Conformational Analysis (ab Initio HF/3-21G*) and Optical Properties of Symmetrically Disubstituted Terthiophenes

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We report a conformational analysis of several substituted terthiophenes using ab initio calculations performed at the HF/3-21G* level. Geometries of terthiophenes having methoxy substituents in 3,3″ positions (DMOTT), methyl groups in the same positions (DMTT), and ethyl substituents in 3′,4′ positions (DETT) are compared with that of the unsubstituted molecule (TT). For all these symmetrical molecules, it is observed that the two dihedral angles are independent of each other. The most stable conformation of TT is found for dihedral angles $\theta = \phi = 147.2°$, whereas three maxima are located at 0°, 90°, and 180°. The insertion of methoxy groups in 3,3″ positions favors a more planar conformation with a higher rotational barrier at 90°. This behavior is explained by the electron donor properties of the methoxy groups. By contrast, the addition of two methyl groups at the same positions induces a twisting in the molecule which is caused by the steric hindrance between the methyl substituents and the sulfur atom. The presence of two ethyl groups in 3′,4′ positions creates an even stronger steric effect, giving rise to a more twisted conformation for DETT compared to that of DMTT. Absorption and fluorescence spectra of each terthiophene derivative are also reported and are correlated with their respective potential energy surfaces. The more planar molecule (DMOTT) shows a red-shifted absorption band with a higher vibrational resolution and a smaller bandwidth. For more twisted molecules, the blue shift and the bandwidth of the absorption bands increase with twisting while the absorption coefficient decreases. The fluorescence bands, in all molecules, show a better vibrational resolution with a smaller bandwidth compared to their absorption counterparts, while their maximum wavelengths are practically the same, showing that in the first excited singlet state, all molecules relax to a more planar conformation.

1. Introduction

Polythiophenes and oligothiophenes show very interesting conductive and optical properties.[1] Since these properties strongly depend on the degree of electronic delocalization present in these materials, the length of the oligomer and the insertion of side chains at specific positions are two parameters that can be used to control the final output. Recently, the effect of the molecular length on spectroscopic and photophysical properties of unsubstituted oligothiophenes has been reported by Becker et al.[2] However the combined effects of the presence of side chains and of the oligomer length on the latter properties have been scarcely investigated. Recently we have studied the effect of the nature and position of alkyl and alkoxy substituents on the optical properties of bithiophene (BT).[3] From these results, it was shown that the presence of substituents in 4,4′ positions does not significantly change the molecular conformation, whereas insertion of groups in 3,3′ positions greatly affects the geometry of the molecules. More recently, we have completed an analysis of the spectroscopic and photophysical properties of alkyl-substituted oligothiophenes, from trimer to hexamer, combined with semiempirical calculations of their respective potential energy surfaces.[4] It is clearly shown that the alkyl groups influence the conformation of the oligomers, but the geometric changes are mostly independent of the length of the oligomers.

To better understand the substitutional effect on oligothiophene molecular conformations and consequently on their physical properties, theoretical calculations have been of prime importance. Ab initio calculations performed at the HF/3-21G* level on many substituted bithiophenes have allowed one to obtain potential energy surfaces that are in good agreement with their spectral data.[5−7] Moreover, these theoretical results have provided rotational barriers[8] that have been correlated with the thermochromism observed on the parent polymers.[9−11] It was shown in these papers[5−7] that the 3-21G* basis set is the minimum ab initio level of calculations that gives results in close agreement with those obtained from more elaborate basis sets and methods including MP2.[12−15] It was also shown that semiempirical AM1 and PM3 methods failed in the prediction of the minimum conformation and rotational barrier for alkoxy- and alkylthio-substituted bithiophenes but give more acceptable results for alkyl-substituted bithiophenes as well as for the unsubstituted molecule.

To the best of our knowledge, the analysis of the substitutional effect using ab initio calculations on longer oligothiophenes is still missing in the literature. On the other hand, the conformation of the unsubstituted terthiophene molecule (TT) using HF/6-21G* calculations has been reported recently.[16] It was shown that the two dihedral angles are independent of each other and are very close to that obtained for BT. We report in this paper the potential energy surfaces of TT and three symmetrical disubstituted terthiophene derivatives (shown in Figure 1) as obtained by HF/3-21G* calculations. Results show that, for each molecule, the two dihedral angles are independent of each

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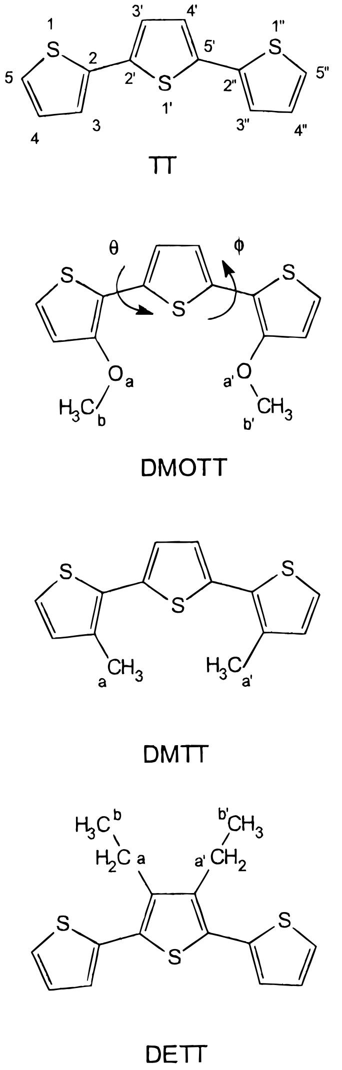

Figure 1. Molecular structures of the substituted terthiophenes investigated.

other. The alkoxy substituents favor a higher planarity of the molecule, while alkyl substituents created steric hindrance and favor more twisted conformations. Absorption and fluorescence spectra of each molecule are also reported and are in good agreement with the molecular torsional potentials. For more planar molecules, the absorption spectrum shows a red shift, a better vibronic resolution, and a smaller bandwidth. Twisted molecules show absorption spectra blue shifted with a lowering in the absorption coefficient and an increase of the bandwidth. Fluorescence spectra show that all molecules relax to a more planar conformation in their first singlet excited state.

