Molecular Structure and Conformational Analysis of Some Alkylthio-Substituted Bithiophenes. Theoretical and Experimental Investigation

Nicolas DiCésare,[†] Michel Belletête,[†] François Raymond,[‡] Mario Leclerc,[‡] and Gilles Durocher*[,†]

Laboratoire de Photophysique Moléculaire and Laboratoire des Polymères Électroactifs et Photoactifs, Département de Chimie, Université de Montréal, C.P. 6128, Succ. A, Montréal, Québec, H3C 3J7, Canada

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The conformational analysis and molecular structure of 3,3′-dimethylthio-2,2′-bithiophene (DMS33BT), 3,4′-dimethylthio-2,2′-bithiophene (DMS34BT), and 3,4′-dimethylthio-3′,4-dimethyl-2,2′-bithiophene (DMSDM34BT) were investigated by ab initio calculations at the Hartree−Fock level (HF/STO-3G and HF/3-21G*) as well as by semiempirical calculations [Austin Model 1 (AM1) and Parametric Method 3 (PM3)]. Ab initio calculations (HF/3-21G*) indicated that the insertion of two alkylthio chains in the 3,3′ positions creates a sufficiently high steric hindrance to twist the molecule to a minimum conformation at 71.0° (and a second minimum at 120°), with an energy barrier of 2.3 kcal mol^{-1} compared with the coplanar trans (180°) conformation. For this molecule (DMS33BT), one can see an absorption band characteristic of a twisted molecule with a large range of conformations. The fluorescence spectrum demonstrates that the molecule adopts, in the first singlet excited state, a more planar conformation. The presence of only one alkylthio substituent in the 3-position (DMS34BT) decreases the steric hindrance such that a more planar conformation (141.5°, (HF/3-21G*)) is obtained, with a lower energy barrier of 0.5 kcal mol^{-1}. The insertion of an alkylthio and a methyl group in the 3,3′ positions (DMSDM34BT) creates the maximum steric hindrance and the more twisted molecule (102.2°), with the higher energy barrier compared with the planar conformation (5 kcal mol^{-1}). It is concluded from these results that the steric hindrance created by an alkylthio group is less than that of a methyl or an ethyl group in the same positions. It is also shown that the ab initio HF/STO-3G and the semiemperical AM1 and PM3 calculations are not sophisticated enough to predict good energy minimum conformers and potential energy surfaces for these kinds of molecules.

1. Introduction

Polythiophenes are frequently studied because of their high conductivity[1] in the doped state and also because of their interesting optical properties.[1,2] These properties make polythiophene a good candidate for electronic and optoelectronic composites.[3,4] To improve the solubility of polythiophene, new substituted polythiophenes with different lateral chains have been synthesized.[5−10] These substituted polythiophenes show new interesting optical properties, such as thermochromism and solvatochromism.[8−11] Variation in the optical properties of the different substituted polymers are related to the change of conformation of the backbone caused by the lateral chain. To have a good description of the conformation and of the effects of the position and nature of the substitution on the optical properties of polythiophene, theoretical and experimental studies of well-defined substituted oligothiophene models have been very useful. Recently, the conformations and spectroscopic properties of bithiophene (BT) and of some alkyl- and alkoxy-substituted bithiophenes have been studied.[12−16] Also, the potential energy surfaces of a series of substituted BTs have been used to obtain a theoretical understanding of the thermochromism observed in the parent polymers.[17] These results have successfully correlated the potential energy surface of the dimer with the thermochromism of many polymers and have allowed successful predictions for the 3,3′-dimethylthio-2,2′-bithiophene (DMS33BT) polymeric system.[18]

To date, the conformational analyses of BT[19,20] and some alkyl derivatives[21,22] have been well studied by ab initio calculations as well as by semiempirical calculations.[12,13,23] The potential energy surface of bithiophene is well defined by using ab initio HF/3-21G* and more elaborated basis sets. On the other hand, using the ab initio HF/STO-3G basis set and semiempirical calculations [Austin Model 1 (AM1) and Parametric Method 3 (PM3)], the potential energy surface is not defined with sufficient precision.[12,13] It is interesting to note that the semiempirical method AM1 predicts good conformers but with bad rotational energy barriers. From the most elaborate methods, two minima are obtained, one at 30° and the global minimum at 150°. Three maxima are found: one at 0°, a second at 90°, and one at 180°. The rotational energy barrier between 0° and 30° is ∼1.3 kcal mol^{-1}, the rotational barrier at 90° is ∼1.5 kcal mol^{-1}, and a low rotational barrier, 0.5 kcal mol^{-1}, is obtained between 150° and 180°. For BT and substituted BTs, two important forces determine the conformation and the rotational barrier of the molecule. One force is the electron delocalization throughout the molecule, which favors a more planar conformation, and the second force is the steric hindrance between the sulfur atom and the group of atoms in the 3-position, a hydrogen atom in the case of BT, which is responsible for the twisting of the molecule.

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* To whom correspondence should be addressed.

[†] Laboratoire de Photophysique Moléculaire.

[‡] Laboratoire des Polymères Electroactifs et Photoactifs.

