Conformational and Spectroscopic Analysis of Selected 2,2′-Bithiophene Derivatives

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Received: July 8, 1996; In Final Form: October 11, 1996⊗

A spectroscopic study has been performed on selected substituted 2,2′-bithiophenes. Absorption and fluorescence spectra of bithiophenes (BT) substituted with alkyl and alkoxy groups in positions 4,4′ and 3,3′ have been measured in solvents of various polarity and viscosity. AM1 and ZINDO/S semiempirical calculations have also been performed on all molecules in order to evaluate the torsional potential energy surfaces and the singlet−singlet transition energies. It is found by a combined theoretical and experimental technique in which 3,3′-derivatives are more twisted than their 4,4′-analogs in the ground state. After excitation, molecules relax to much more planar S_1 excited states. The sole exceptions are 3,3′-alkoxybithiophene derivatives which seem to remain in the same conformation in their respective relaxed S_1 excited state. For molecules in their T_1 excited states, planar and perpendicular conformations are the most stable. It is also observed that fluorescence quantum yields of all bithiophene derivatives are weak but weaker for 3,3′-substituted compounds. Results are interpreted in terms of a possible substitutional effect on the intersystem crossing process involved in these systems.

1. Introduction

The preparation of soluble conjugated polythiophenes can be done by the incorporation of relatively long and flexible side chains.[1] This approach is based upon a decrease in attractive interchain interactions and the introduction of favorable interactions between the substituents and the solvent. But, the introduction of substituents may have a strong influence on the electronic structure of the resulting material and, consequently, on its optical properties. For instance, some substituted polythiophenes exhibit intriguing thermochromic (in the solid state and in solution) properties.[2−5] These unusual optical effects are believed to be related to a reversible "transition" between a coplanar (highly conjugated) and a nonplanar (less conjugated) conformation of the conjugated main chain.[6,7] Other studies have revealed the strong dependence of the thermochromic properties upon the position and the nature of the substituents.[8−10] Several explanations of the driving force of these optical phenomena have been proposed (crystallization, aggregation, thermally induced steric interactions, etc.), but a detailed description of the structural parameters involved in these optical effects is still lacking.

Knowledge of the structure−property relationships in substituted polythiophenes is still rudimentary.[1] The polymers are complex materials exhibiting a broad and not fully characterized range of conjugation lengths and a distribution of molecular environments and excitonic effects that makes difficult the measurement of vibrationally resolved optical spectra and simple fluorescence decay kinetics. For this reason, we think it is important to focus our attention on the most easily studied oligothiophenes, *i.e.*, substituted bithiophenes. A thorough understanding of the optical properties of these molecules upon the nature and the position of the substituents should provide the basis for determining such structural properties as conformation and conjugation length in the more complex polythiophenes.

Recently, gas phase electron diffraction performed at 97−98 °C on the unsubstituted bithiophene molecule (BT) has shown the existence of two conformations, *anti*-like and *syn*-like, with torsional angles of 148 and 36° and conformational weights of 56 and 44%, respectively.[11] These results are in very good agreement with the most recent *ab initio* calculations performed with large basis sets.[12−16] We have recently applied semiempirical quantum-chemical calculation methods (AM1, PM3, and ZINDO/S) to study the ground and excited state conformations of BT as well as other oligothiophenes.[17−19] It was found that the PM3 method does not reproduce accurately the torsional potential of BT. On the contrary, AM1 calculations reproduce minima and maxima at angles similar to those obtained using *ab initio* calculations and in agreement with most stable conformers of BT measured in the vapor phase. The torsional potential curve is flat such that multiple conformations may coexist in the gas phase and in solution. ZINDO/S calculations performed on AM1 optimized conformers predict a fully planar *anti* conformation for BT but give a torsional barrier between thiophene rings close to the experimental values (5 ± 2 kcal mol^{-1}).[20,21] Moreover, these calculations suggest that, after excitation, all molecules relax to nearly planar excited singlet electronic states.[18,19] ZINDO/S also predicts that the most stable conformations of BT in its first excited triplet state are planar ($\phi = 0$ and 180°), but a local minimum is also predicted for the perpendicular conformation.

The conformation of many alkyl-substituted thiophene oligomers has been studied theoretically.[13,14,16,22−24] Results indicate that 4,4′-dialkylbithiophenes behave similarly to the unsubstituted compound. On the contrary, due to strong repulsive interactions 3,3′-dialkylbithiophenes give conformers with high torsional angles between thiophene rings. These results are conformed with the absorption spectra of these molecules.[24]

The fluorescence quantum yield of BT is very small.[25,26] It has been observed that the intersystem crossing is the major mode of relaxation of the first excited singlet state which is favored by the presence of two heavy atoms.[26] From the first excited triplet state, the system returns to the ground state via intersystem crossing such that no phosphorescence is observed. To our knowledge, the photophysics of substituted bithiophenes is still unknown.

To shed more light on the conformational changes involved

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⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1997.

