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Investigation of Barriers To Conformational Interchange in Oligothiophenes and Oligo(Thienyl)furans

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The conformational analysis of unsubstituted and alkyl-substituted oligothiophenes and oligo(thienyl)furans by dynamic NMR (DNMR) spectroscopy and ab initio calculations is described. The DNMR studies of oligothiophenes indicate that the conformational exchange is fast even on the ^{13}C chemical shift scale and that the barriers are too low to be measured by this technique. Ab initio 6-31G** and MP2/6-31G** calculations are in agreement with these experimental findings. Moreover, it is found that the torsional barriers do not change significantly as the chain length is increased. Torsional parameter sets for the MM2 force field are derived for substituted oligothiophenes and oligo(thienyl)furans using the ab initio torsional energy profiles for the appropriate dimers, with the expectation that these parameter sets will be transferable to larger oligomers.

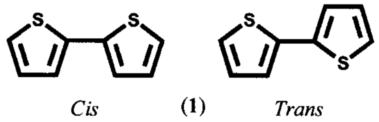
Introduction

Since the first observation of electrical conductivity in the oxidized form of polyacetylene,[1] conjugated polymers have received a great deal of attention both for their fundamental properties and their potential applications.[2] More recently, the luminescent properties of conjugated polymers have been the subject of intense research.[3] Polythiophenes are an interesting class of conjugated polymers owing to their high chemical and electrochemical stability in neutral and oxidized states.[4,5] Unsubstituted polythiophene is insoluble and intractable, and this not only prevents extensive characterization of the material but also limits its potential application. Substitution at the 3 position with various substituents has led to materials which are soluble in common organic solvents[6,7] and even water.[8,9] Substituted poly(thienyl)furans are currently being investigated as potential materials for luminescent devices as a result of their enhanced photoluminescence quantum yields.[10] This enhanced efficiency has been attributed to the presence of a lighter atom (oxygen) in the polymer chain. Heavy atoms increase the probability for intersystem crossing, thereby decreasing the quantum yield in photoluminescence.[11] Physical properties such as electrical conductivity and luminescence are a result of conjugation along the polymer chain, derived from the overlap of p atomic orbitals, and are dependent on the conformations adopted by these polymers. A detailed study of the conformational behavior of these polymers is therefore of interest for the understanding of structure−property relationships.

A number of theoretical[12−42] and experimental[17−21,32,40−44] studies of conformations of oligo- and polythiophenes has been reported. The theoretical studies have ranged from molecular mechanics[12,18−22] to ab initio[17,35−42] calculations. The latter, performed at Hartree−Fock, DFT, and MP2 levels with various basis sets ranging from 3-21G* to 6-311G**, consistently indicate that cis and trans conformers are nonplanar. The energies, and thus populations, of these conformers are comparable, and their interconversion barriers are very low. The height of the barriers reduces dramatically with substitution at the 3,3′ positions. Inclusion of the effects of electron correlation does not change the overall conclusions appreciably. Thus, Bongini and Bottoni[39] showed that Hartree−Fock calculations of methyl-disubstituted bithiophenes gave a single minimum at 90° whereas inclusion of electron correlation (MP2) gave a minimum at 60°. DFT calculations, on the other hand, indicated the presence of both the 60° and 90° minima but separated by a barrier of only 1 kcal mol^{-1}. Removal of the barrier of 1 kcal mol^{-1} will therefore lead to one minimum.

Experimental studies of oligothiophenes range from X-ray crystallographic studies[18,20,21,43,45−47] to gas-phase[17,48] and solution conformational studies.[40−42,44,49−51] The X-ray crystal structure of 2,2′-bithiophene (**1**) is characterized by the fully coplanar trans conformation,[43] perhaps as a result of crystal packing forces. Other crystal structures of alkyl-substituted oligothiophenes exhibit disorder due to the presence of a significant amount (up to 40%) of thiophene rings in the cis conformation.[20,52]

CHART 1



(1)

Moreover, in contrast to the general perception that the trans conformer is dominant, 3,3′,4″,3‴-tetramethyl-2,2′:5′,2″:5″,2‴-tetrathiophene was found to crystallize in the cis conformation about the HH linkages.[20] This observation is consistent with the results of ab initio calculations, which indicated that the energy difference between the cis and trans conformers is very small.

The earliest gas-phase electron diffraction conformational study of 2,2′-bithiophene (**1**)[48] was consistent with the existence

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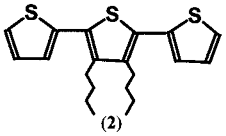
of two twisted conformers having dihedral angles of 95° and 146°. However, the uncertainties associated with this earlier study prompted a more recent study,[17] coupled with ab initio calculations using standard 3-21G* and 6-31G** basis sets. The experimental data at 97−98 °C were found to be consistent with the presence of two conformations, trans (148°) and cis (36°), with populations of 56% and 44%, respectively, suggesting that the trans conformation is more stable than the cis conformation by about 0.18 kcal/mol.

The conformations of oligothiophenes in solution have also been investigated. An early study, of 2,2′-bithiophene (**1**) by liquid crystal NMR spectroscopy[44] indicated the presence of a mixture of cis and trans conformations, having populations of 30% and 70%, respectively. This suggests that the trans conformation is more stable than the cis conformation by about 0.2 kcal/mol. The energy barrier for conformational interchange was determined to be 5 ± 2 kcal/mol. The relatively large magnitude of this barrier compared to that obtained by the theoretical calculations has been associated with a possible structural deformation of solutes in liquid crystal solvents.[23] Other measurements of the torsional barriers, based on dynamic NMR data, have also been reported.[49−51] Thus, an inter-ring rotational barrier of 19.7 kcal/mol in 2,5-bis(2′-thienyl)-3,4-dibutylthiophene (**2**) was assigned,[49] but this claim was subsequently retracted,[50] and an energy barrier of 8 kcal/mol, based on the temperature dependence of the proton chemical shifts, was estimated. The barrier to rotation in a substituted tetrathiophene was also reported to be about 20 kcal mol^{-1}.[51]

CHART 2



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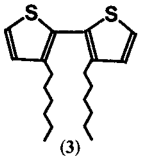