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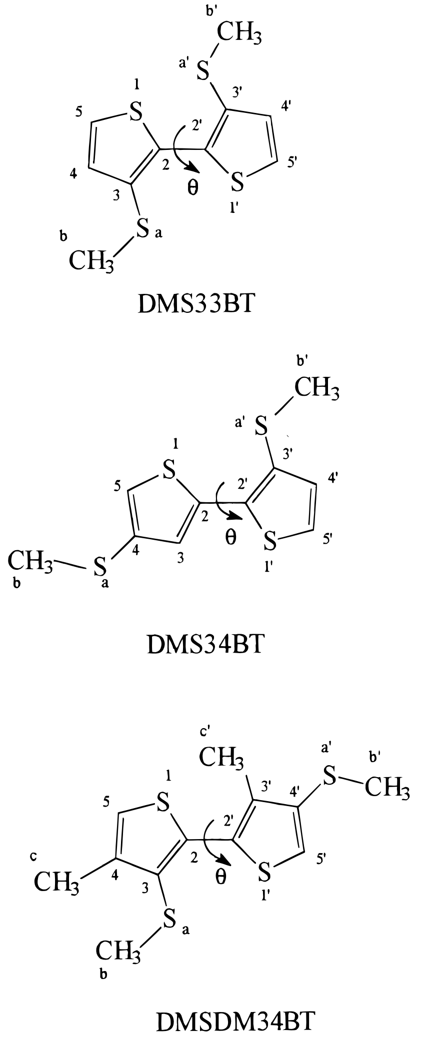

DMS33BT

DMS34BT

DMSDM34BT

Figure 1. Molecular structures of the substituted bithiophenes investigated.

For the first time, we propose in this paper a theoretical analysis of alkylthio substituents on BT. The effects of the nature and of the position of the substituent are discussed together with the potential energy surfaces and the geometry. It is shown that the insertion of two alkylthio lateral chains in the 3,3′-positions creates sufficiently high steric hindrance to induce a large twisting of the molecule. The presence of only one alkylthio lateral chain in the 3-position creates less steric hindrance and gives rise to a molecular structure much less twisted, near the conformation of BT. The presence of an alkylthio and a methyl group in the 3,3′-positions, on the other hand, creates the most important steric hindrance, with a concomitant high rotational energy barrier compared with the planar trans conformation. It is also shown that the basis set HF/STO-3G from ab initio calculations and the semiempirical AM1 and PM3 methods are not sophisticated enough in comparison with the ab initio HF/3-21G* basis set to make good predictions on the minimum energy conformers and on the potential energy surfaces. The molecular structures investigated are shown in Figure 1.

2. Methodology

2.1. *Ab initio* Calculations. The ab initio calculations were performed on a Silicon Graphics Challenge R4000 work station at the University of Montreal using the Gaussian 90 program.[24] The conformational analysis was done by changing the torsional angle θ by 30° steps. The geometries were optimized at the Hartree−Fock (HF) level with the STO-3G and 3-21G* basis sets. The Berny analytical gradient method was used for the optimizations. In the geometry optimization of the DMS33BT, a local C_2 symmetry restriction was applied between the two rings to reduce the calculation time, but no constraint was applied to the side groups. No constraint was applied on the other molecules. The requested HF convergence on the density matrix was 10^{-8}, and the threshold values for the maximum force and the maximum displacement were 0.00045 and 0.0018 au, respectively. To obtain the final torsional angles of the most stable conformers, calculations of these geometries were performed without constraint on the dihedral angle.

2.2. Semiempirical Calculations. Semiempirical calculations were performed using the HYPERCHEM package, release 4.5, for Windows from Hypercube, Inc., on a Pentium personal computer. This package has been used to draw the molecules and roughly optimize their geometry using the MM+ force field, which is an extension of MM2 developed by Allinger.[25] A more precise geometry optimization was obtained using the AM1 or PM3 semiempirical methods, including the sulfur atom parameter. AM1 is a modified MNDO method proposed and developed by M. J. S. Dewar and co-workers at the University of Texas at Austin.[26−29] For all derivatives, the dihedral angle (θ) between the two thiophene rings was varied in 15° increments from planar trans conformation ($\theta = 180°$) to the planar cis conformation ($\theta = 0°$). For each increment, θ was held fixed while the remainder of the molecule was optimized using AM1. A root-mean-square (rms) gradient in the energy of 0.1 kcal mol^{-1} was use for the optimization criterion.

2.3. Materials. Hexane was purchased from Aldrich Chemicals (99+%, anhydrous) and used as received. Prior to use, the solvent was checked for spurious emissions in the region of interest and found to be satisfactory. The synthesis of 3,3′-dibutylthio-2,2′-bithiophene (DBS33BT) will be described in a forthcoming publication.[18] All NMR and elemental analysis data were consistent with the expected structure.

2.4. Instrumentation. Absorption spectra were recorded on a Varian spectrometer model Cary 1 Bio using 1-cm path length quartz cells and a solute concentration of 2.18×10^{-5} M. It has been shown that the Beer−Lambert law applies for the concentration used. Fluorescence spectra corrected for the emission detection were recorded on a Spex Fluorolog-2 spectrophotometer with a F2T11 special configuration. The excitation and emission band-passes used were 2.6 and 1.9 nm, respectively. Each solution was excited near the absorption wavelength maximum using a 1-cm path length quartz cell, and the concentration used was 2.18×10^{-5} M, giving an absorbance near 0.1 to avoid any inner filter effects. A study was made of the effect of concentration (C) on the fluorescence intensity (I_F), and all measurements were made in the linear region of the I_F versus C curve.

3. Results and Discussion

We have used the HF/3-21G* method as the more elaborated calculation in this paper to have reasonable calculation times and because this basis set gives similar results in comparison with more elaborated basis sets. We used the results obtained with this basis set for comparison with the other methods. For BT, it was shown that a basis set without polarization functions is not good enough to predict good potential energy surfaces.[19,22] Methods and basis sets HF/3-21G*,[20,21] HF/6-31G*,[20,22] HF/6-31G**,[21]HF/ 6-311G**,[22] and MP2/6-31G*[20] give very similar potential energy surfaces with the same minima and similar