S1089-5639(96)01997-4 CCC: $14.00

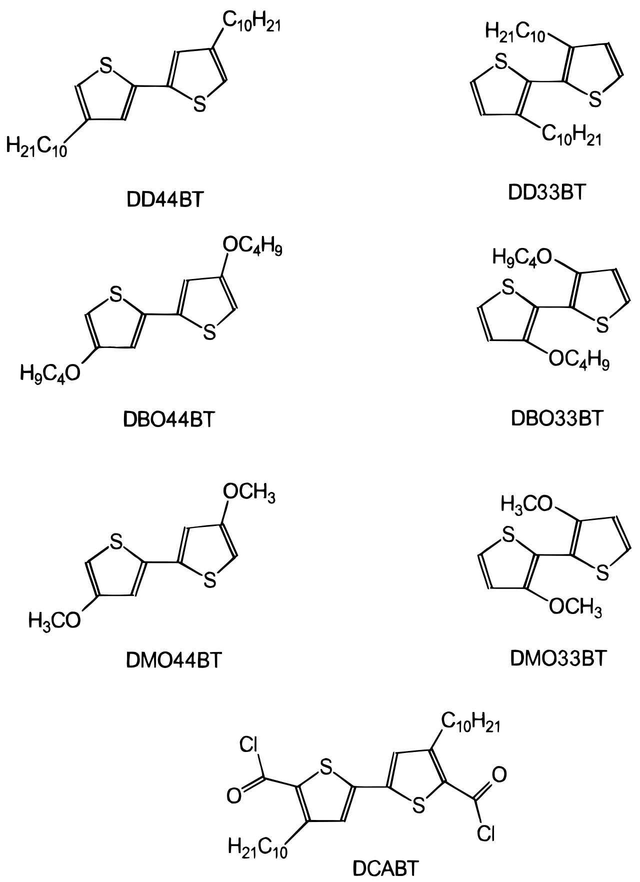

Figure 1. Molecular structures of the substituted bithiophenes investigated.

in substituted polythiophenes, optical and photophysical properties of bithiophenes having alkyl or alkoxy groups in the 3,3′ or 4,4′ positions have been investigated. 4,4′-Didecyl-2,2′-bithiophene-5,5′-dicarbonyl dichloride (DCABT) has also been investigated. In these simple systems, irregular effects caused by the polymer are eliminated such that absorption and fluorescence bandwidths are smaller and more structured. The study of small oligomers allows also for the use of semiempirical calculations for the interpretation of experimental results. The main objective here in this work is to describe the substituent effect (nature and position) on the molecular conformation and electronic properties of these thiophene dimers. The bithiophenes have been divided in two groups: 4,4′- and 3,3′-substituted molecules. The molecules investigated are shown in Figure 1.

2. Experimental Section

2.1. Materials. All solvents were purchased from Aldrich Chemicals (99+%, anhydrous) and used as received. Prior to use, the solvents were checked for spurious emission in the region of interest and found to be satisfactory. 4,4′-Didecyl-2,2′-bithiophene (DD44BT),[27] 4,4′-didecyl-2,2′-bithiophene-5,5′-dicarbonyl dichloride (DCABT),[28] and 3,3′-didecyl-2,2′-bithiophene (DD33BT)[29] were prepared according to previously published procedures. All alkoxy-substituted bithiophenes were prepared from 3,3′-dibromo-2,2′-bithiophene or 4,4′-dibromo-2,2′-bithiophene following procedures described in a previous publication.[30]

2.2. Instrumentation. The absorption spectra were recorded on a Phillips UV/vis spectrometer using 1 cm quartz cells and solute concentrations of (1−3) × 10^{-5} M. The spectra were then digitized with the use of a GRAPHPAD/IBM-AT system. It has been verified that the Beer−Lambert law is well-respected for these compounds for solute concentrations up to 10^{-4} M. 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 for each derivative studied was (0.1−2.0) × 10^{-5} M, giving absorbance of less than 0.1 to avoid any inner-filter effects. For all molecules, a study of the concentration (C) effect has been done on the fluorescence intensities (I_F) and all measurements have been performed in the linear region of the I_F *vs* C curve. Quantum yields of fluorescence were determined at 298 K against DD44BT in chloroform ($\phi_f = 0.017$)[28] as a standard. All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra.

2.3. Theoretical Methods. Semiempirical calculations were performed using the Hyperchem package, release 4.5, for Windows from Hypercube, Inc., on a Pentium computer with an internal memory of 16 Mb. This package has been used to draw the molecules and optimize roughly their geometry using the MM+ force field, which is an extension of MM2 developed by Allinger.[31] A more precise geometry optimization was obtained using the AM1 (Austin Model 1) semiempirical method, 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.[32−35] For all derivatives, the dihedral angle (ϕ) between the two thiophene rings was varied in 15° increment from planar cis conformation ($\phi = 0°$) to the planar trans conformation ($\phi = 180°$). For each increment, ϕ was held fixed while the remainder of the molecule was reoptimized using AM1. We have developed a subroutine to couple CHEMPLUS and EXCEL to make full use of the automatic phipsi routine of HYPERCHEM after optimization by AM1 at each torsional angle. An root mean square (RMS) gradient in the energy of 0.1 kcal mol^{-1} was use for the optimization criterion.