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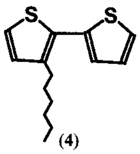

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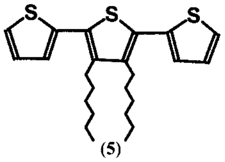


(5)

The contradictory results described in the foregoing sections have led to a great deal of confusion over this subject. Some researchers have classified polythiophenes as rigid polymers,[49−51,53] while others have regarded them as flexible polymers.[21,44,54] The present work attempts to resolve the controversy by simultaneous application of dynamic NMR spectroscopy and ab initio calculations. Since electron correlations do not seem to produce a significant effect, we restricted ourselves to Hartree−Fock calculatons at the 6-31G** level. The results of the ab initio calculations were also used to derive a set of torsional parameters for the MM2 force field. This set was specifically optimized for the study of the conformational behavior of oligomers and can perhaps be used for even polymers of thiophenes and (thienyl)furans. A convenient and reliable method of computation for more complex oligomers is highly desired. In a companion paper, we show that the new MM2 parameters, when used in a molecular dynamics protocol, predict accurately the experimental conformational behavior of oligothiophenes and oligo(thienyl)furans derived by quantitative NOE experiments.[55]

Experimental Section

General. Melting points were determined on a Fisher-Johns apparatus. Gas chromatographic analysis was performed on a HP-5890A using an initial temperature of 60 °C for 1.00 min, followed by a heating rate of 20 °C/minute until the final temperature of 275 °C was reached. Column chromatography, unless otherwise stated, was performed over Kieselgel 60 (230−400 mesh) according to a published procedure.[56] Thin-layer chromatography (TLC) was performed on precoated aluminum plates with Merck silica gel 60-F_{254}. Development of TLC plates was carried out under UV light or by exposure to iodine vapors.

Variable-temperature NMR experiments, unless otherwise stated, were acquired on an AMX400 Bruker instrument operating at 400.13 MHz. Low-temperature NMR spectra were measured in a mixture of trichlorofluoromethane: dichloromethane (85:15). The high-temperature NMR spectra on *ter*-thiophene with hexyl or butyl substituents were measured in toluene-d_8. Typically, the experiments were acquired on 16 K data sets, using a sweep width of 10 ppm and 32 scans. The temperature of the probe, monitored with a thermocouple, is believed to be accurate to 0.1 K.

All reactions, unless otherwise stated, were performed under a nitrogen or argon atmosphere. Glassware was placed in an oven at 110 °C for at least 12 h and subsequently dried under vacuum with a Bunsen burner. Solvents were dried using standard protocols. Butyllithium solutions were titrated prior to use with a 1M solution of 1-butanol in xylenes using anhydrous 1,10-phenanthroline as an indicator. $CuCl_2$ was dried at 130 °C for 24 h under vacuum.

Microanalyses were performed by M. K. Yang of the Simon Fraser University microanalytical laboratory.

Ab initio MO calculations were performed using General Atomic and Molecular Electronic Structure System (GAMESS)[57] version = 1 December, 1998 in a Unix environment and version = 18 March, 1997 in a Windows 95/NT environment, except for the torsional energy profiles for 2-(2′-thienyl)furan and 2-(3′-methyl-2′-thienyl)furan, which were carried out with Gaussian 94[58] revision D.1 on a Silicon Graphics workstation. All ab initio calculations were performed at the Hartree−Fock level with the 6-31G** basis set. Vibrational analysis was employed to verify the nature of the optimized structures.

Molecular mechanics calculations using the MM2−1991 force field were conducted using Tinker version 3.6, as provided by Ponder and co-workers.[59−62] Energy optimization was performed using a truncated Newton method,[62] with its default settings and a 0.000 001 kcal/mol/Ang root mean square (RMS) gradient cutoff. Torsional potential energy curves were obtained in 10° steps by constraining the inter-ring dihedral angle as defined by the heteroatoms in the system. Furthermore, the inter-ring carbon−carbon bond was constrained to be coplanar with both rings. The dihedral angles were constrained with a flat-welled harmonic potential in which no energy penalty is associated if the angle is within 0.01° of the specified value. Outside this allowed range, a harmonic potential with a force constant of 1.0 kcal/degree^2 was applied. The structures were allowed to relax during the minimization process. Since MM2-(91) lacks the required torsional parameter for an alkane carbon directly bonded to a thiophene ring, the corresponding torsional parameters for an alkene type of carbon bonded on the ring was employed instead. Using the atom types defined in MM2, the torsional parameters for 42−2−2−2 (42 for sulfur, 2 for alkene) were set to the parameters for the torsional angle defined