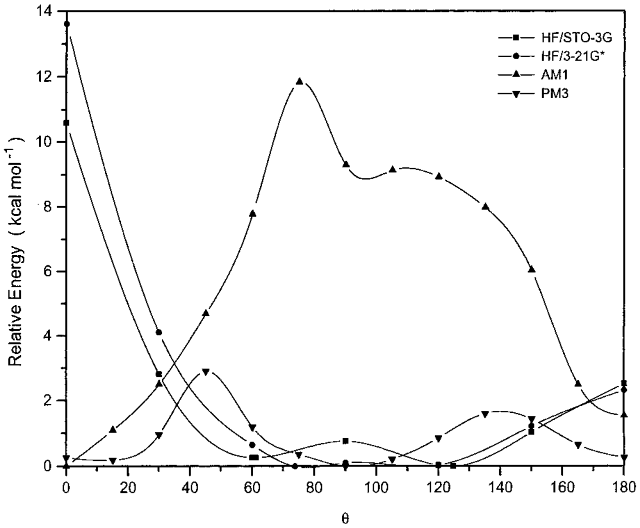

Figure 2. Potential energy surfaces for the ground state of DMS33BT.

potential energy barriers. For the alkyl-substituted bithiophenes in the 3,3′-positions,[21] it is also clear that the HF/3-21G* and the HF/6-31G** basis sets give identical potential energy surfaces with similar energy barriers and minima. From these results, the use of polarization functions seems essentials and the HF/3-21G* is the minimal basis set acceptable for the determination of potential energy surfaces. Moreover, results obtained with the basis set HF/3-21G* have been recently shown to give a very good correlation between the calculated conformation and the rotational energy barrier of substituted BTs and the experimental optical properties of the parent polymer.[17]

If one compares the structural parameters of BT with the basis sets HF/3-21G*,[21] HF/6-31G*,[20] HF/6-31G**,[21] and MP2/6-31G*,[20] very similar values are obtained. Indeed, we have compared the optimized geometries obtained from HF/3-21G*, HF/6-31G*, and MP2/6-31G* with experimental results from electronic diffraction.[30] Standard deviations (SDs) on the bond lengths (including carbon−hydrogen bond lengths) of 0.024 Å for HF/3-21G*, 0.024 Å for HF/6-31G*, and 0.022 Å for MP2/6-31G* are obtained. For the angles, SDs of 0.81° for HF/3-21G*, 1.04° for HF/6-31G*, and 1.10° for MP2/6-31G* are obtained. Now, if we compare the calculated planar *trans* conformations with the crystallographic results,[31] which show BT as planar, we obtain for bond lengths (excluding carbon−hydrogen bond lengths) SDs of 0.035 Å for HF/3-21G*, 0.037 Å for HF/6-31G*, and 0.027 Å for MP2/6-31G*. For the angles, we obtain SDs of 6.4° for HF/3-21G*, 6.5° for HF/6-31G*, and 6.5° for MP2/6-31G*. From these data, one can see that the MP2/6-31G* method seems to give better results on bond lengths but not necessarily on bond angles. The results obtained using the two other Hartree−Fock methods on bond lengths are very close to those obtained from MP2/6-31G*.

We have also confirmed that even the semiempirical methods (AM1 and PM3) give good structural parameters on BT such that any differences observed in the potential energy surfaces based on the dihedral angle from one calculation to the other cannot be ascribed or correlated to any structural parameter defects. In the following, the molecular structures as obtained from HF/3-21G* will be described and a comparison of the energy surfaces, based on the dihedral angle, calculated from various methods will be discussed.

3.1. 3,3′-Dimethylthio-2,2′-bithiophene (DMS33BT). The potential energy surfaces of DMS33BT calculated from various methods are represented in Figure 2. The rotational barrier and the minimum conformations calculated from HF/3-21G* are shown in Table 1. Very shallow minima are obtained at 71.0° and at 120°. The geometry at 120° was optimized without constraint on the dihedral angle and we obtained a relaxed conformation at 73.8°, which is very close to the 71.0° angle previously obtained. For this reason we can confirm that the minimum obtained at 71.0° in Figure 2 is the global minimum. The energy barrier between these two minima is very low, 0.11 kcal mol^{-1}. In comparison with *kT* at room temperature (298 K), 0.59 kcal mol^{-1}, one can expect that many conformers will coexist at room temperature in solution or in the gas phase. At 180°, we obtain a rotational barrier of 2.3 kcal mol^{-1}. This barrier corresponds to the steric hindrance existing between the methylthio side group and the sulfur atom of the thiophene ring. This rotational barrier is very similar to that obtained with one ethyl side group in the 3-position,[32] but is higher than the one obtained with one methyl group in the 3-position.[21,22] From these results, one can see that the presence of two methylthio groups creates the same steric hindrance as one ethyl side group. In other words, the steric hindrance of one methylthio group is less than that of one ethyl side group as will be shown later for 3,4′-dimethylthio-2,2′-bithiophene (DMS34BT). For the coplanar syn conformation ($\theta = 0°$), one obtains a high rotational barrier of 13.6 kcal mol^{-1} because of the steric hindrance caused by the presence of two lateral chains very close each other. This rotational barrier is smaller than that found for the 3,3′-diethyl derivative,[32] showing that two methylthio groups on the same side of the molecule create less steric hindrance than two ethyl groups at the same positions.

TABLE 1: Relative Energy (in kcal mol^{-1}) and Torsional Angle (θ) Obtained by the 3-21G* Basis Set

molecule	syn[a]	syn-gauche	perpendicular	anti-gauche	anti[a]
DMS33BT	13.6	0.0 (71.0°)	0.11	0.031 (120°)	2.3
DMS34BT	2.1	0.049 (50.0°)	0.86	0.0 (141.5°)	0.31
DMSDM34BT	15.0	−	0.0 (102.3°)	−	4.5

[a] Syn, $\theta = 0°$; anti, $\theta = 180°$.