2. Methodology

2.1. Ab Initio Calculations. Ab initio calculations were performed on a Silicon Graphics Challenge R4000 workstation at the University of Montreal using the Gaussian 90 program.[17] The conformational analysis was done by changing the torsional angle θ (and/or ϕ) by 30° steps. The geometries were optimized at the HF level with the 3-21G* basis set. The Berny analytical gradient method was used for the optimizations. In the geometry optimization of TT, DMOTT, and DMTT, a locally C_2 symmetry restriction was applied between the thiophene rings for $\theta = \phi$ to reduce the calculation time, but no symmetric constraint was applied to the side groups. No symmetric constraint was applied on DETT and for all molecules where $\theta \neq \phi$. 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 conformers in each minima, calculations of these geometries were performed without constraint on the dihedral angle.

TABLE 1: Optimized Structural Parameters of TT

parameter	bond length (Å)	parameter	angle and dihedral angle
S_1-C_2	1.7351	$S_1-C_2-C_3$	110.981
C_2-C_3	1.3538	$C_2-C_3-C_4$	112.948
C_3-C_4	1.4335	$C_3-C_4-C_5$	112.509
C_4-C_5	1.3475	$C_4-C_5-S_1$	111.968
C_5-S_1	1.7206	$C_5-S_1-C_2$	91.590
C_3-H_3	1.0694	$C_2-C_3-H_3$	123.363
C_4-H_4	1.0687	$C_3-C_4-H_4$	123.514
C_5-H_5	1.0672	$C_4-C_5-H_5$	127.136
C_2-C_2'	1.4570	$S_1-C_2-C_2'$	121.232
$S_1'-C_2'$	1.7342	$S_1'-C_2'-C_3'$	110.941
$C_2'-C_3'$	1.3534	$C_23-C_3-C_4$	113.123
$C_3'-C_4'$	1.4292	$C_5'-S_1'-C_2'$	91.871
$C_3'-H_3'$	1.0692	$S_1-C_2'-C_2$	121.165
		$C_2'-C_3'-H_3'$	123.382
		$S_1-C_2-C_2'-S_1'$	147.6

2.2. Materials. Terthiophene (TT) and *n*-hexane were purchased from Aldrich Chemicals (99% for TT and 99+%, anhydrous for *n*-hexane) and used as received. Prior to use, the compounds were checked for spurious emissions in the region of interest and found to be satisfactory. 3′,4′-Dihexyl-2,2′:5′,2″-terthiophene (DHTT) and 3′,3″-dimethyl-2,2′:5′,2″-terthiophene (DMTT) were prepared according to previously published procedures.[18,19] 3′,3″-Dimethoxy-2,2′:5′,2″-terthiophene (DMOTT) was prepared following procedures similar to those previously reported in the literature.[20]

2.3. Instrumentation. Absorption spectra were recorded on a Varian spectrometer model Cary 1 Bio using 1 cm quartz cells and solute concentrations of $(5-8) \times 10^{-6}$ M. It has been shown that the Beer–Lambert law applies for the concentrations 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 concentrations used were $(5-8) \times 10^{-6}$ M, giving absorbances near 0.1 to avoid any inner-filter effects. A study of the concentration (C) effect has been done on the fluorescence intensity (I_F), and all measurements have been performed in the linear region of the I_F versus C curve.

3. Results and Discussion

3.1. Structural and Conformational Analysis. The use of the 3-21G* basis set in the ab initio calculations has been justified in previous papers.[5,7] Indeed this level of calculations gives similar potential energy surfaces as those obtained from more elaborate basis sets and methods (including MP2) for 2,2′-bithiophene[12,14] and substituted bithiophenes.[12,13,15] Due to the size of the molecules investigated in this paper, we have limited our calculations at this level.

3.1.1. Terthiophene (TT). Since a C_2 symmetry was used in the geometry optimization, the two thiophene rings at each molecular end are identical, whereas the central ring is symmetric. The structural parameters of TT are listed in Table 1. All geometric parameters are close to those found from X-ray

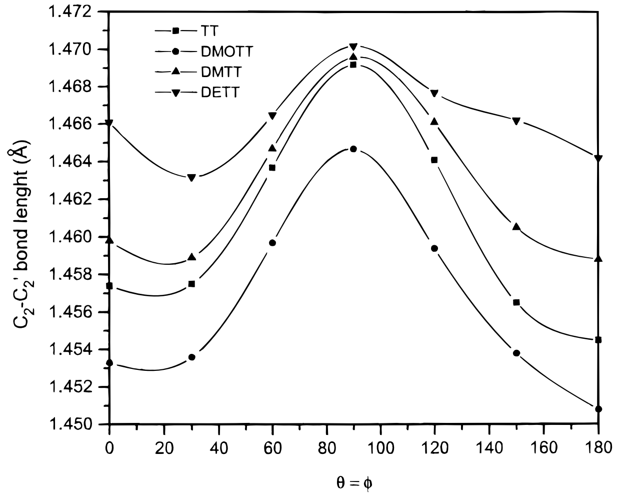

Figure 2. Variation of the C2−C2′ bond length with the dihedral angles θ and ϕ.