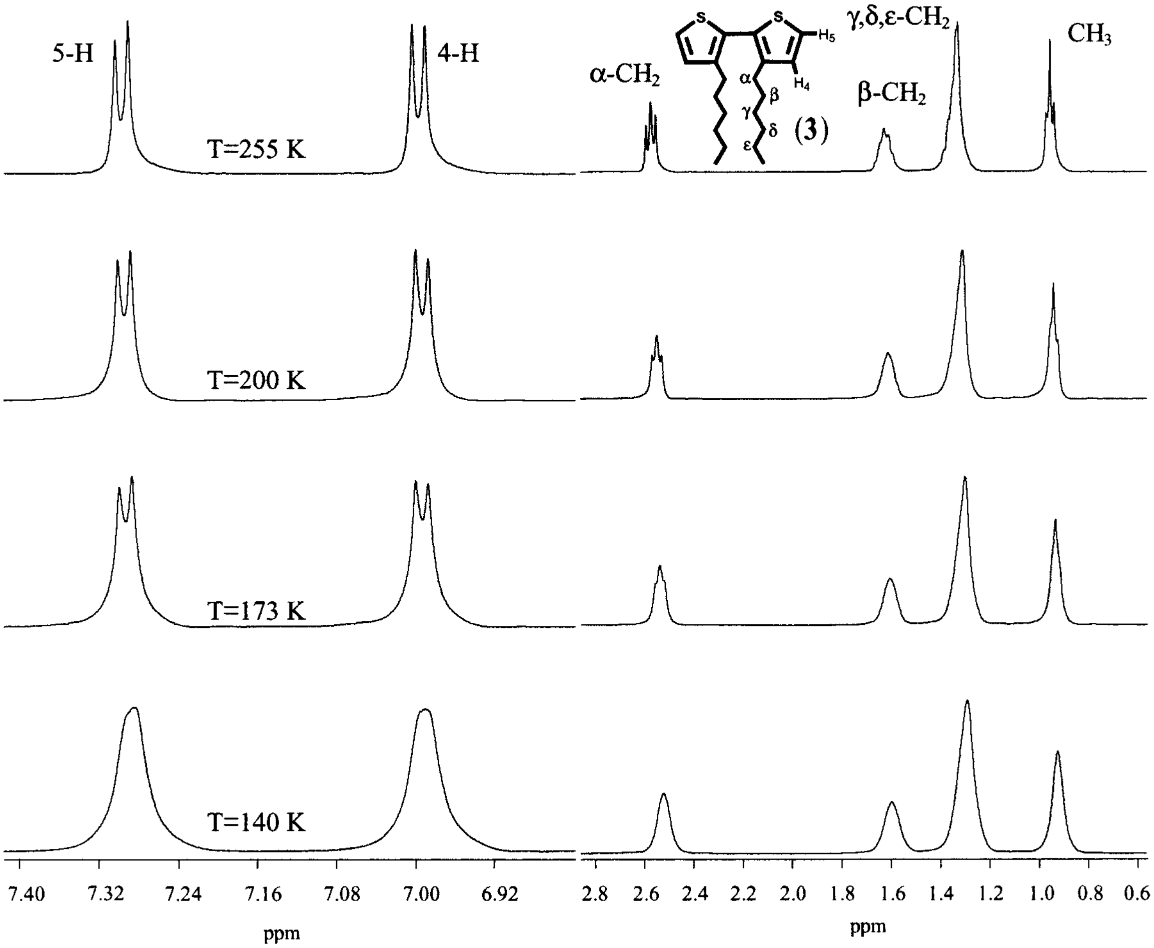


Figure 1. ^{1}H NMR spectra in $CFCl_3$:CD_2Cl_2 (85:15) of 3,3′-dihexyl-2,2′-bithiophene (**3**) as a function of temperature. Conformationally averaged spectra were observed even at temperatures as low as 140 K. Line broadening at low temperatures is consistent with the increased solvent viscosity.

by 42−2−2−1 (1 for alkane). Specifically, $\mathbf{V_1}$ was set to 0.000, $\mathbf{V_2}$ to 15.000, and $\mathbf{V_3}$ to 2.600.

Syntheses. The syntheses of the oligothiophene derivatives together with the experimental details are described in the Supporting Information. The syntheses of the oligo(thienyl)furans have been described previously.[10]

Results and Discussion

Dynamic NMR Studies. The NMR spectrum of 3,3′-dihexyl-2,2′-bithiophene (**3**) at room temperature was consistent with the presence of a conformationally averaged system. A series of low-temperature spectra (see Figure 1) is also consistent with a system that is in the fast exchange regime even at temperatures as low as 140 K. Broadening of the NMR lines is consistent with the increased solvent viscosity at lower temperatures. This was confirmed from line width measurements of the solvent (CD_2Cl_2) signal and the other signals of the compound of interest. An increase of ~6 Hz in line width of all signals, including the solvent, was observed from a temperature of 255 K to 140 K.

A second oligomer, 2-(2′-thienyl)-3-hexylthiophene (**4**), was also examined at low temperatures. No significant changes (see Figure 2) were observed in the NMR spectra as the temperature was lowered other than the expected line broadening due to solvent viscosity. The spectra were consistent with the system being in the fast exchange regime even at temperatures as low as 137 K.

The inability to observe slow or intermediate exchange rates on the chemical shift time scale with the compounds described above prompted us to examine the low-temperature behavior of 2,5-bis(2′-thienyl)-3,4-dihexylthiophene (**5**). This oligomer is analogous to that reported by Blanchard et al.,[49,50] except that it has hexyl substitutents as opposed to butyl substituents. The NMR spectra as a function of temperature (see Figure 3) are consistent with the presence of a conformationally averaged system even at temperatures as low as 149 K.

In view of this result and since Blanchard and co-workers[49,50] had attributed significant line broadening in the temperature range of 85 to 90 °C to coalescence of signals, ^{1}H NMR spectra of 2,5-bis(2′-thienyl)-3,4-dihexylthiophene (**5**) in the temperature range of 295−383 K were recorded using toluene-d_8 as the solvent. No evidence of such line broadening was observed, as illustrated by Figure S1. Therefore, 2,5-bis(2′-thienyl)-3,4-dibutylthiophene (**2**) itself was studied by variable-temperature NMR spectroscopy using toluene-d_8 as the solvent. Contrary to the results reported,[49] the NMR line widths did not vary significantly even at temperatures as high as 383 K (see Figure 4). The coalescence of the aromatic signals that they observed could not be seen. The spectra appeared to be the same below their “coalescence temperature”. In all cases, the NMR spectra reflected a system in the fast exchange regime. These results suggest that the rotational barriers are much lower than those quoted by Blanchard et al.[49,50]

Since the rate constant at coalescence is directly proportional to the chemical shift difference of spins in the two different exchanging sites and ^{13}C chemical shift differences are much larger than ^{1}H chemical shift differences, ^{13}C NMR spectroscopy

