies along the series 2,2′-bithiophene, 4,4′, 3,4′, and 3,3′-dimethyl-2,2′-bithiophene. It is important to point out that the higher degree of coplanarity which has been found in the 3,4′ isomer with respect to the 3,3′ isomer explains the increase of conjugation pointed out by the ipsochromic effect found in 3,3′-dimethyl-2,2′-bithiophene when compared to 4,4′ and 3,4′-dimethyl-2,2′-bithiophene.

All of these results point out that, to obtain a reliable description of the conformational properties of oligo and polythiophenes, two requirements must be fulfilled: (a) the correlation energy effects must be taken into account in the computations; (b) the correlated method which is chosen must be able to provide a balanced description of these contributions. Our results and their comparison with the experimental evidence indicate that this task is better carried out by the DFT method (in particular the B3LYP functional which clearly shows the existence of a second anti-gauche minimum) than the MP2 method.

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(24) To further test the reliability of the DFT approach we have investigated at the B3LYP/6-31G* level the torsional potential curve for the nonalkylated system 2,2′-bithiophene. The curve is characterized by the presence of two minima at $\omega = 30°$ and 150°. These values agree very well with the experimental values of 36° and 148°.