Using the basis set HF/STO-3G, one obtains a potential energy surface very similar to that calculated from HF/3-21G*. This basis set predicts two minima, at 61.1° and 124.8°. The barrier at 90° is higher but the rotational barrier at 0° is lower. The barrier at 180° is also similar with that calculated from HF/3-21G*. For this molecule, one can see that HF/STO-3G is quite good though it cannot reproduce the fine details of the more elaborate basis set and it gives always a higher rotational barrier at 90° and a lower barrier for the syn conformation. The same behavior has been found for BT[33,34] and alkyl derivatives.[32] As for the semiempirical AM1 calculations, the potential energy surface obtained is not at all realistic. The minimum obtained is for the coplanar syn conformation where there is the larger steric hindrance. For PM3, the surface looks better. We obtain the global minimum at 90° but the energy falls off for the planar conformations, syn and anti, which is not realistic either. It is surprising that the results obtained by these two semiempirical methods are so different because they were much more similar when applied to BT. These results were rather similar to the ab initio results,[23,35] except that the rotational barriers were largely underestimated compared with that obtained at the ab initio level.

The molecular structure parameters of the lowest energy conformer of DMS33BT using the four theoretical methods already described are listed in Table 2. A restricted C_2 symmetry between the two thiophene rings has been applied

TABLE 2: Optimized Geometry for the Lowest Energy Conformer of DMS33BT

parameter[a]	HF/3-21G*	HF/STO-3G	AM1	PM3
C2−C2′	1.4651	1.4901	1.4191	1.4456
S1−C2	1.7321	1.7477	1.6971	1.7464
C2−C3	1.3546	1.3493	1.3945	1.3803
C3−C4	1.4399	1.4603	1.4375	1.4415
C4−C5	1.3450	1.3325	1.3716	1.3628
C5−S1	1.7195	1.7276	1.6671	1.7173
C4−H4	1.0683	1.0802	1.0931	1.0964
C5−H5	1.0673	1.0793	1.0892	1.0893
C3−Sa	1.7661	1.7733	1.6730	1.7462
Sa−Cb	1.8232	1.8028	1.7519	1.8062
C2′−C2−C3	120.553	128.080	129.021	126.710
S1−C2−C3	111.376	112.076	110.496	111.605
C2−C3−C4	112.278	111.631	111.135	111.530
C3−C4−C5	112.832	112.762	112.400	112.958
C4−C5−S1	111.871	112.779	111.725	1112.464
C5−S1−C2	91.641	90.749	94.159	91.441
C3−C4−H4	122.588	122.889	122.422	121.691
C4−C5−H5	127.084	126.706	125.604	125.346
C2−C3−Sa	124.900	124.677	124.730	124.503
C3−Sa−Cb	98.948	99.019	106.393	103.597
C2−C3−Sa−Cb	94.202	126.189	153.228	164.870
S1−C2−C2′−S1′	71.044	124.773	0.000	90.000

[a] Distance in angstroms, and angle and dihedral angle in degrees.

such that only parameters of one thiophene ring and one side group is shown. From the results in Table 2 we can see that few parameters are quite different from one method to another. The bond length between the two thiophene rings, C2−C2′, is much higher for ab initio methods than for semiempirical methods. The double bonds in the thiophene ring, C2−C3 and C4−C5, are predicted to be smaller by the ab initio calculations in comparison with the semiemperical methods. This result shows the difference in the electronic distribution taken care of by the ab initio and semiemperical methods. The bond lengths between the sulfur atom and carbons in the ring, S1−C2 and C5−S1, are much smaller for the AM1 method compared with other methods, which is the reason the potential energy barrier calculated by ab initio methods are higher than those obtained by semiempirical methods for the planar conformation (180°). These small bond lengths explain the favored planar conformation calculated by AM1 because of the more compact ring giving rise to less steric hindrance between the sulfur atom and the group in the adjacent thiophene ring. Another difference is the bond length of the carbon and the sulfur of the side group, C3−Sa, which is larger for the ab initio methods compared with semiemperical methods. It is also noteworthy that the side group is perpendicular to the thiophene ring (C2−C3−Sa−Cb = 94.202°) for HF/3-21G*, which decreases the resonance of the nonbonding electron lone-pair on the sulfur atom with the aromatic ring.

The absorption and fluorescence spectra of BT, DBS33BT, and decyl- and butoxy-substituted bithiophenes in the 3,3′-positions are shown in Figure 3 and the spectroscopic parameters for these molecules are reproduced in Table 3. The absorption spectrum of BT has already been discussed.[13] The first absorption band is well explained by using a twisted angle of 150° with a certain distribution of conformers. The absorption spectrum of 3,3′-dibutoxy-2,2′-bithiophene (DBO33BT) is characteristic of a planar conformation.[36] On the other hand, the absorption spectrum of 3,3′-didecyl-2,2′-bithiophene (DD33BT) is characteristic of a twisted conformation of ∼100°, as shown recently.[12] Figure 3A shows that the absorption band maximum of DBS33BT is not far from that of DD33BT, and in both cases the absorbtivity coefficient is less than that of BT and DBO33BT. This result clearly shows that DBS33BT is on the average much more twisted than BT or DBO33BT but probably a little less twisted than DD33BT. Indeed, the minimum obtained by HF/3-21G*, 120° (or 71.0°), is between the minima of BT (150°)[20] and DE33BT (101.5°),[32] which shows the good evaluation of the minimum energy conformer by using the HF/3-21G* basis set.