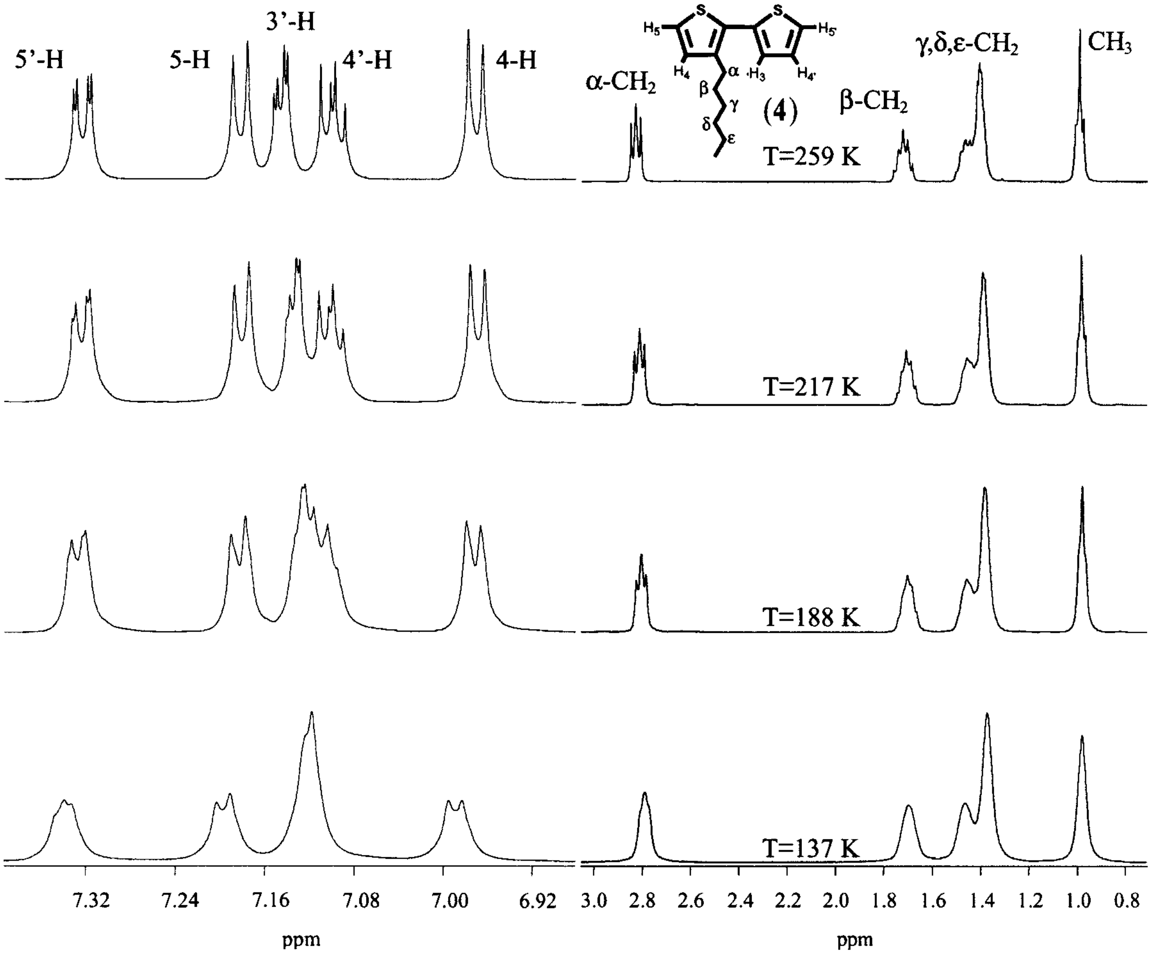


Figure 2. ^{1}H NMR spectra in $CFCl_3$:CD_2Cl_2 (85:15) of 2-(2′-thienyl)-3-hexylthiophene (**4**) as a function of temperature. Conformationally averaged spectra were observed even at temperatures as low as 137 K. Line broadening at low temperatures is consistent with the increased solvent viscosity.

should be suitable for observation of coalescence at higher temperatures. The ^{13}C NMR spectra of 2,5-bis(2′-thienyl)-3,4-dihexylthiophene (**5**) as a function of temperature were found to be consistent with a system in the fast exchange regime on the ^{13}C NMR time scale even at temperatures as low as 164 K (see Figure 5). The variable-temperature ^{1}H NMR and ^{13}C NMR spectra therefore indicate that the barriers to conformational interchange in oligothiophenes are too low to be measured by dynamic NMR spectroscopy. The conclusions reported by Muguruma et al.[51] about the high barriers in tetrathiophenes can also be questioned and are likely a result of the misinterpretation of the effects of chemical-shift changes with temperature.

Theoretical Studies

Ab Initio Calculations. *Torsional Energy Profiles for the 2,2′-Bithiophene System.* The ab initio inter-ring torsional energy profiles were obtained by scanning the S−C−C−S torsion angle in 10° steps. Figure 6 depicts the energy profile for 2,2′-bithiophene (**1**) and its alkyl substituted derivatives (**9**, **10**, and **14**). The relative stability of molecular conformations is determined by the balance of two competing inter-ring energy terms—steric repulsion that minimizes at a torsion angle of about 90° and conjugative stabilization that reaches its maximum for planar structures (0° and 180°) and vanishes at 90°. It can be concluded from Figure 6 that the stable cis and trans conformers of 2,2′-bithiophene (**1**) are not fully coplanar but, rather, are twisted due to the steric interactions, with dihedral angles of about 40° and 150°, respectively. The cis and trans conformers are more stable than the corresponding fully coplanar cis and trans conformations by about 1.1 and 0.3 kcal/mol, respectively (see Table 1). The trans conformer was more stable than the cis conformer by approximately 0.7 kcal/mol. The energy barrier for cis to trans interconversion is on the order of 1.0 kcal/mol. Introduction of a methyl substituent at the 4 position did not significantly alter the energy profile and the energy barrier (1.1 kcal/mol) remained practically the same for cis to trans interconversion. On the other hand, the steric interactions increased significantly when the methyl subtituent was located at the 3 position. In this case, the fully coplanar cis and trans conformations were greatly destabilized by approximately 2.8 and 1.7 kcal/mol with respect to the stable cis (60°) and trans (120°) conformers, respectively. The cis conformer was more stable than the trans conformer by approximately 0.06 kcal/mol, and the energy barrier for cis to trans interconversion was only about 0.2 kcal/mol.

A similar trend was observed for 2,2′-bithiophene (**1**) substituted at the 3 position with an ethyl group (**14**). The steric interactions for the cis and trans conformers were enhanced even more to the point that the potential energy well, in the region between 70° and 110°, was virtually flat. The cis (0°) and trans (180°) conformations were destabilized by approximately 4.1 and 3.0 kcal/mol with respect to the cis-like (∼70°) and trans-like (∼110°) conformers, respectively. The cis-like conformer was only slightly more stable (0.05 kcal/mol) than the trans-like conformer.