data.[21] In the crystal, TT adopts a nearly planar conformation, about 5−10° from planarity. Moreover two different conformations are obtained; the majority of the molecules are in an anti−anti conformation (97%), but some anti−syn conformers are present (3%). Table 1 shows that the parameters of each thiophene ring are very close to each other. Only the C3′−C4′ bond length and C2′−C3′−C4′ and C5′−S1′−C2′ bond angles differ significantly from equivalent parameters found in the first thiophene ring. The decrease of the C3′−C4′ bond length suggests that the π charge density is higher in the central thiophene ring, resulting in the higher values of the angles mentioned above. As the molecular twisting varies, two parameters, namely, C2−C2′ and C3′−C4′ bond lengths, are mainly affected. The C2−C2′ bond length variation as a function of θ ($=\phi$) is illustrated in Figure 2. It is shown that the C2−C2′ bond length increases from 1.4545 Å for the anti−anti planar conformation to reach its maximum value at 1.4692 Å for the perpendicular conformer and decreases as the syn−syn planar geometry is reached (1.4574 Å). A similar effect, but to a lesser extent, is also found for the C3′−C4′ bond length (figure not shown). These structural changes are caused by a reduction of the electronic delocalization as the twisting between adjacent thiophene rings increases. It is worth noting that C2−C2′ and C3′−C4′ bond lengths are shorter for the planar anti−anti conformer compared to the respective values in the planar syn−syn conformer. This shows the importance of nonbonded interactions (steric hindrance) in the latter conformation causing an increase in the bond length. A similar behavior has been observed in bithiophene.[7,12] Table 1 also shows that all bond lengths and angles for the most stable conformation of TT are very similar to those obtained for BT[7,12−14] (a difference smaller than 0.001 Å has been found for bond lengths). Moreover each molecule has about the same dihedral angle between thiophene rings, namely, 147.2° for TT and 147.7° for BT.[7] These results clearly indicate that the thiophene rings at the ends of the molecule are mostly independent of the length of the oligomer. On the other hand, as mentioned above, the central thiophene ring shows small differences.

Potential energy surfaces for $\theta = \phi$ are displayed in Figure 3. Energies and relaxed optimized geometries for minima and maxima are listed in Table 2. As mentioned above, potential energy surfaces involving one dihedral angle (θ or ϕ) are independent of the value of the other dihedral angle. Thus we present only the results of the diagonal energy matrix (θ by ϕ) to illustrate torsional potentials in two dimensions and because it represents the most probable conformations, the global minimum conformation being located on the diagonal. Figure 3A shows that the potential energy surface of TT is very similar to that obtained for BT.[7,12−14] Indeed two minima, a local minimum at 42.8° and the global minimum at 147.2°, are obtained compared to the respective minima of BT located at 44.7° and 146.3°.[7] However the minima obtained for TT are slightly shifted toward more planar conformations. This behavior may be due to the increase in the electronic delocalization going from the dimer to the trimer, but the changes are too small to have any significant importance on the geometry. Three maxima are also observed on the potential energy surface, two for the planar conformations and one for the perpendicular one. The barriers of rotation displayed in Table 2 involve the torsion of the two thiophene rings. However, if we compare the potential energy surface for one dihedral angle, the second remaining fixed at any value (the two dihedral angles are independent of each other), with that obtained for BT,[7] we can observe a decrease in the energy barrier for the planar conformations of TT. Indeed $\Delta E = 0.31$ and 1.64 kcal mol^{-1} for planar anti and syn conformations, respectively, whereas the respective energy barrier values of BT are 0.39 and 1.72 kcal mol^{-1}. These small differences are probably due to the

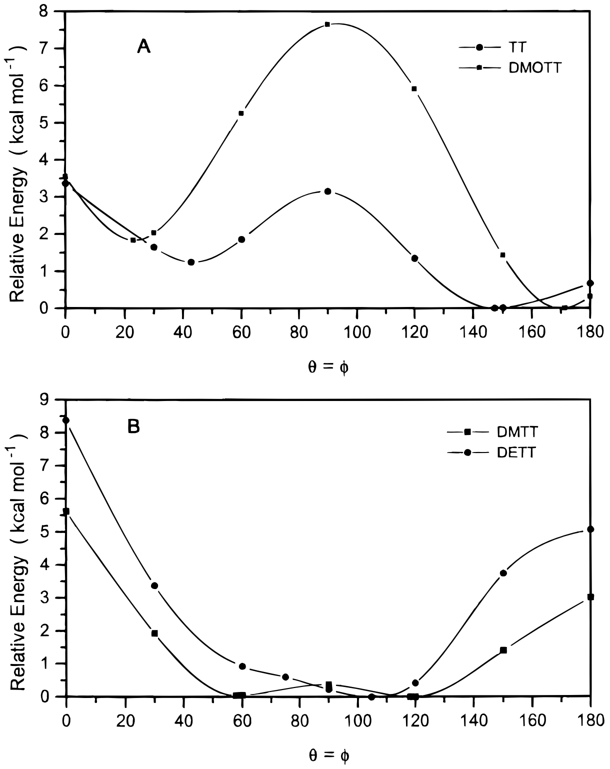

Figure 3. Ground-state potential energy surfaces for dihedral angles $\theta = \phi$.