The electronic transition energies have been calculated within the framework of the semiempirical ZINDO/S method including configuration interaction (CI). ZINDO/S is a modified INDO method parametrized to reproduce UV/visible spectroscopic transitions.[36,37] The electron-repulsion integrals were evaluated using the Mataga−Nishimoto formula. For the singlet−singlet transition, all singly excited configurations involving the five highest occupied and the five lowest unoccupied orbitals (CI = 5/5) were included whereas CI = 3/3 was used for the triplet−triplet energy calculation. The ZINDO/S method also provides the ground state and the first excited triplet energies of the molecule. From these values and the transition energies (singlet−singlet and triplet−triplet), the first excited singlet (S_1) and triplet (T_1) state energies were obtained for each torsional angle. The geometry used for ZINDO/S calculations is that optimized at each torsional angle from the AM1 method.

3. Results and Discussion

3.1. Optical Properties. The absorption and fluorescence spectra have been taken in a series of *n*-alkanes (pentane to hexadecane) as well as in perfluorohexane, methanol, hexanol, chloroform, tetrahydrofuran (THF), and acetonitrile. We observed that the absorption and fluorescence maxima of these thiophene derivatives are similar in all solvents. In general, a small red shift (2−3 nm) has been observed in the spectra going from *n*-pentane to *n*-hexadecane. A small red shift is also observed (1−2 nm) in these spectra as the polarity of the solvent increases. Figures 2 and 3 show the absorption and fluorescence

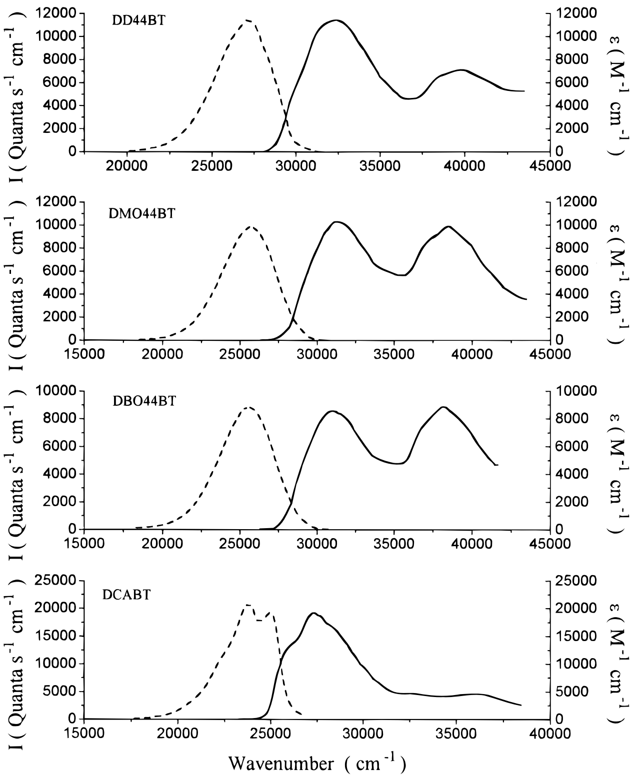

Figure 2. Absorption (—) and fluorescence (- -) spectra of 4,4′-substituted molecules in *n*-hexane.

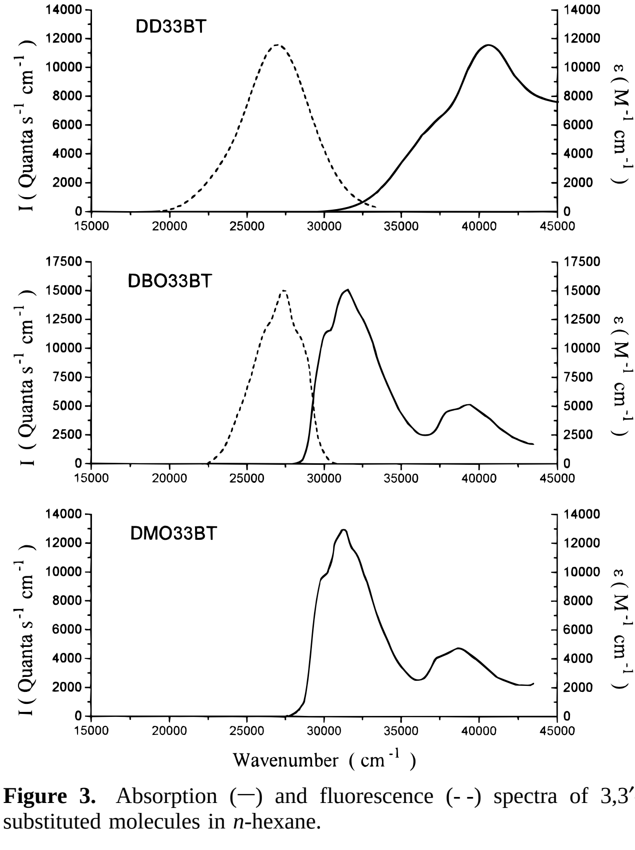

Figure 3. Absorption (—) and fluorescence (- -) spectra of 3,3′-substituted molecules in *n*-hexane.

spectra of the bithiophenes in *n*-hexane, and Table 1 reports the spectral data.