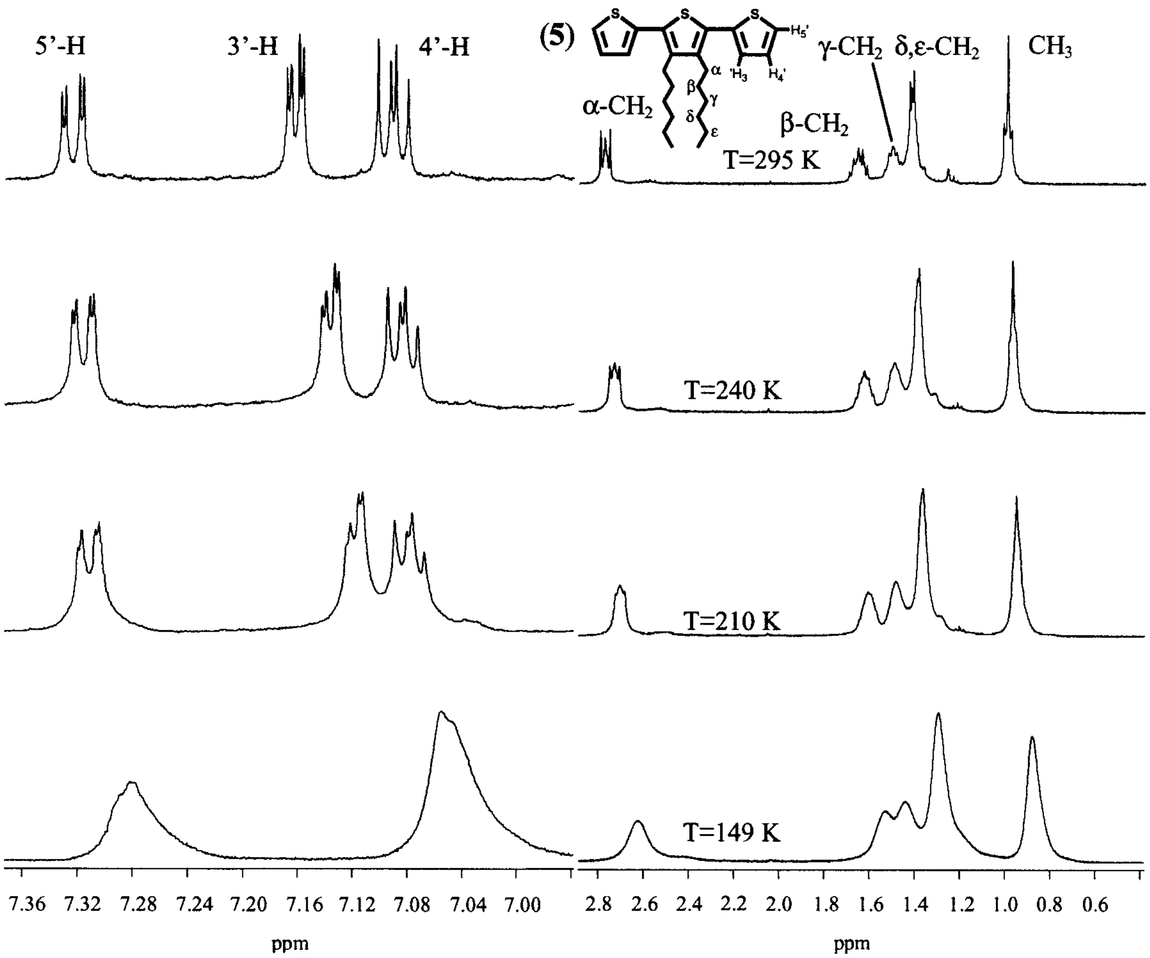
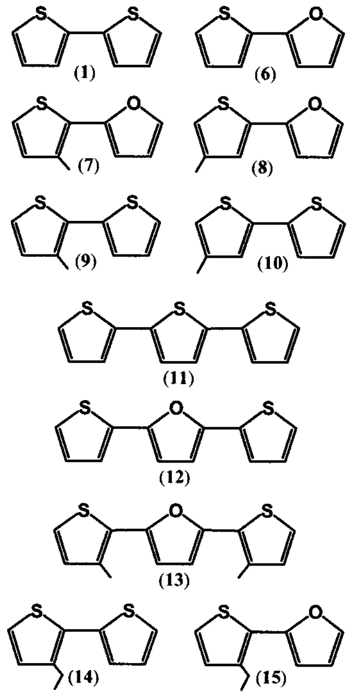


Figure 3. ^{1}H NMR spectra in $CFCl_3$:CD_2Cl_2 (85:15) of 2,5-bis(2′-thienyl)-3,4-dihexylthiophene (**5**) as a function of temperature. Conformationally averaged spectra were observed even at temperatures as low as 149 K. Line broadening at low temperatures is consistent with the increased solvent viscosity.

CHART 3



Torsional Energy Profiles for the 2-(2′-Thienyl)Furan System. In contrast to 2,2′-bithiophene (**1**), 2-(2′-thienyl)furan (**6**) exhibits two almost fully coplanar cis and trans conformers, the trans conformer being more stable than the cis conformer by approximately 0.56 kcal/mol (see Figure 7). Inter-ring steric repulsion is presumably weaker in (**6**) because of the smaller van der Waals radius of oxygen. The energy barrier for conformational interconversion was found to be 3.6 kcal/mol (see Table 2), approximately twice as large as the value obtained for 2,2′-bithiophene (**1**). A methyl substituent at the 4 position (**8**) in the thiophene ring of 2-(2′-thienyl)furan (**6**) did not have any appreciable effects on the potential energy curve. A significant effect was observed when the methyl substituent was placed at the 3 position (**7**). Two twisted cis and trans conformers were observed at dihedral angles of 20° and 150°, respectively, as a result of the increased steric interactions. Moreover, the cis conformer was found to be more stable than the trans conformer by about 0.25 kcal/mol. The energy barrier for cis to trans interconversion decreased to a value of 1.8 kcal/mol. This decrease in the magnitude of the energy barrier is consistent with increased destabilization of the fully coplanar cis and trans conformations as a result of steric interactions. Replacing the methyl substitutent by an ethyl group at the 3 position led to a greater destabilization of the cis conformer. The trans (40°) conformer was now more stable than the cis (140°) conformer by 0.3 kcal/mol. The magnitude of the potential energy barrier for conformational interconversion was on the order of 1.2 kcal/mol.