TABLE 2: Relative Energy (in kcal mol^{-1}) and Torsional Angle ($\theta = \phi$) Obtained from ab Initio Calculations (HF/3-21G*) for the Molecules Investigated

molecule	syn[a]		perpendicular		anti[a]
DMOTT	3.5	1.8 (22.9°)	7.7	0.0 (171.3°)	0.32
TT	3.4	1.2 (42.8°)	3.2	0.0 (147.2°)	0.67
DMTT	5.6	0.047 (57.9°)	0.37	0.0 (118.2°)	3.0
DETT	8.4		0.23	0.0 (104.7°)	5.1

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

TABLE 3: Optimized Structural Parameters of DMOTT

parameter	bond length (Å)	parameter	angle and dihedral angle
S_1-C_2	1.7372	$S_1-C_2-C_3$	110.384
C_2-C_3	1.3530	$C_2-C_3-C_4$	113.672
C_3-C_4	1.4339	$C_3-C_4-C_5$	112.108
C_4-C_5	1.3441	$C_4-C_5-S_1$	112.122
C_5-S_1	1.7231	$C_5-S_1-C_2$	91.708
C_4-H_4	1.0680	$C_3-C_4-H_4$	123.214
C_5-H_5	1.0669	$C_4-C_5-H_5$	127.112
C_3-O_a	1.3757	$C_2-C_3-O_a$	122.582
O_a-C_b	1.4592	$C_3-O_a-C_b$	116.293
C_2-C_2'	1.4511	$S_1-C_2-C_2'$	122.250
$S_1'-C_2$	1.7380	$S_1'-C_2'-C_3'$	111.167
$C_2'-C_3'$	1.3559	$C_2'-C_3'-C_4'$	113.123
$C_3'-C_4'$	1.4232	$C_5'-S_1-C_2'$	91.420
$C_3'-H_3'$	1.0697	$C_2'-C_3'-H_3'$	123.790
		$S_1'-C_2'-C_2$	122.070
		$C_2-C_3-O_a-C_b$	254.4
		$S_1-C_2-C_2'-S_1'$	171.3

increase in the electronic delocalization found in TT which favors more planar conformations. This effect can also explain the small increase in the rotational barrier at 90° observed for TT (1.53 and 1.49 kcal mol^{-1} for TT and BT, respectively).

3.1.2. 3,3″-Dimethoxy-2,2′:5′,2″-terthiophene (DMOTT). Structural parameters of DMOTT are displayed in Table 3 . One can see that bond lengths of end thiophene rings are close to those found for TT. However, small structural changes are observed between these two molecules. For instance, S1−C2 and C5−S1 bond lengths slightly increase whereas the C4−C5 bond length decreases for DMOTT. However, Table 3 shows that changes are more important for C2−C2′ and C3′−C4′ bond lengths, which are shorter than those obtained for TT. It is worth mentioning here that this behavior is also observed for TT and DMOTT, having identical torsional angles between adjacent thiophene rings, as illustrated in Figure 2. As mentioned above, C2−C2′ and C3′−C4′ bond lengths are largely dependent on the electronic delocalization along the long molecular axis. The electron donor properties of the methoxy groups in 3,3″ positions increase the electronic conjugation, favoring a more planar conformation, which reduces the C2−C2′ and C3′−C4′ bond lengths. A similar behavior has been observed for methoxy-substituted bithiophenes.[5] Figure 2 also shows that the variation of the C2−C2′ bond length with the torsion is less for DMOTT than for TT. Indeed, for DMOTT, the difference between planar *anti* and perpendicular conformations is 0.0139 Å, whereas a value of 0.0147 Å is observed for TT. Finally, one can see that methoxy groups are nearly perpendicular (angle of 254°, see Table 3) to the molecular plane (see Figure 4), as observed for 3,4′-dimethoxy-2,2′-bithiophene (DMO34BT).[5]

The potential energy surface of DMOTT shows two minima, one at 22.9° and the global minimum located at 171.3° (see Figure 3B). As discussed above, the increase of the molecular planarity following insertion of methoxy groups is due to the increase of the electronic delocalization along the molecular frame caused by the electron donor properties of these substituents. According to the ab initio calculations, this effect is stronger than the steric hindrance created by the methoxy groups which should favor twisted conformations. However, steric effects induced by methoxy groups are reflected in the values of the rotational barriers at the planar syn and anti conformations. Indeed, the fact that rotational barriers for these two conformations are similar to the respective values obtained for TT (see Figure 3) can be explained in terms of two opposing forces, *i.e.*, higher steric effects and a higher electronic delocalization, which act in opposite directions with about the same magnitude. For the perpendicular conformation, the rotational barrier of DMOTT is higher than that obtained for TT because the electronic delocalization is no longer playing any role at all. The potential energy surface involving the rotation of only one thiophene ring (the other remaining constant at its minimum conformation) shows a global minimum slightly more planar (171.3°) than that obtained for DMO34BT (170.6°).[5] This shift toward planarity is very small as observed going from BT to TT. However the rotational barriers seem a little more affected by the length of the molecule. Indeed, the barrier to rotation of one thiophene ring of DMOTT at the perpendicular conformation (4.08 kcal mol^{-1}) is higher than that observed for DMO34BT (3.88 kcal mol^{-1}).[5] Thus, as observed for TT, the increase in the molecular length seems to provoke a small increase of the rotational barrier at 90°. It is interesting to note that the rotational barrier for the planar anti conformation is slightly higher for DMOTT (0.16 kcal mol^{-1}) than for DMO34BT (0.13 kcal mol^{-1}), whereas the reverse is true for rotational barriers for planar syn conformations (DMOTT 1.79 kcal mol^{-1}, DMO34BT 1.19 kcal mol^{-1}). This seems to indicate that the location of the sulfur atom and the methoxy substituent on the same side of the molecule creates a stronger steric hindrance for a longer oligothiophene chain.