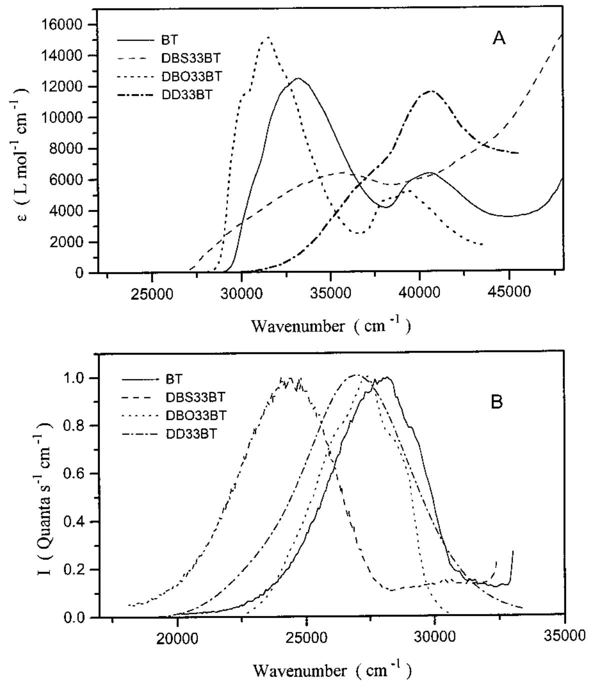

Figure 3. (**A**) Absorption and (**B**) normalized fluorescence spectra of BT (2,2′-bithiophene), DBS33BT (3,3′-dibutylthio-2,2′-bithiophene), DBO33BT (3,3′-dibutoxy-2,2′-bithiophene) and DD33BT (3,3′-didecyl-2,2′-bithiophene) all taken from ref 12. All spectra were measured in *n*-hexane at room temperature.

We can see that the absorption band of DBS33BT is spread over a large wavelength region. The part of the band in the region of lower energy shows the presence of more planar conformers. The absorption band of DBS33BT extends to the red of that of DBO33BT in the region of 27 500 cm^{-1}, this suggesting that the methylthio group has better electron donor properties compared with the butoxy group. This result is in agreement with the spectral data observed on substituted

TABLE 3: Spectroscopic Parameters of Bithiophene and Bithiophene Derivatives in *n*-Hexane at Room Temperature (298 K)

molecule	λ_{Abs}[a] (nm)	$\bar{\nu}_{Abs}$[a] (cm^{-1})	ϵ (M^{-1} cm^{-1})	FWHM$_{Abs}$[b] (cm^{-1})	λ_F[a] (nm)	$\bar{\nu}_F$[a] (cm^{-1})	fwhm$_F$[b] (cm^{-1})	Δ[c] (cm^{-1})
BT	300	33300	12490	5560	355	28100	4310	5200
DBS33BT	280	35700	7530	-	410	24400	4470	11300
O3BT[d]	293	34100	-	5870	366	27300	4550	6800
DBO33BT[e]	317	31500	15000	4440	370	27000	4000	4500
DD33BT[f]	280	35700	4380	-	374	26700	5050	9000

[a] Taken at the maximum of the band. [b] Full-width at half-maximum. [c] Stokes shift between absorption ($\bar{\nu}_A$) and fluorescence ($\bar{\nu}_F$) bands. [d] 3-Octyl-2,2′-bithiophene, ref 14. [e] 3,3′-Dibutoxy-2,2′-bithiophene, ref 12. [f] 3,3′-Didecyl-2,2′-bithiophene, ref 12.

thiophenes. Indeed the maximum of the absorption band of thiophene is at 231 nm,[37] that of 3-methoxythiophene is at 255 nm,[37] and that of the 3-methylthiothiophene is at 270 nm.[38] The same behavior has been observed on the 4,4′-substituted-2,2′-bithiophenes.[12,39,40] It is worth mentioning that ZINDO/S calculations performed on HF/3-21G*-optimized geometries of DMO33BT and DMS33BT do not predict the methythio substituent as a better electron donor group. Indeed, the calculated energies of the first electronic transition of each compound are very similar.

DBS33BT possesses a very particular absorption spectrum that allows for many possible conformers at room temperature because the rotational energy barrier is quite low (see Figure 2 and Table 1). We have already mentioned that the minima of the potential energy surfaces of DMS33BT and of the ethyl substituents in the 3,4′-positions are in the same position and that the surfaces between 90° and 180° are very similar. In agreement with these results, it is observed that the absorption spectra of DBS33BT and 3-octyl-2,2′-bithiophene (O3BT)[14] (parameters are reported in Table 3) are much blue-shifted in comparison with the BT absorption spectrum. These spectra are also very wide, which is a characteristic of twisted molecules with a large distribution of conformers. However, it is worth pointing out that the first absorption band of DBS33BT shows a larger blue-shift, is less intense, and is spread over a larger region compared with that of O3BT.

The fluorescence spectrum of DBS33BT shows a large red-shift in comparison with the absorption band (the Stokes shift is 11 300 cm^{-1}) and a decrease of the bandwidth. For the BT derivatives, it is well-known that, in the first excited singlet state, the planar conformation is favored.[12] The spectral data reported here lead us to the same conclusion for this molecule. However, the fluorescence band of DBS33BT is much red-shifted in comparison with that of alkyl- and alkoxy-substituted BTs (see Table 3). This result is in agreement with the assumption already mentioned that the methythio substituent is a better electron donor group than alkyl and alkoxy substitutents. But another contribution to the red shift observed may also involve conformational changes of the methythio group in the excited state. Indeed in the ground state, ab initio calculations performed at the HF/3-21G* level predict that this side group is perpendicular to the molecular frame (see Table 2). Thus, it is quite possible that in the first relaxed singlet excited state, the methylthio group reaches a more coplanar conformation, which should induce a better electronic delocalization along the molecular frame.