Effect of Oligomer Length on the Inter-Ring Torsional Energy. To determine whether the torsional energy profiles for systems

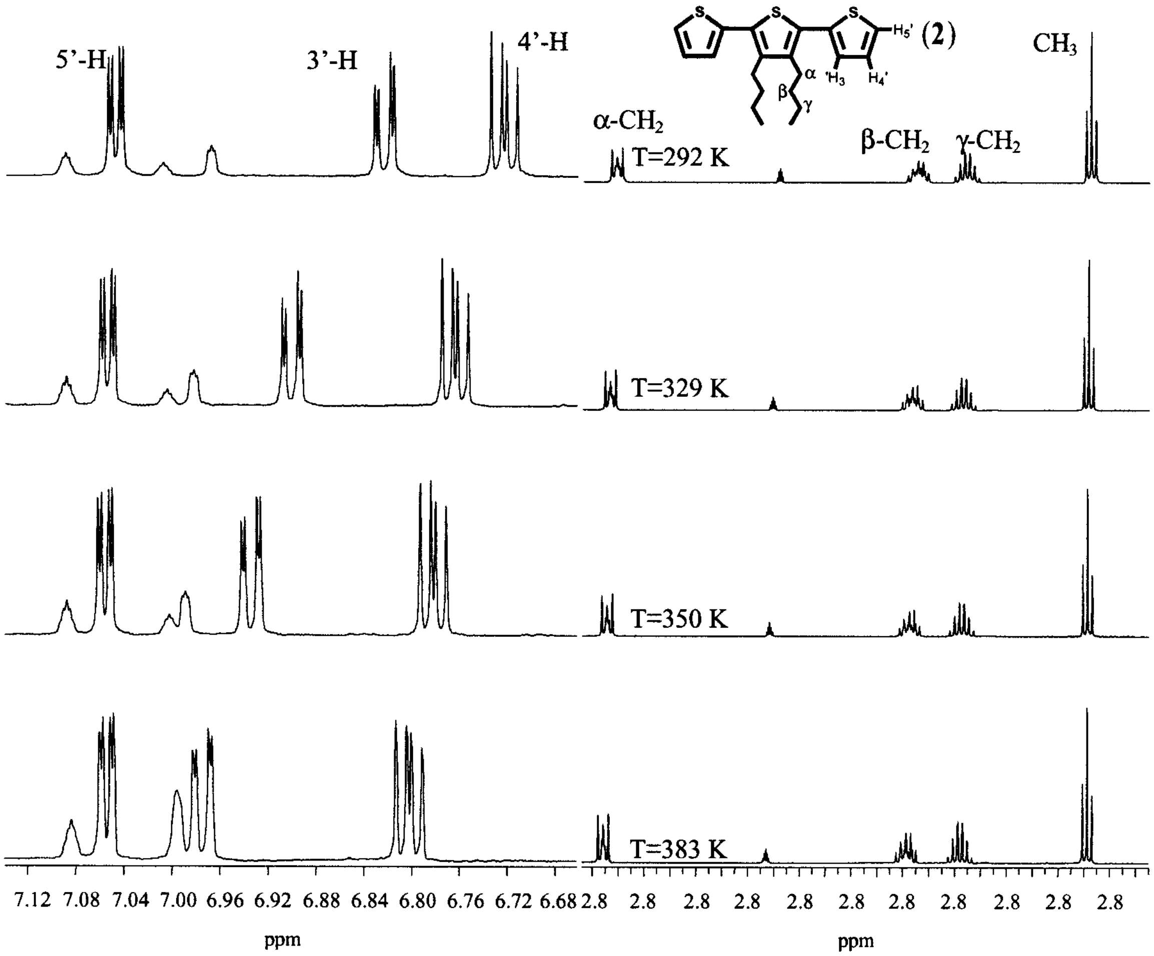


Figure 4. ^{1}H NMR spectra in toluene-d_8 of 2,5-bis(2′-thienyl)-3,4-dibutylthiophene (**2**) as a function of temperature. Conformationally averaged spectra were observed in all cases, and no significant line broadening was observed at high temperatures.

with only two heteroaromatic rings were suitable as models for longer oligomers, the minimum-energy conformers and transition states for *ter*-thiophene (**11**), 2,5-bis(2′-thienyl)furan (**12**) and 2,5-bis(3′-methyl-2′-thienyl)furan (**13**) were calculated. The results are shown in Figures S2−S4.

The torsional barriers for *ter*-thiophene (**11**) (Figure S2) were slightly greater than those found for 2,2′-bithiophene (**1**). The cis-cis to cis-trans and cis-trans to trans-trans barriers were determined to be 1.05 and 1.11 kcal/mol, respectively. This represents an increase of approximately 0.07 kcal/mol over the magnitude of the barrier for cis to trans interconversion in 2,2′-bithiophene (**1**) (1.04 kcal/mol). The energy barriers for the reverse processes, cis−trans to cis−cis and trans−trans to cis−trans, were determined to be 1.89 and 1.88 kcal/mol, respectively. The highest of these barriers was approximately 0.17 kcal/mol greater than that associated with the trans to cis exchange in 2,2′-bithiophene (**1**).

The same pattern was observed for 2,5-bis(2′-thienyl)furan (**12**) (Figure S3). The torsional barriers for the cis−cis to cis−trans and cis−trans to trans−trans exchange were determined to be 3.11 and 3.19 kcal/mol, respectively. The highest of these barriers was 0.14 kcal/mol greater than that for cis to trans interconversion in 2-(2′-thienyl)furan (**6**). Conformational exchange in the opposite direction, cis-trans to cis−cis and trans−trans to cis−trans, gave torsional barriers of 3.87 and 3.65 kcal/mol, respectively. The highest of these, was only 0.27 kcal/mol greater than the barrier for trans to cis exchange in 2-(2′-thienyl)furan (**6**). It can therefore be concluded that the rotational barriers do not change as the length of the oligomer chain increases.