TABLE 4: Optimized Structural Parameters of DMTT

parameter	bond length (Å)	parameter	angle and dihedral angle
S_1-C_2	1.7380	$S_1-C_2-C_3$	111.709
C_2-C_3	1.3538	$C_2-C_3-C_4$	111.766
C_3-C_4	1.4414	C_3-C_4-Cs	113.213
C_4-C_5	1.3455	$C_4-C_5-S_1$	111.881
C_5-S_1	1.7177	$C_5-S_1-C_2$	91.426
C_4-H_4	1.0698	$C_3-C_4-H_4$	122.851
C_5-H_5	1.0675	$C_4-C_5-H_5$	126.940
C_3-C_a	1.5087	$C_2-C_3-C_a$	125.955
C_2-C_2'	1.4665	$S_1-C_2-C_2'$	119.629
$S_1'-C_2'$	1.7326	$S_1'-C_2'-C_3'$	110.967
$C_2'-C_3'$	1.3521	$C_2'-C_3'-C_4'$	113.073
$C_3'-C_4'$	1.4312	$C_5'-S_1'-C_2'$	91.919
$C_3'-H_3'$	1.0691	$C_2'-C_3'-H_3'$	123.071
		$S_1'-C_2'-C_2$	121.878
		$S_1-C_2-C_2'-S_1'$	118.2

3.1.3. 3′,3″-Dimethyl-2,2′:5′,2″-terthiophene (DMTT). Structural parameters of DMTT are displayed in Table 4. All parameters are comparable with the crystallographic data.[22] In the crystalline phase, DMTT adopts a twisted conformation of about 30° from planarity with a proportion of 85% in the anti−syn conformation and 15% in the anti−anti conformation. The fact that DMTT adopts a more planar conformation in the crystalline phase compared to that found for the optimized geometry at the ab initio level is attributed to packing forces which favor more planar conformations as observed for TT. All geometrical changes induced by the methyl groups are attributed to the change of conformation going from TT to DMTT except for S1−C2, C3−C4, and C2−C2′ bond lengths, which are longer compared to that found for TT having the same conformation as DMTT (120°). As mentioned above for TT, S1−C2 and C3−C4 are nearly independent of the twisting of thiophene rings such that the increase in these bond lengths is due to the insertion of methyl groups themselves without involving any significant changes in the torsional angle. The higher value of C2−C2′ observed in the case of DMTT can be attributed to the steric hindrance caused by the methyl groups. This steric hindrance causes a smaller variation of the C2−C2′ bond length as the molecule becomes more twisted (see Figure 2). As a result, one can see in Figure 2 that the steric hindrance

TABLE 5: Optimized Structural Parameters of DETT

parameter	bond length (Å)	parameter	angle and dihedral angle
$S_1{-}C_2$	1.7352	$S_1{-}C_2{-}C_3$	111.021
$C_2{-}C_3$	1.3506	$C_2{-}C_3{-}C_4$	113.003
$C_3{-}C_4$	1.4356	$C_3{-}C_4{-}C_5$	112.394
$C_4{-}C_5$	1.3477	$C_4{-}C_5{-}S_1$	111.990
$C_5{-}S_1$	1.7199	$C_5{-}S_1{-}C_2$	91.589
$C_3{-}H_3$	1.0691	$C_2{-}C_3{-}H_3$	122.987
$C_4{-}H_4$	1.0688	$C_3{-}C_4{-}H_4$	123.623
$C_5{-}H_5$	1.0675	$C_4{-}C_5{-}H_5$	126.982
$C_2{-}C_2'$	1.4695	$S_1{-}C_2{-}C_2'$	121.664
$S_1'{-}C_2'$	1.7290	$S_1'{-}C_2'{-}C_2$	120.160
$C_2'{-}C_3'$	1.3528	$S_1'{-}C_2'{-}C_3'$	112.055
$C_3'{-}C_4'$	1.4491	$C_2'{-}C_3'{-}C_4'$	112.263
$C_4'{-}C_5'$	1.3528	$C_3'{-}C_4'{-}C_5'$	112.263
$C_5'{-}S_1'$	1.7290	$C_4'{-}C_5'{-}S_1'$	112.052
$C_5'{-}C_2''$	1.4694	$C_5'{-}S_1'{-}C_2'$	91.364
$S_1''{-}C_2''$	1.7352	$S_1'{-}C_5'{-}C_2''$	120.089
$C_2''{-}C_3''$	1.3508	$S_1''{-}C_2''{-}C_5'$	121.707
$C_3''{-}C_4''$	1.4355	$S_1''{-}C_2''{-}C_3''$	111.014
$C_4''{-}C_5''$	1.3477	$C_2''{-}C_3''{-}C_4''$	113.001
$C_5''{-}S_1''$	1.7199	$C_3''{-}C_4''{-}C_5''$	112.400
$C_3''{-}H_3''$	1.0691	$C_4''{-}C_5''{-}S_1''$	111.986
$C_4''{-}H_4''$	1.0688	$C_5''{-}S_1''{-}C_2''$	91.593
$C_5''{-}H_5''$	1.0675	$C_2'{-}C_3'{-}C_a$	124.020
$C_3'{-}C_a$	1.5117	$C_3'{-}C_a{-}C_b$	110.980
$C_a{-}C_b$	1.5471	$C_3'{-}C_4{-}C_a'$	123.614
$C_4'{-}C_a'$	1.5118	$C_4'{-}C_a'{-}C_b'$	110.960
$C_a'{-}C_b'$	1.5471	$C_2''{-}C_3''{-}H_3''$	122.990
		$C_3''{-}C_4''{-}H_4''$	123.617
		$C_4''{-}C_5''{-}H_5''$	126.987
		$C_2'{-}C_3'{-}C_a{-}C_b$	91.181
		$C_3'{-}C_4'{-}C_a'{-}C_b'$	274.657
		$S_1{-}C_2{-}C_2'{-}S_1'$	255.711
		$S_1'{-}C_5'{-}C_2''{-}S_1''$	254.354

caused by the methyl groups is high enough in the planar syn conformation such that the C2−C2′ bond length is longer than that observed for the 30° conformation.