3.2. 3,4′-Dimethylthio-2,2′-bithiophene (DMS34BT). The potential energy surface of DMS34BT is presented in Figure 4. From the basis set HF/3-21G*, two minima are obtained: one minimum at 50° and the global minimum at 141.5°. Three maxima are also obtained, at 0°, 90°, and 180°. The rotational barrier for these maxima are listed in Table 1. For this molecule, the steric hindrance created by only one alkylthio group is smaller and one obtains a more planar conformation in comparison with the 3,3′-substituted compound. If one compares the potential energy surfaces of DMS34BT and BT,[19,20] it is seen that these two surfaces are quite similar. The minimum energy conformations of each molecule are close; for BT there are two minima, one at 44.7° and the global minimum at 146.3°. The energy barriers are also very similar, for BT, the barrier at 180° is 0.39 kcal mol^{-1} in comparison with 0.31 kcal mol^{-1} for DMS34BT: at 90°, the barrier for BT is 1.49 kcal mol^{-1} compared with 0.860 kcal mol^{-1} for DMS34BT; and at 0°, the barrier for BT is 1.72 kcal mol^{-1} in comparison with 2.1 kcal mol^{-1} for DMS34BT. These similarities does not mean that the steric hindrance caused by an alkylthio group is similar to that of a hydrogen atom in the unsubstituted BT. It is more plausible that the more planar conformation obtained for DMS34BT is due to the donor effect of the alkylthio group that improves the delocalization over the molecular frame, which favors the planar conformation. The delocalization effect of a donor group in position 3 has also been clearly demonstrated with the results on the alkoxy substituted BTs.[36] The maximum of the absorption band of DMS34BT is at 331 nm,[39,40] which is at the same position as the 4,4′-methylthio-2,2′-bithiophene (327 nm).[39,40] The absorption spectra of these two compounds are very similar,[38] except for the second transition, at 265 nm, where the intensity in comparison with the intensity of the first transition is higher for the 4,4′-substituted derivative. As already mentioned, the substitution in the 4,4′-positions does not influence the conformation[12] and a minimum conformation at 150° is expected for the 4,4′-derivative with a similar potential energy surface as that of BT. The fact that the 3,4′-derivative possesses a similar spectrum suggests that the conformation and the distribution of conformers in solution are rather identical as those of the 4,4′-substituted derivative and also nearly identical as those of BT.

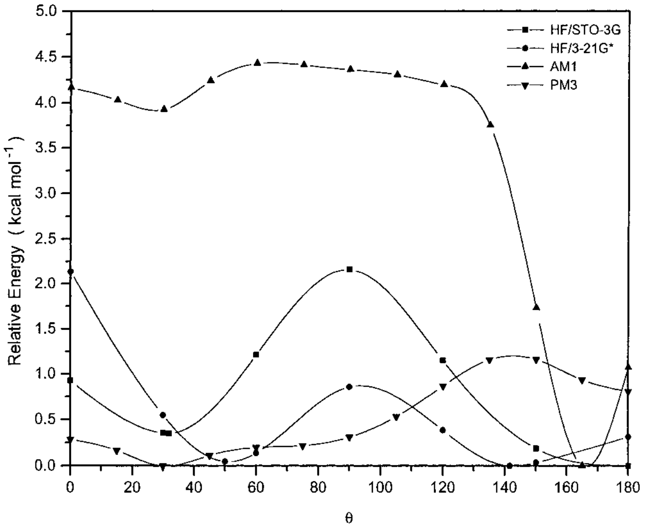

Figure 4. Potential energy surfaces for the ground state of DMS34BT.

The ab initio HF/STO-3G basis set gives a similar potential energy surface but the two minima are moved in the direction of the more planar conformations. This shift of the minima is also observed in the case of BT where the two minima are at 180° and 0°. We have observed that the HF/STO-3G basis set favored the planar conformations for many molecules,[32,36] except for the molecules with very high steric hindrance. This result is because of the inability of this basis set to explain the fine details in the conformational analysis of the thiophene oligomers. The rotational barrier at 90° is also often larger than the energy barrier obtained by HF/3-21G*. It seems that the HF/STO-3G basis set put too much emphasis on the delocalization rather than on the nonbonded interactions, in other words, HF/STO-3G underestimates the steric hindrance and/or overestimates the electronic delocalization. Finally, for this molecule, AM1 calculations fell again. The minimum obtained, 175°, is close to one of the minima obtained by the ab initio methods but the other part of the surface makes no sense. The potential energy surface obtained by PM3 calculations gives a preference for the syn conformer. We obtained the global minimum at 30° and a little minimum at 180°. This preference of the syn

TABLE 4: Optimized Geometry for the Lowest Energy Conformer of DMS34BT

parameter[a]	HF/3-21G*	HF/STO-3G	AM1	PM3
C2−C2′	1.4625	1.4842	1.4232	1.4407
S1−C2	1.7380	1.7459	1.6947	1.7472
C2−C3	1.3545	1.3465	1.3840	1.3739
C3−C4	1.4343	1.4554	1.4304	1.4374
C4−C5	1.3510	1.3391	1.3872	1.3728
C5−S1	1.7129	1.7295	1.6562	1.7166
C3−H3	1.0691	1.0797	1.0923	1.0977
C5−H5	1.0675	1.0793	1.0904	1.0910
C4−Sa	1.7652	1.7732	1.6797	1.7429
Sa−Cb	1.8232	1.8027	1.7491	1.8029
C2′−C2−C3	125.697	125.481	129.545	125.488
S1−C2−C3	110.736	111.099	111.085	111.116
C2−C3−C4	113.354	113.657	111.727	112.881
C3−C4−C5	111.771	110.918	111.083	111.740
C4−C5−S1	112.613	113.560	112.559	112.812
C5−S1−C2	91.523	90.765	93.547	91.449
C2−C3−H3	123.770	123.681	124.973	123.915
C4−C5−H5	126.120	126.464	123.901	125.380
C3−C4−Sa	123.977	124.739	127.443	126.525
C4−Sa−Cb	99.620	98.981	104.996	104.678
C3−C4−Sa−Cb	277.582	58.161	−6.874	−1.660
S1′−C2′	1.7342	1.7494	1.6692	1.7485
C2′−C3′	1.3600	1.3536	1.4007	1.3846
C3′−C4′	1.4388	1.4599	1.4258	1.4409
C4′−C5′	1.3446	1.3319	1.3778	1.3631
C5′−S1′	1.7182	1.7266	1.6688	1.7142
C4′−H4′	1.0682	1.0804	1.0924	1.0923
C5′−H5′	1.0672	1.0791	1.0889	1.0896
C3′−Sa′	1.7675	1.7734	1.6857	1.7470
Sa′−Cb′	1.8221	1.8031	1.7567	1.8030
C2−C2′−C3′	130.407	130.564	121.384	127.635
S1′−C2′−C3′	110.862	111.756	110.933	111.328
C2′-C3′−C4′	112.452	111.589	111.526	111.532
C3′−C4′−C5′	112.972	113.070	111.416	113.048
C4′−C5′−S1′	111.732	112.547	112.016	112.469
C5′−S1′−C2′	91.978	91.037	94.092	91.618
C3′−C4′−H4′	122.359	122.553	123.208	122.753
C4′−C5′−H5′	127.177	126.581	125.379	125.329
C2′−C3′−Sa′	126.052	126.581	118.321	124.394
C3′−Sa′−Cb′	99.753	98.670	104.519	105.121
C2′−C3′−Sa′−Cb′	281.682	239.557	131.890	174.164
S1−C2−C2′−S1′	141.534	180.000	165.000	30.000