If one compares the three 4,4′-substituted bithiophene derivatives with the unsubstituted molecule (BT: $\lambda_{abs} = 301$ nm, $\lambda_f = 360$ nm),[24] it is possible to analyze the influence of the nature of the substitution on the first electronic transition, assuming that the equilibrium geometry is similar for all of the molecules investigated. We will see later that this assumption is reasonable.

It is observed that the addition of decyl chains to the bithiophene chromophore (BT) provokes a red shift of the absorption and fluorescence bands (see Figure 2 and Table 1). This is surely due to the inductive effect of the decyl chains. These results are in agreement with measurements reported for 4,4′-dioctyl-2,2′-bithiophene[24] and 4,4′-dimethyl-2,2′-bithiophene.[38] The absorption and fluorescence spectra of DD44BT do not show any vibrational fine structure, meaning that this molecule is quite flexible in its ground (S_0) and first relaxed excited singlet states (S_1). However, it can be observed that the DD44BT fluorescence band is sharper than its absorption band (see Figure 2 and Table 1), suggesting that the molecule is on average more rigid in the S_1 state. This suggests that the barrier to rotation is higher when the molecule is in its first relaxed singlet excited state. This will be confirmed by ZINDO/S calculations in the next section.

The substitution of BT with methoxy and butoxy groups in the 4,4′ positions provokes red shifts in the absorption and fluorescence spectra which are larger than those observed by the incorporation of decyl chains. These results show that, as expected, alkoxy substituents are better electron donors than alkyl groups. Table 1 also shows that the butoxy substituent is a better electron donor group than the methoxy substituent when the molecule is in the ground state whereas this trend is reversed for the molecule in the S_1 relaxed excited state. The stokes shifts (difference between absorption and fluorescence energy maxima) of DMO44BT and DBO44BT are larger compared to that measured for DD44BT (see Table 1). This indicates that the conformational changes occurring during the relaxation of the Franck−Condon excited state is more important for 4,4′-alkoxy- than for 4,4′-alkylbithiophene derivatives. Like those for DD44BT, absorption and fluorescence bands of alkoxy derivatives are structureless (see Figure 2), showing the mobility of the thiophene rings in both S_0 and S_1 states.

The absorption bands of 3,3′-alkoxybithiophene derivatives appear at approximately the same wavelengths as those of 4,4′ analogs. This shows that steric effects are not the only factors influencing electronic transition energy values for these systems. The positions of substituents also play a role. Indeed, we have shown by ZINDO/S calculations that alkoxy substituents in the 3-position give $S_1 \leftarrow S_0$ elctronic transitions which are red-shifted compared to those observed for 4,4′ analogs having the same torsional angles. These calculations together with the absorption spectra suggest that 3,3′-alkoxybithiophenes are more twisted than 4,4′-alkoxy analogs but have similar singlet−singlet transition energies due to better electron donor properties of substituents in 3- and 3′-positions. But, conversely to 4,4′-alkoxy compounds, the absorption spectra of 3,3′-alkoxy bithiophenes are structured. Moreover the bandwidths are smaller by about 1000 cm^{-1} compared to those of 4,4′-alkoxybithiophenes. These results seem to indicate that the 3,3′-alkoxy derivatives are more rigid (higher barrier to rotation) such that the number of conformers available is reduced. This will be confirmed later by semiempirical calculations.

The fluorescence spectrum of DMO33BT is very wide in all of the solvents investigated. Moreover the bandwidths increase with time even if the solutions are kept in the dark. For this reason, it is not possible to assign the fluorescence wavelength at the center of mass of the peak with good accuracy. This behavior is not observed in the DMO33BT absorption spectrum. We believe that this behavior is due to a small degradation of the molecule. The new species is not detected in the absorption

TABLE 1: Spectroscopic Parameters of the Bithiophene Derivatives Studied in *n*-Hexane at Room Temperature (298 K)

molecule	λ_A[a] (nm)	$\bar{\nu}_A$[b] (cm^{-1})	ϵ (M^{-1} cm^{-1})	fwhm$_A$[c] (cm^{-1})	λ_F[d] (nm)	$\bar{\nu}_F$[e] (cm^{-1})	fwhm$_F$[f] (cm^{-1})	Δ[g] (cm^{-1})
DD44BT	309	32 200	11 000	4700	375	26 700	3960	5500
DMO44	316	31 650	10 300	5200	395	25 300	4000	6350
DBO44B	320	31 250	8 500	5550	393	25 400	4150	5850
DCABT	361	27 700	18 000	5200	422	23 700	3500	4000
DCABT[h]	346	28 900	26 700	4700	413	24 200	3700	4700
DD33BT	280[i]	35 700	4 380		374	26 700	5050	9000
DMO33	319	31 350	12 900	4300				
DBO33B	317	31 500	15 000	4440	370	27 000	4000	4500

[a] Absorption wavelengths taken at the center of mass of the absorption band. [b] Absorption wavenumbers taken at the center of mass of the absorption band. [c] Full width at half-maximum (fwhm) of the absorption band. [d] Fluorescence wavelengths taken at the center of mass of the fluorescence band. [e] Fluorescence wavenumbers taken at the center of mass of the fluorescence band. [f] Full width at half-maximum (fwhm) of the fluorescence band. [g] Stokes shift between absorption ($\bar{\nu}_A$) and fluorescence ($\bar{\nu}_F$) bands. [h] Measure taken in methanol. [i] Measure evaluated at the shoulder.