The DMTT potential energy surface shows two minima located at 57.9° and 118.2° which are very close in energy (see Figure 3B). The equivalence of these two minima are reflected in the crystallographic data of this compound, where a majority of syn−anti conformations is observed.[22] Twisted conformations predicted by ab initio calculations are surely due to the steric hindrance induced by the methyl groups. Moreover, the minima obtained are very close to those found for 3,4′-dimethyl-2,2′-bithiophene (DM34BT).[7] A very low rotational energy barrier at 90° is observed, which allows a wide range of conformations for this molecule. The rotational energy barriers against planarity are much higher than those observed for TT or DMOTT. The barrier for the rotation of only one thiophene ring (the other remaining fixed at its minimum conformation) at the planar anti conformation (1.43 kcal mol^{-1}) is smaller than that found for DM34BT (2.29 kcal mol^{-1}), showing that the increase of the molecular length stabilizes the anti planar conformation. The rotational barriers at 90° (0.18 kcal mol^{-1} for DMTT and 0.16 kcal mol^{-1} for DM34BT) and for the syn planar conformation (2.84 kcal mol^{-1} for DMTT and 2.89 kcal mol^{-1} for DM34BT) are much less affected by the number of thiophene rings involved.

3.1.4. 3′,4′-Diethyl-2,2′:5′,2″-terthiophene (DETT). Structural parameters of DETT are listed in Table 5. All parameters are in good agreement with the crystallographic data of 3′,4′-dibutyl-2,2′:5′,2″-terthiophene (DBTT).[23] In the crystalline phase, DBTT adopts a conformation of about 30° from planarity with a majority of anti−anti conformers. Even though the geometry optimization was done without any symmetry restriction, a symmetrical molecule is obtained both in thiophene rings and ethyl lateral chain parameters. This confirms the molecular symmetry of this molecule and justifies the C_2 local symmetry used for the other molecules when $\theta = \phi$. Most of the structural parameters are similar to those obtained for DMTT except for C3−C4, C3′−C4′, and S1′−C2′ bond lengths. The increase in the C3′−C4′ bond length observed for DETT is caused by the steric effects of the two ethyl chains on the same thiophene ring. Ethyl groups are perpendicular to the plane of the central thiophene ring and point in opposite directions (see Figure 4 and Table 5). It has been calculated that the conformation having ethyl groups pointing in the same direction is less stable by about 1 kcal mol^{-1} compared to that having ethyl groups pointing in opposite directions. By contrast, DBTT in the solid phase shows that the two butyl chains are pointing in the same direction. The reason for this behavior might involve packing forces which should be stronger for the latter conformation because molecules are allowed to approach closer to each other. It is also possible that the minimum energy conformation calculated in the gas phase has no crystalline form (the compound having hexyl chains on the central thiophene ring (DHTT) is liquid at room temperature). The variation of the C2−C2′ bond length with the twisting is much smaller than that observed for other molecules (see Figure 2). This bond length is much longer for the planar syn conformation than for the 30° conformation compared to that of DMTT and is still relatively long for the planar anti conformation. This clearly indicates the high steric hindrance created by the two ethyl chains in the 3′,4′ positions. The steric effect in all of these substituted terthiophene derivatives is emphasized by the fact that the increase in the C2−C2′ bond length varies as the

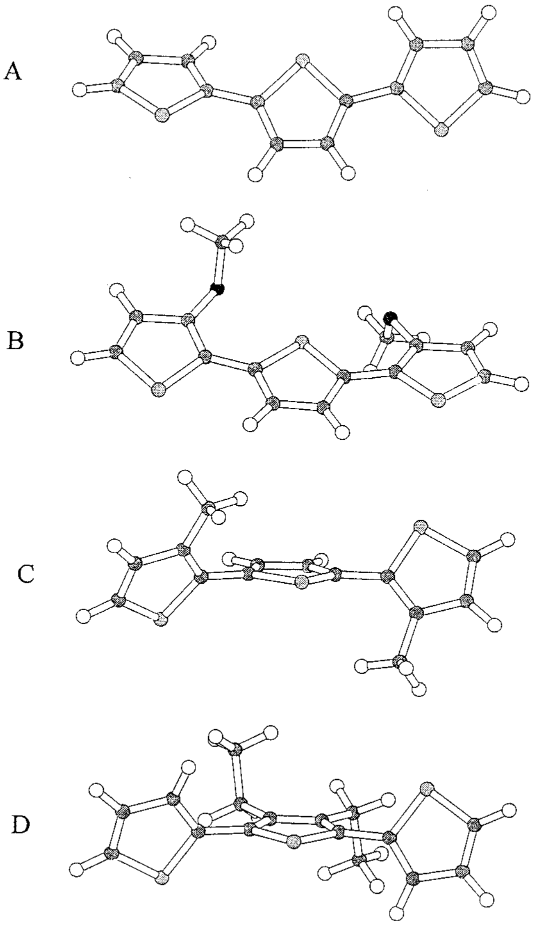

Figure 4. Optimized molecular structures of the molecules investigated: (A) TT, (B) DMOTT, (C) DMTT, and (D) DETT.