[a] Distances in angstroms, and angle and dihedral angle in degrees.

conformation for PM3 calculations has also been found for BT[23,34] and the reasons have been discussed.[35]

The optimized geometries of the lowest energy conformers for each theoretical method are presented in Table 4. The geometric parameters of DMS34BT and of DMS33BT, for the HF/3-21G* basis set, are very similar without any important difference except for the angles between the two cycles, C2′−C2−C3 and C2−C2′−C3′, which are larger for the latter compound. For the asymmetric DMS34BT, some structural parameters of each thiophene ring differ. The bond length C2−C3 is smaller than the bond length C2′−C3′ and the bond C4−C5 is larger than the bond C4′−C5′. The angles C2′−C2−C3 and C2−C2′−C3′ are also different. These differences show clearly the effect of the steric hindrance caused by the alkylthio group in position 3 and the possibility of the asymmetric molecule to adopt a conformation that will favor a more planar conformation with a lower rotational barrier. Again for this molecule, the position of the two alkylthio groups is perpendicular to the plane of the thiophene ring. As for the difference between the methods, again, the bond length between the two cycles, C2−C2′, is smaller for the semiemperical methods. As for the other geometric parameters, the same effects observed for the DMS33BT can also be observed here.

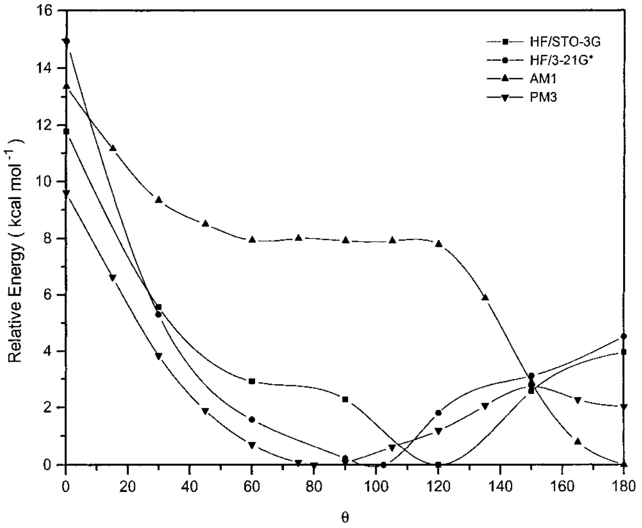

Figure 5. Potential energy surfaces for the ground state of DMSDM34BT.

3.3. 3′,4-Dimethyl-3′,4-dimethylthio-2,2′-bithiophene (DMSDM34BT).

The potential energy surface of DMSDM34BT is shown in Figure 5, which shows one minimum at 102.3°, a rotational barrier of 4.5 kcal mol^{-1} at 180°, and a barrier of 15.0 kcal mol^{-1} at 0°. The minimum obtained for this molecule is approximately at the same position as that observed for the 3,4′-dimethyl-2,2′-bithiophene[21] and the 3,4′-diethyl-2,2′-bithiophene.[32] But, the rotational barriers for both planar conformations are higher for the DMSDM34BT than for the diethyl substituents in the 3,4-positions. From these results, it is clear that the methyl group in the 3-position in DMSDM34BT creates a more important steric hindrance and is responsible for the twisted conformation. The presence of the alkylthio group in the 3-position does not play an important role in the determination of the conformation of the molecule, as seen for DMS34BT, which presents a similar potential energy surface as BT but plays a more important role in the rotational barrier as indicated by the comparison of the potential energy surface of DMSDM34BT and DM34BT.[21] At 0°, the presence of the two substituents face to face creates the maximum steric hindrance and is responsible of the high rotational barrier. This rotational barrier is grossly identical to that observed for the 3,3′-dimethyl- and 3,3′-diethyl-2,2′-bithiophene.[21,32] The rotational barrier at 180° is higher for DMSDM34BT because there are two substituents in the 3-position such that the molecule cannot relax like the asymmetric one (DMS34BT). Rather, this barrier at 180° for DMSDM34BT is of the same order as those of the methyl and ethyl substituents in the 3,3′-positions.

The potential energy surface for the ab initio HF/STO-3G basis set is relatively similar to that obtained by HF/3-21G*. The important difference is that HF/STO-3G gives a more planar conformation, at 120°, but the rotational barriers at 180° are predicted to be very similar by both methods. For this molecule, AM1 fell again for the prediction of the minimum conformation and the potential energy surface. Calculations on BT[13,23] and on alkyl-substituted BT[12,23] by AM1 were good enough for the prediction of the minimum conformations and for the determination of rotational barriers but not for this molecule containing these kinds of lateral chains. PM3 can reproduce quite well the potential energy surface except for the planar trans conformation, where one observes a shallow minimum.