TABLE 2: Fluorescence Quantum Yields ($\times 10^3$) of the Bithiophene Derivatives in *n*-Hexane, *n*-Hexadecane, Methanol, and *n*-Hexanol at Room Temperature (298 K)

solvent	DD44BT	DMO44BT	DBO44BT	DCABT	DD33BT	DMO33BT	DBO33BT
n-hexane	17	18	22	77	0.77	2.9	3.9
n-hexadecane	19	27	30	73		6.2	6.3
methanol	15	27	25	94	0.72	1.8	1.7
n-hexanol	18	27	32	168	1.4	5.7	3.3

spectra but shows a weak luminescence spectrum which overlaps the DMO33BT fluorescence band. The same phenomena are observed for DBO33BT in chloroform, THF, and acetonitrile, but, in *n*-alkanes and in *n*-alcohols, the fluorescence bands are much sharper and do not show any changes with time.

It is observed that the fluorescence band of DBO33BT in *n*-hexane is blue shifted by 23 nm compared to DBO44BT, whereas the emission bandwidths of both molecules are similar (see Table 1). Since absorption bands of both molecules appear at similar wavelengths, these results suggest that the DBO33BT first relaxed excited state is less planar than that of DBO44BT. However, the presence of vibrational structure in the DBO33BT fluorescence spectrum indicates that this molecule remains rigid in the S_1 relaxed excited state. The vibrational Franck−Condon envelope of the absorption and fluorescence spectra is identical, showing that the DBO33BT geometries in S_0 and S_1 are very close.

Figure 3 shows that the first electronic absorption band of DD33BT appears as a shoulder around 280 nm. This is an indication that the torsional angle between thiophene rings is very large for this molecule. This will be confirmed below by semiempirical calculations. The absorption spectrum of DD33BT is very similar to that of 3,3′-dioctyl-2,2′-bithiophene reported by Van Hutten *et al.*[24] However, the first absorption band of the methyl analog derivative is reported at 268 nm,[38] which suggests that methyl groups create a slightly larger steric hindrance than longer alkyl chains. The fluorescence band of DD33BT is very weak but appeared at 374 nm, giving a very large Stokes shift of 9000 cm^{-1}. It thus seems that, in the relaxed S_1 excited state, electronic delocalization is favored in such a way that the steric hindrance caused by the alkyl chains is not very effective. Indeed, Table 1 shows that the energetic positions of the fluorescence bands of DD44BT and DD33BT are very close. But one can see that the fluorescence spectrum of DD33BT is wider than that of DD44BT, suggesting that more conformers are present in the S_1 state of DD33BT.

Figure 2 and Table 1 show that the addition of carbonyl chloride groups to the DD44BT molecule to form the DCABT derivative provokes a large red shift of the absorption band (4500 cm^{-1}). This shows that the conjugation length increases by adding two double bonds to the molecular frame. The effect of this process on the geometry of the DCABT molecule will be discussed below. However the fact that the absorption spectrum is structured seems to indicate that the DCABT molecule is more rigid than DD44BT. Like its absorption spectrum, the fluorescence band of DCABT is red-shifted by a large amount (3000 cm^{-1}) compared to that of DD44BT. This is in agreement with the observation that the DCABT fluorescence band is structured. Indeed, a better electronic delocalization should reduce the mobility of the thiophene rings. The small value of the Stokes shift observed (see Table 1) strongly suggests that conformational changes occurring upon the relaxation of the S_1 state are less important than those found in other molecules.

In methanol, the DCABT absorption band shows a hypsochromic shift of 1200 cm^{-1} compared to that in *n*-hexane. This blue shift may be interpreted in terms of the formation of hydrogen bonds between the alcohol as proton donor and the carbonyl groups. This should increase the electron acceptor properties of each carbonyl substituent at both ends of the bithiophene, thus reducing the electron density between thiophene rings. The resulting effect would be a more twisted geometry for DCABT in alcohols. A similar blue shift is observed for the fluorescence spectrum of DCABT in methanol, showing that hydrogen bonds are also playing a role in the S_1 relaxed excited state.

Table 2 reports the fluorescence quantum yields (ϕ_F) of the molecules investigated in *n*-hexane, *n*-hexadecane, methanol, and *n*-hexanol. Amid the bithiophene derivatives investigated, DCABT possesses the stronger fluorescence ($\phi_F = 0.077$), probably due to a better electronic delocalization in the S_1 relaxed excited state. For the other 4,4′-substituted compounds, the fluorescence quantum yields observed are close to the one reported for BT in dichloromethane and in dioxane (0.018).[25,26] It thus seems that the alkyl or alkoxy chains at the 4,4′-positions do not affect much the radiative and/or the nonradiative properties of these molecules. Moreover Table 2 shows that fluorescence quantum yields of these molecules are not much affected by the viscosity of the environment. This suggests that the internal conversion deactivation process is not very important for these derivatives.