TABLE 6: Spectroscopic Parameters of Terthiophene Derivatives in *n*-Hexane at Room Temperature

molecule	λ_A^a (nm)	$\bar{\nu}_A^a$ (cm^{-1})	ϵ^b (M^{-1} cm^{-1})	fwhm$_A^c$ (cm^{-1})	λ_F^a (nm)	$\bar{\nu}_F^a$ (cm^{-1})	fwhm$_F^c$ (cm^{-1})	Δ^d (cm^{-1})	$\theta = \phi^e$ (deg)
DMOTT	372	26 900		4600	431	23 200	3600	3700	171.3
TT	349	28 700	28 700	5200	422	23 700	3400	5000	147.2
DMTT	335	29 900	16 100	6100	419	23 900	3600	6000	118.2
DHTT[f]	331	30 200	13 400	6700	426	23 500	3500	6700	104.7

[a] Taken at the band maxima. [b] Molar absorption coefficient at the band maxima. [c] Full width at half-maximum. [d] Stokes shift between maxima of absorption and fluorescence bands. [e] Dihedral angle of the minimum energy conformer obtained from the HF/3-21G* basis set.

twisting proceeds and is directly proportional to the reciprocal of the energy barrier against planarity (see Figures 2 and 3).

As one can see in Figure 3B, the insertion of two ethyl groups on the same thiophene ring induces a more important twisting between the rings compared to that found for DMTT. This demonstrates the increase in the steric hindrance of the ethyl groups in these positions where the presence of a second ethyl chain prevents the first ethyl chain from adopting an energy-favored conformation. However, it is worth mentioning here that ethyl groups create stronger steric effects than methyl substituents.[7] This behavior may be partly responsible for the more twisted conformation found in DETT. By contrast with DMTT, we observed that only one minimum at 104.7° is observed for DETT. This is in agreement with crystallographic data showing mainly the presence of anti conformers. Both rotational barriers against planarity (syn and anti) are larger than that obtained for DMTT, reflecting the larger steric hindrance created by the ethyl groups in the $3',4'$ positions. An experimental determination of the rotational barrier of DBTT has been reported by DeWitt et al.[23] From NMR measurements, they have obtained a value of 8 kcal mol^{-1} for the ground-state rotational barrier, which is larger than that calculated for the anti conformation (5.1 kcal mol^{-1}) but similar to that predicted for the syn conformation (8.4 kcal mol^{-1}). Recently, we have reported a conformational analysis of DHTT using AM1 and PM3 semiempirical methods.[4,24] Two minima located at 60° and 120° have been obtained, but the rotational barriers are smaller than those obtained at the ab initio level. Smaller rotational barriers obtained with the semiemperical AM1 method have also been observed for unsubstituted oligothiophenes[25,26] as well as for alkyl-substituted bithiophenes.[7,26] The presence of two minima in the DHTT potential energy surface suggests that AM1 underestimates the steric hindrance of the two alkyl chains, giving steric effects similar to those created by the insertion of methyl substituents in positions 3 and $3''$ as in DMTT (see Figure 3B).

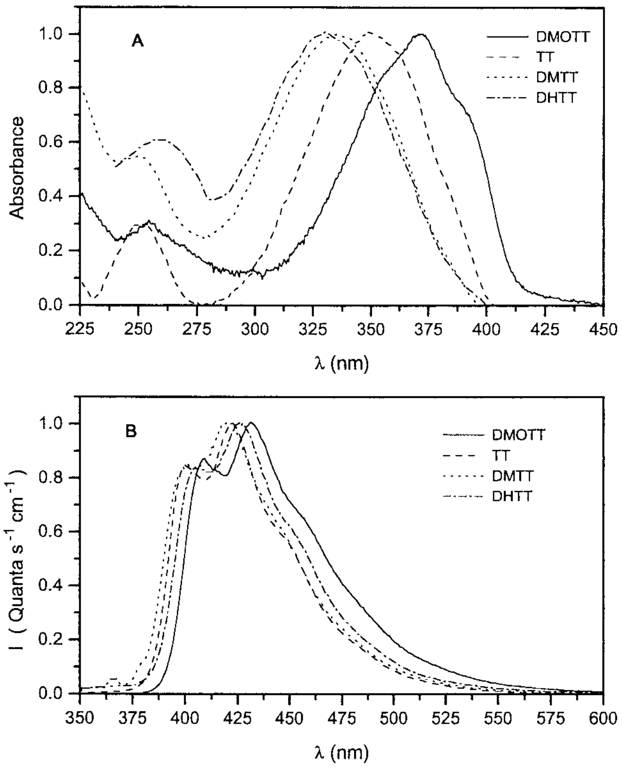

Figure 5. Absorption (A) and fluorescence (B) spectra of TT, DMTT, DMOTT, and DHTT. All spectra have been measured in *n*-hexane at room temperature.