In the case of **13**, the presence of methyl substituents at the 3 positions on both thiophene rings led to a decrease in the height for the torsional energy barriers. This is consistent with the pattern observed for the biheterocyclic systems where introduction of an alkyl group at the 3 position destabilized the ground-state conformations as a result of steric interactions. As illustrated in Figure S4, the inter-ring torsional energy barriers for 2,5-bis(3′-methyl-2′-thienyl)furan (**13**) for the interconversion from the cis−cis to cis−trans and cis−trans to trans−trans conformers were 1.74 and 2.05 kcal/mol, respectively. The largest was only 0.25 kcal/mol greater than the energy barrier for cis to trans interconversion for 2-(3′-methyl-2′-thienyl)furan (**7**). A similar pattern was observed for conformational exchange in the opposite direction. In fact, the inter-ring torsional energy barriers for exchange starting from trans−trans to cis−trans and from cis−trans to cis−cis were 1.76 and 1.86 kcal/mol, respectively. This is to be compared to the energy barrier for trans to cis interconversion for 2-(3′-methyl-2′-thienyl)furan (**7**) which is approximately 1.55 kcal/mol. This corresponds to a maximum increase of 0.31 kcal/mol, and thus, it reinforces the conclusion that the inter-ring torsional barriers do not change as the length of the oligomer increases.

Parametrization of the MM2 Force Field. Since ab initio methods may not be applied to large systems, one needs to resort to a simpler type of calculations such as molecular mechanics

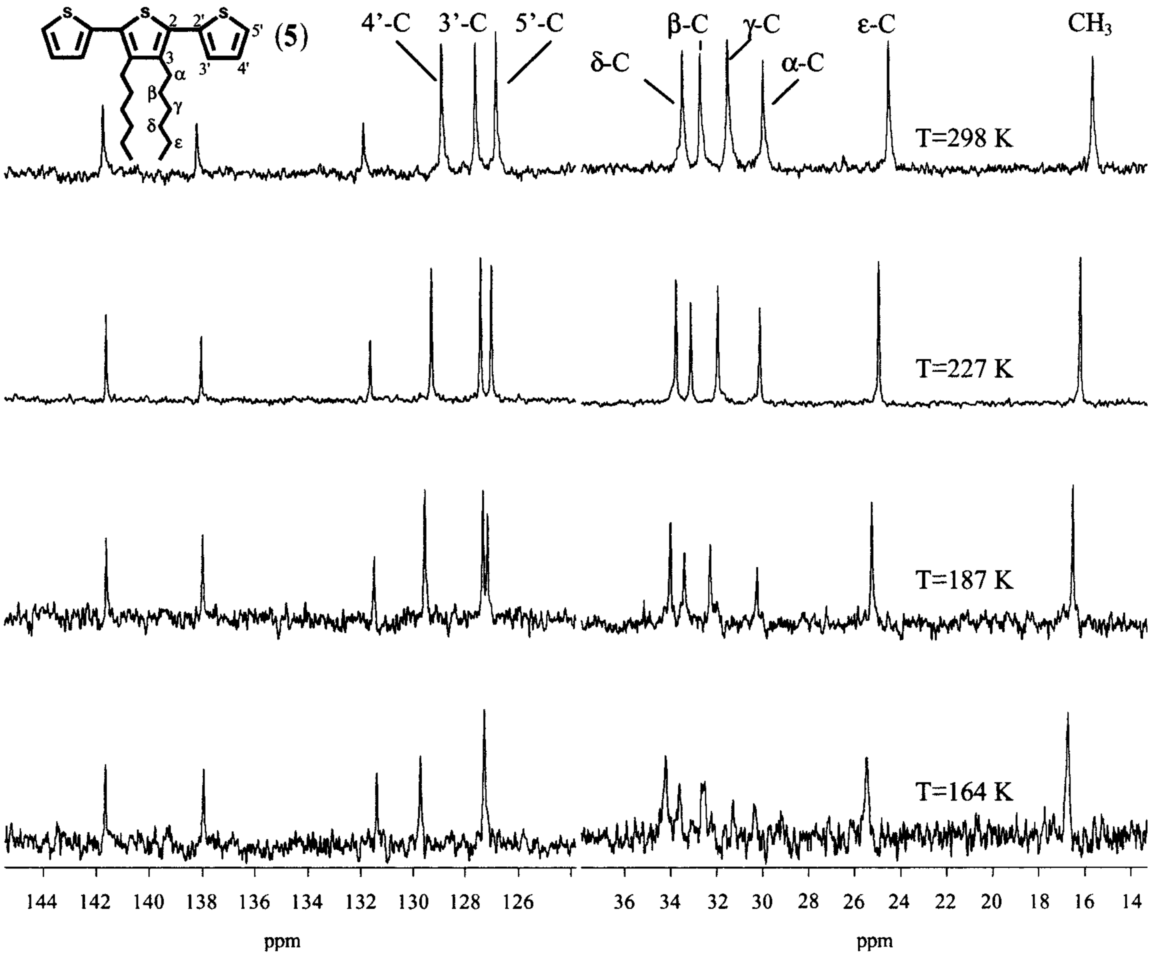


Figure 5. ^{13}C NMR spectra in $CFCl_3$:CD_2Cl_2 (85:15) of 2,5-bis(2′-thienyl)-3,4-dihexylthiophene (**5**) as a function of temperature. Conformationally averaged spectra were observed even at temperatures as low as 164 K. Line broadening at low temperatures is consistent with the increased solvent viscosity.