For 3,3′-substituted alkoxybithiophenes, Table 2 shows that ϕ_F are about 10 times less than that of the 4,4′ analogs. Conversely to the 4,4′ compounds, 3,3′ derivatives show a variation in their fluorescence quantum yields with the viscosity of the environment. It is difficult to believe that this behavior

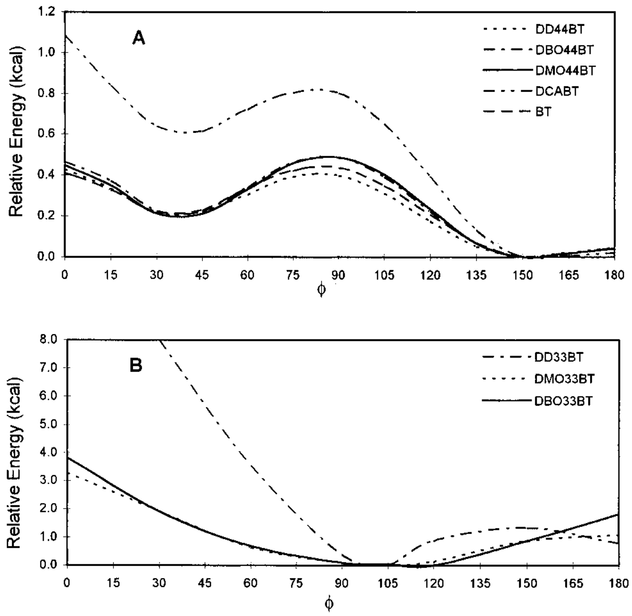

Figure 4. Potential energy curves for the ground state of the 4,4′-substituted molecule (A) and of the 3,3′-substituted molecule (B) obtained by AM1 semiempirical methods.

is linked to the internal conversion process since, as observed above, 3,3′ derivatives seem more rigid than 4,4′-substituted bithiophenes. Recently it has been found that the main deactivation pathway involved in the relaxation of the BT S_1 state is an intersystem crossing process.[26] At present, the substitutional effect on this process is unknown for bithiophene derivatives. We are currently working on this aspect of the problem. However, Rossi *et al.* have reported the triplet quantum yield (ϕ_T) of several 2,2′:5′,2″-terthiophene derivatives.[39] It was found that the compound having the highest ϕ_T value is the one showing maximum steric effects between thiophene rings. Thus, it is plausible to think that the same behavior can be observed for bithiophene derivatives. The intersystem crossing process involved should be related to the S_1-T_n energy gap of the BT derivatives. We have checked this using ZINDO/S calculations. It was found that the S_1-T_n energy gap decreases as the dihedral angle between thiophene rings increases as observed for the unsubstituted BT molecule.[18] These results will be reported elsewhere. Thus, we think that 3,3′-bithiophene derivatives would have weaker fluorescence quantum yields due to an enhanced intersystem crossing involved in these molecules. The viscosity effects observed on ϕ_F values would be related to an energy barrier involved in the $S_1 \rightarrow T_n$ crossing. For the 4,4′ derivatives, this barrier is probably higher such that the radiationless process is independent of the viscosity of the environment.

3.2. Conformational Analysis. *3.2.1. AM1 Calculations.* A conformational analysis has been carried out on all molecules using the semiempirical AM1 method. For each molecule, a geometry optimization is performed on each value of the dihedral angle between the two rings (ϕ) from the fully planar *syn* ($\phi = 0°$) to the fully planar *anti* ($\phi = 180°$) conformation at each 15° using AM1 calculations. The difference between the total energy of each optimized geometry and the energy of the most stable conformer has been plotted as a function of the dihedral angle in Figure 4A for the 4,4′-substituted bithiophenes and in Figure 4B for the 3,3′ analogs. Figure 4A also reports the potential energy surface of the unsubstituted bithiophene molecule (BT). Recently, we have discussed in detail the AM1 torsional potential of BT.[17,18] It was found that a qualitative agreement exists between AM1 results and the most recent calculations performed at the *ab initio* level using large basis sets. In particular, the energy minima were reproduced at similar dihedral angles.

Figure 4A shows that 4,4′ derivatives have similar potential energy surfaces; *i.e.*, energy minima and maxima appear at similar dihedral angles. The DD44BT potential curve reported here is in good agreement with the AM1 curve obtained for the dioctyl analog[24] and qualitatively similar to that of the 4,4′-methyl derivative as obtained by *ab initio* calculations.[14] The two minima observed are the result of a compromise between steric effects between hydrogen and sulfur atoms, which tend to increase the torsional angle between thiophene rings, and the electronic conjugation along the molecular frame which favors a planar conformation. The fact that the perpendicular and the *cis* conformations have about the same energy shows the strong steric hindrance between sulfur atoms in the *cis* conformation.