The structural parameters for the lowest energy conformations are listed in Table 5. The angle C2′−C2−C3 is greater for DMSDM34BT than for DMS33BT. This difference can be

TABLE 5: Optimized Geometry for the Lowest Energy Conformer of DMSDM34BT

parameter[a]	HF/ 3-21G*	HF/ STO-3G	AM1	PM3
C2−C2′	1.4690	1.4916	1.4228	1.4471
S1−C2	1.7282	1.7455	1.6687	1.7422
C2−C3	1.3560	1.3481	1.4014	1.3800
C3−C4	1.4491	1.4685	1.4317	1.4486
C4−C5	1.3465	1.3350	1.3821	1.3685
C5−S1	1.7199	1.7294	1.6644	1.7148
C5−H5	1.0679	1.0787	1.0889	1.0901
C3−Sa	1.7677	1.7764	1.6866	1.7567
Sa−Cb	1.8220	1.8039	1.7579	1.8063
C4−Cc	1.5066	1.5212	1.4702	1.4776
C2′−C2−C3	128.2855	127.9203	121.892	126.857
S1−C2−C3	111.3327	112.1434	111.050	111.986
C2−C3−C4	112.8293	112.0361	111.490	111.448
C3−C4−C5	111.5692	111.8284	111.000	112.348
C4−C5−S1	112.7497	113.3559	112.320	112.839
C5−S1−C2	91.5183	90.636	94.137	91.369
C4−C5−H5	126.3493	126.3777	124.860	125.042
C3−C4−Cc	123.5613	122.9839	124.115	124.128
C2−C3−Sa	124.0156	125.4768	118.421	124.187
C3−Sa−Cb	99.5918	98.4176	105.116	102.571
C2−C3−Sa−Cb	271.074	280.3823	122.256	−119.555
S1′−C2′	1.7352	1.7446	1.6940	1.7423
C2′−C3′	1.3525	1.3456	1.3884	1.3770
C3′−C4′	1.4485	1.4692	1.4391	1.4490
C4′−C5′	1.3499	1.3363	1.3833	1.3715
C5′−S1′	1.7095	1.7315	1.6568	1.7132
C5′−H5′	1.0675	1.0767	1.0900	1.0912
C3′−Cc′	1.5068	1.5216	1.4693	1.4775
C4′−Sa′	1.7661	1.7678	1.6808	1.7450
Sa′−Cb′	1.8233	1.7976	1.7496	1.8026
C2−C2′−C3′	127.6814	127.9203	129.709	125.541
S1′−C2′−C3′	112.0189	112.1735	111.270	111.958
C2′−C3′−C4′	111.6715	112.1856	111.149	111.881
C3′−C4′−C5′	112.4781	111.7155	111.359	111.698
C4′−C5′−S1′	112.4925	113.2825	112.564	113.251
C5′−S1′−C2′	91.3365	90.6428	93.657	91.212
C4′−C5′−H5′	125.8725	127.3743	124.177	125.384
C2′−C3′−Cc′	125.3772	126.0658	125.971	124.898
C3′−C4′−Sa′	124.4237	119.1487	119.715	120.835
C4′−Sa′−Cb′	99.9307	100.616	104.297	104.185
C3′−C4′−Sa′−Cb′	273.2314	180.4771	−176.289	176.360
S1−C2−C2′−S1′	102.292	120.9197	180.000	80.000

[a] Distances in angstroms, and angle and dihedral angle in degrees.

correlated with the higher steric hindrance caused by the presence of the methyl group in the 3-position, which forces the two rings to adopt this conformation to reduce the steric hindrance. When we compare the structural parameters of DMSDM34BT with those of DMS34BT, we see that the structural parameters of the two rings for the former are very similar, which is in contrast with the asymmetric DMS34BT. As observed in the other molecules, the bond length C2−C2′ obtained by HF/STO-3G is the largest and it is the smallest from AM1. All the methods give a twisted conformation for the alkylthio group in the 3-position, but HF/STO-3G and the semiempirical methods suggest a planar conformation for the alkylthio group in the 4′-position.

4. Concluding Remarks

The results reported here show that insertion of two alkylthio substituents in positions 3,3′ creates a sufficiently important steric hindrance to twist the molecule. The potential energy surface of this molecule is very similar to those obtained for the 3,4′-dimethyl- and 3,4′-diethyl-2,2′-BTs. The low rotational energy barrier allows for the presence of many conformations, which is responsible for the wide, diffuse, and unstructured absorption spectrum observed. The electron donor property of the alkylthio group is important, so the fluorescence is red-shifted in comparison with that of the alkyl- and alkoxy-substituted BTs. The blue-shift of the absorption band caused by the twisted conformations and the red-shift of the fluorescence band caused by the electron donor properties of a more planar conformer are responsible for the very large Stokes shift observed that characterizes the spectral properties of this 3,3′-substituted derivative. The presence of only one alkylthio lateral chain does not create such a large steric hindrance and gives rise to a potential energy surface that is very similar to that of BT. The presence of the methyl group in the DMSDM34BT is responsible for the twisted conformation obtained for this molecule, but the presence of the alkylthio group in the 3-position creates a sufficiently high steric hindrance to give a high rotational barrier for the planar trans conformation. The semiemperical AM1 method fails in the determination of the minimum energy conformer and potential surfaces of these kinds of substituted molecules. On the other hand, HF/STO-3G and the semiemperical PM3 method give better results. Among the theoretical methods investigated in this paper, however, the ab initio HF/3-21G* method is the only one capable of explaining the fine details of the energy surfaces necessary to make good correlations with experiments.

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