3.2. Optical Properties. The normalized absorption and fluorescence spectra of the molecules investigated are shown in Figure 5. All spectroscopic parameters are listed in Table 6. It is important to note that experimental measurements have been done for DHTT and not for DETT because DETT was not available. However, it is well-known that the length of the side chains does not practically influence the potential energy surface such that similar ab initio torsional potentials are expected for DHTT and DETT.[3,4] All spectral measurements have been done in many solvents without showing any important changes in spectroscopic parameters. Figure 5A shows that the absorption spectrum of TT is broad and does not show any resolvable vibrational structures that are characteristics of a nonrigid system giving rise to a wide range of conformations. This result is in agreement with the TT potential energy surface, where the global minimum corresponds to a twisted anti conformation having a low rotational barrier. The absorption spectrum of DMOTT is red shifted, shows vibrational structures, and is sharper than that of TT. The bathochromic shift observed is attributed both to the electron donor properties of the methoxy groups and to an increase in the molecular planarity. ZINDO/S calculations[3,24] performed on the optimized geometry obtained from the ab initio HF/3-21G* show that the former is responsible for about half of the red shift observed. The presence of vibrational structures is a characteristic of more planar rigid systems, whereas sharper bands indicate a narrower distribution of conformers. This agrees quite well with theoretical results predicting a more planar conformation for DMOTT. Moreover the rotational barrier at 90° is higher than that found for TT, which should favor a smaller number of conformers for DMOTT. Compared to TT, the absorption spectrum of DMTT is blue shifted, its absorption coefficient is much reduced, and its bandwidth is larger (see Table 6). This is experimental evidence that DMTT molecules are very twisted. Indeed a larger twisting between adjacent thiophene rings induces a reduction in the electronic delocalization, causing an increase in the transition energy as well as a decrease in the oscillator strength (which is proportiona1 to the absorption coefficient). ZINDO/S shows that this blue shift is even counterbalanced by a 10 nm red shift caused by the methyl groups in the $3,3''$ positions. This emphasizes the importance of the steric effect between the methyl group and the sulfur atoms in this molecule. On the other hand, the broad and unstructured band indicates the presence of a wider distribution of conformations. All these results are corroborated by the potential energy surface of DMTT. Finally the absorption spectrum of DHTT is slightly blue shifted and its absorption coefficient is reduced compared to that of DMTT. This behavior indicates the presence of higher twisting between thiophene rings in DHTT, as suggested by the comparison of the potential energy surfaces of DMTT and DETT in Figure 3B. It is worth noting that again here for the same dihedral angle in TT and DETT, ZINDO/S shows a bathochromic shift of about 7 nm in the latter compound. Thus, blue shifts observed in the absorption spectra of DMTT and DHTT caused by the twisting of thiophene rings are always counterbalanced by the donor properties of the allyl chains and would be even larger without the inductive effect of these substituents.

Figure 5B shows that the fluorescence maxima of all the molecules are closer to each other compared to their respective absorption spectra. Moreover, all fluorescence bands have the same vibrational structure and have similar bandwidths. This strongly suggests that all molecules adopt about the same conformation in the first relaxed singlet excited state. More structured and sharper fluorescence bands compared to their respective absorption bands also suggest that the molecules adopt more planar conformations in their first relaxed singlet excited states with higher barrrier to rotation.

The red shift of the DMOTT fluorescence band compared with that of TT is attributed to the electron donor properties of the methoxy groups. However this spectral shift is much smaller than that found in the absorption spectra. Since an increase of the donor properties of the methoxy groups is expected in the excited state, the reduction in the red shift is explained by a larger conformational change of TT compared to DMOTT between the ground and first relaxed singlet excited states, as shown in Figure 3A, comparing both minima to 180°. It is also worth noting that a change of the conformation of methoxy groups in the first singlet excited state would also contribute to the red shift observed for the fluorescence band of DMOTT.

Table 6 shows that the fluorescence band maximum of DMTT is very close to that observed for TT. Since a red shift of the DMTT fluorescence band should be observed for a conformation similar to that of TT, we believe that DMTT in the first relaxed singlet excited state is more twisted than TT. The steric hindrance induced by the methyl groups is probably too large for the molecules to reach totally planar conformations, as observed in the crystallographic data[22] for the ground electronic state. Along the same line, we do not believe that the excited-state conformation of DHTT is more planar than that of DMTT, as suggested by their respective fluorescence maxima. The red shift observed for the DHTT fluorescence band relative to that of TT is probably due to the donor properties of the hexyl chains.

Conformational changes between the ground state and first relaxed singlet excited state are well illustrated by the Stokes shifts. Indeed one can see in Table 6 that, as the ground-state conformation of terthiophenes becomes more twisted, the Stokes shift increases, indicating an important conformational change between these two states.

4. Concluding Remarks

Ab initio calculations at the HF/3-21G* level performed on terthiophene derivatives have shown that the structural parameters of thiophene rings are little affected by the length of the molecule and the presence and/or the nature of substituent. On the other hand, the inter-ring bonds (C2−C2′) and bond angles are the most affected because they depend directly on the electronic delocalization, which is strongly related to the molecular conformation. Indeed, the C2−C2′ bond length is shorter for the planar anti−anti conformers and increases as the twisting proceeds between 180° and 90°. This increase has been shown to vary from molecule to molecule and depends linearly on the reciprocal of the potential energy barrier against planarity, which is obviously related to the minimum energy dihedral angle of each thiophene oligomer.

It has been shown that the insertion of methoxy groups in the 3,3″ positions of terthiophene (DMOTT) improves the molecular planarity and rigidity due to the electron donor properties of the methoxy substituents. On the other hand, the steric hindrance caused by the insertion of methyl groups in the same positions (DMTT) induces a large twisting between thiophene rings and produces a more flexible molecule. For these molecules, potential energy surfaces are very close to that of the respective 3,4′-substituted bithiophenes, showing the local effect of the substitution. The presence of two ethyl chains on the central thiophene ring (DETT) seems to produce an even larger steric hindrance, giving rise to a more twisted conformation. Indeed, the rotational barrier against planarity is much higher for DETT compared to those for DMTT, DMOTT, and TT.

Absorption measurements are in good agreement with theoretical results. Indeed the almost planar conformation of DMOTT predicted by ab initio calculations is reflected in its absorption band, which is red shifted, more structured, and sharper than that of the unsubstituted molecule. On the other hand, twisted molecules (DMTT and DHTT) show absorption bands that are blue shifted, unstructured, and broad. Moreover absorption coefficients are smaller for twisted molecules.

After excitation, all terthiophenes become more planar, following the relaxation of the first excited singlet state. This is reflected by sharper fluorescence bands showing resolvable fine structures. We suggest that the relaxed conformations of DMTT and DHTT in the S_1 excited state are less planar than that of TT and DMOTT.

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