The rotational barrier, as calculated by the AM1 method, is about 0.4 kcal mol^{-1} for BT, DD44BT, DMO44BT, and DBO44BT, showing that the equilibrium geometry of these molecules is not much influenced by the substituents in the 4,4′ positions. Thus, it was well-justified to interpret changes in the absorption spectra in terms of inductive effects rather than conformational changes. However, the potential energy curves are rather flat, allowing many conformers for these molecules in their ground state. This is in agreement with the relatively large structureless absorption bands observed (see Figure 2). The barrier to rotation of DCABT (0.8 kcal mol^{-1}) is higher than those observed for the other 4,4′-bithiophenes, showing the increase in the π-electron delocalization for this molecule. This should increase the rigidity of this molecule, which is reflected by a sharper absorption band that shows a vibrational progression (see Figure 2).

Figure 4B shows the potential energy curves of 3,3′-substituted bithiophenes. For these molecules, the energy of the planar *cis* conformations ($\phi = 0°$) are very large, showing strong steric interactions between sulfur and alkoxy or alkyl substituents. Moreover, this energy is much higher for the DD33BT molecule. This indicates that CH_2 groups show much more steric hindrance than oxygen atoms. This is in good agreement with results obtained on poly(3,3′-dialkyl-2,2′-bithiophenes)[29] and poly(3,3′-dialkoxy-2,2′-bithiophenes).[30] We have observed that the length of the alkyl chains has no effect on the conformational analysis. The AM1 curve of DD33BT is in good agreement with the one reported for the dioctyl analog[24] and with the potential energy curve of the dimethyl analog as obtained by *ab initio* calculations.[14] The planar trans conformations ($\phi = 180°$) are also destabilized compared to those of the 4,4′ analogs. The equilibrium geometry of these molecules is much more twisted ($\phi = 120°$ for DBO33BT and $\phi = 105°$ for DMO33BT and DD33BT). The barrier to rotation is higher for the 3,3′ derivatives compared to the 4,4′ derivatives, which suggests that the molecular frame is more rigid. This is in agreement with the shape of the absorption bands of these systems. Indeed, Table 1 and Figure 3 show that the first absorption bands of DMO33BT and DBO33BT are sharper and more structured compared to the 4,4′ analogs. But, the vibrational Franck–Condon envelope of the alkoxy compounds shows a (0,0) transition lower in intensity compared to other vibronic transitions, which is a characteristic of nonplanar aromatic skeleton. And since the fluorescence spectrum of DBO33BT is an approximate mirror image of the absorption spectrum, it is suggested that the molecule is also twisted in its first relaxed excited singlet state, as suggested in part 3.1.

3.2.2. ZINDO/S Calculations. For each AM1 optimized geometry, the energies of the ground state (S_0), of the first

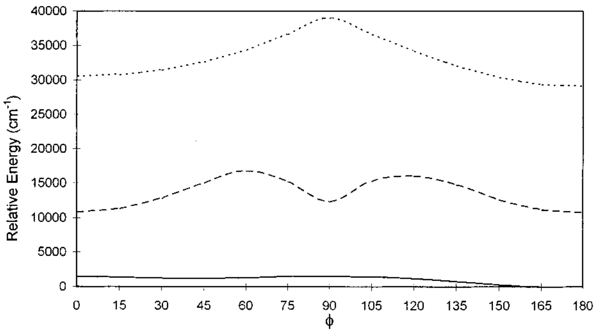

Figure 5. Variation of S_0 (—), S_1 (- -) and T_1 (— —) state energies of DMO44BT as a function of the dihedral angle between the two thiophene rings.

excited singlet (S_1) and triplet (T_1) states, and of the first electronic transition ($S_1 \leftarrow S_0$) have been calculated using the ZINDO/S semiempirical method. The potential energy surfaces of S_0, S_1, and T_1 of DMO44BT are shown in Figure 5 and are representative of all of the molecules investigated. The ground state geometry predicted by ZINDO/S is planar even for the 3,3′ derivatives. This clearly indicates that ZINDO/S underestimates small steric effects and puts more emphasis on the electronic conjugation between thiophene rings. However, the fact that *cis* conformations are destabilized by 1500−5000 cm^{-1} depending on the nature and the position of the substituent compared to *trans* conformations shows that ZINDO/S takes care of important repulsion forces. One can see on Figure 5 that the fully planar *cis* and *trans* conformations are the most stable for the S_1 excited state. It is thus predicted that, after excitation, the molecules should relax to planar S_1 states. This is in agreement with the large Stokes shifts generally found for oligothiophenes (see Table 1) and the observation that fluorescence bands are always sharper than corresponding absorption bands. It has to be pointed out here that just like that for the ground state of the 3,3′ derivatives, ZINDO/S failed to predict any distorsion in the S_1 state geometry of the 3,3′-alkoxy derivatives. Figure 5 also shows that the most stable conformations of the T_1 state are planar ($\phi = 0$ and 180°). However, contrary to singlet states, potential energy surfaces show local minima when the thiophene rings are in perpendicular arrangement, showing the biradical nature of the first triplet state.

It is well-known that even if ZINDO/S sometimes failed to optimize the ground and excited state geometry perfectly, it is, however, an excellent method for predicting electronic transition energies.[17−19,36,37] Then, another way to estimate the ground state geometry of the bithiophenes can be done by correlating the $S_1 \leftarrow S_0$ electronic transition energy (ν) calculated for each AM1 optimized geometry with the first absorption band energy obtained experimentally. Since no vibronic interactions are involved in ZINDO/S calculations, results obtained refer to the 0,0 electronic transition of isolated molecules (vapor phase). The experimental $\nu(0,0)$ of the various molecules have been estimated from the crossing of absorption and fluorescence spectra. To evaluate the $\nu(0,0)$ of the molecules in the vapor phase, the wavenumbers have been plotted as a function of the polarizability function as described elsewhere.[17] The polarizability function is defined by the relation $f(n^2) = 2(n^2 - 1)/(2n^2 + 1)$, where n represents the refractive index of the alkane. At $n = 1$, $f(n^2) = 0$ such that the extrapolated curves give the estimated $\nu(0,0)$ values for the molecules in the gas phase. Figure 6 shows such a plot for the DMO44BT bithiophene derivative. Table 3 reports the best fits between extrapolated and calculated $\nu(0,0)$ values and the corresponding geometry. It is worth noting here that the ZINDO/S method calculates about the same energies for conformations having complementary dihedral angles. Table 3 reports only *trans* conformations. Moreover, ZINDO/S is not parametrized for the chlorine atom such that, in the case of DCABT, Table 3 reports calculations where chlorine atoms are replaced by hydrogen and fluorine atoms. In general, the ground state geometry of these bithiophenes obtained from ZINDO/S are in excellent agreement with those calculated from the AM1 method (see Figure 4).

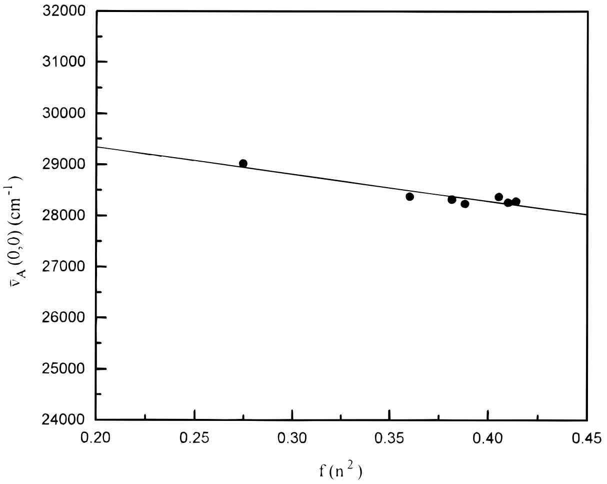

Figure 6. Plot of the 0,0 absorption wavenumber as a function of the polarizability function $f(n^2)$ of the nonpolar solvents for DMO44BT.

TABLE 3: Dihedral Angle Giving the Best Correlation between $\bar{\nu}_A(0,0)$ Extrapolated at $n = 1$ and ZINDO/S Calculations ($E(S_1 \leftarrow S_0)$) for Bithiophene Derivatives

molecule	$\bar{\nu}_A(0,0)$ (cm^{-1})	$\bar{\nu}(S_0 \rightarrow S_1)$ (cm^{-1})	ϕ
DD44BT	30 800	30 400	150
DMO44BT	30 395	30 095	150
DBO44BT	30 040	30 070	150
DCABT	27 800	27 400^a	135
		27 640^b	135
DD33BT	35 700^c	36 400	90
		34 900	105
DMO33BT	31 400^c	31 300	120
DBO33BT	31 300	31 670	120

[a] Value obtained using an hydrogen atom as a replacement for the chlorine atom. [b] Value obtained using a fluorine atom as a replacement for the chlorine atom. [c] Value taken at the maximum of absorption.

4. Concluding Remarks

This paper shows that electronic spectroscopy coupled with semiempirical calculations can provide valuable information about the conformations adopted by substituted bithiophenes in their ground and excited states. AM1 and ZINDO/S semiempirical calculations coupled with the analysis of absorption spectra predict that 3,3′ twisted conformers are more stable when compared to the 4,4′ analogs. Fluorescence spectra as well as ZINDO/S calculations suggest that, after excitation, molecules relax to much more planar S_1 excited states. The sole exceptions are 3,3′-alkoxy derivatives which seem to remain in the same conformation in their S_1 relaxed excited states if one correlates the shape of their absorption and fluorescence spectra. ZINDO/S calculations also predict that bithiophene derivatives in their T_1 excited states are characterized by planar as well as perpendicular conformations.

Fluorescence spectra show that 3,3′-alkoxybithiophenes are more rigid than their 4,4′ analogs in their relaxed S_1 excited state. However, their fluorescence quantum yields are smaller by 1 order of magnitude compared to those of 4,4′-alkoxy derivatives. We suggest that an enhanced intersystem crossing deactivation process for the 3,3′ derivatives might be responsible for this behavior.

Acknowledgment. The authors are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Fonds FCAR (Quebec) for their financial support. N.D.C. is grateful to the NSERC for a graduate scholarship. F.R. thanks also NSERC for a B. Sc. scholarship.

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