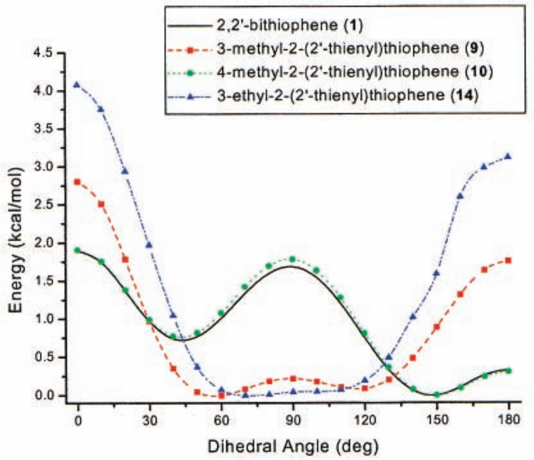
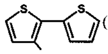
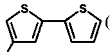
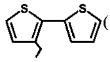


Figure 6. Ab initio 6-31G** inter-ring torsional profiles for 2,2′-bithiophene (**1**) and its alkyl derivatives **9**, **10**, and **14**.

TABLE 1: Comparison of the Main Features of the Torsional Energy Profiles for 2,2′-bithiophene (1) and Its Alkyl-substituted Derivatives (9, 10, and 14)

	DIHEDRAL ANGLE		ENERGY (kcal/mol)		
	Cis	*Trans*	*Trans* relative to *cis*	Energy Barrier (*cis* to *trans*)	Energy Barrier (*trans* to *cis*)
 (1)	44.41°	147.48°	-0.68	1.04	1.72
 (9)	56.59	118.84	0.061	0.25	0.19
 (10)	43.59	148.27	-0.72	1.10	1.82
 (14)	~70(a)	~110(a)	~-0.05(a)	N/A	N/A

(a) Values were estimated from the torsional energy profile.

calculations. This requires the choice of a suitable force field. Although the MM2 force field has been parametrized by Allinger[63] to reproduce, to a high degree of accuracy, crystal structure geometries for thiophene, furan and 2,2′-bithiophene (**1**), the inter-ring torsional energy barrier for 2,2′-bithiophene (**1**) was greatly overestimated by approximately 8.5 kcal/mol. Moreover, this force field lacked the required torsional parameters for 2-(2′-thienyl)furan (**6**) and its alkyl-substituted derivatives (**7**, **8**, **15**) and alkyl-substituted 2,2′-bithiophenes (**9**, **10**, **14**). In view of these problems, it was necessary to develop a suitable set of torsional parameters for the unsubstituted and alkyl-substituted thiophenes and (thienyl)furans for the study of the conformational behavior of these systems.

Procedure. The MM2 force field was parametrized to match as closely as possible the 6-31G** ab initio inter-ring torsional energy profiles. The MM2 inter-ring torsional energy in the force field is due to the sum of four torsional contributions: **S−C−C−X**, **S−C−C−C**, **C−C−C−C**, and **C−C−C−X** (X= S, O). Only the torsional energy parameters for the torsion angle **S−C−C−X** defined by the heteroatoms were modified in order to have the smallest possible impact on the original MM2 force field. Each of these torsional components is

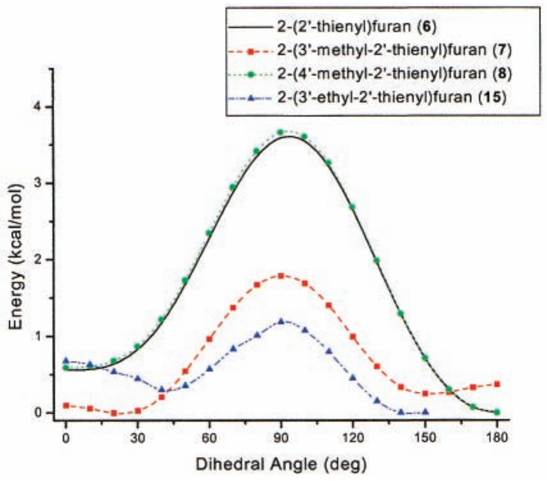
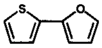
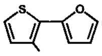
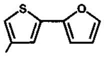
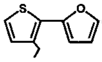


Figure 7. Ab initio 6-31G** inter-ring torsional profiles for 2-(2′-thienyl)furan (**18**) and its alkyl derivatives **7**, **8**, and **15**.

TABLE 2: Comparison of the Main Features of the Torsional Energy Profiles for 2-(2′-thienyl)furan (6) and Its Alkyl-substituted Derivatives (7, 8, and 15)

	DIHEDRAL ANGLE		ENERGY (kcal/mol)		
	Cis	*Trans*	*Trans* relative to *cis*	Energy Barrier (*cis* to *trans*)	Energy Barrier (*trans* to *cis*)
 (6)	4.95°	179.72	-0.56	3.05	3.61
 (7)	~20(a)	~150(a)	~0.25(a)	~1.80(a)	~1.55(a)
 (8)	4.84	-179.95	-0.64	3.10	3.74
 (15)	~40(a)	~140(a)	~0.30(a)	~0.88(a)	~1.19(a)

(a) Values were estimated from the torsional energy profiles.

described by the following equation:

$$\mathbf{V}(\phi) = \frac{1}{2}\mathbf{V_1}(1 + \cos\phi) + \frac{1}{2}\mathbf{CV_2}(1 - \cos(2\phi)) + \frac{1}{2}\mathbf{V_3}(1 + \cos(3\phi)) \quad (1)$$

where $\mathbf{V_1}$, $\mathbf{V_2}$, and $\mathbf{V_3}$ are torsional constants and **C** is a scaling factor dependent on the degree of conjugation.

As a first step, the **S−C−C−X** torsion energy contribution to the total MM2 energy was excluded by setting to zero the appropriate torsion parameters, and the modified MM2 torsion profile was calculated in 10° steps. Then, this energy profile was subtracted from the ab initio energy profile. The resultant difference is attributed to the suppressed **S−C−C−X** torsion term and can be used to estimate the respective torsion parameters. This was achieved by fitting the resultant energy curve, via a least squares procedure, to eq 2, which is a MM2 torsional energy function modified by addition of a constant term $\mathbf{V_4}$:

$$\mathbf{V}(\phi) = \frac{1}{2}\mathbf{V_1}(1 + \cos\phi) + \frac{1}{2}\mathbf{CV_2}(1 - \cos(2\phi)) + \frac{1}{2}\mathbf{V_3}(1 + \cos(3\phi)) + \mathbf{V_4} \quad (2)$$

The extra $\mathbf{V_4}$ term represents the difference in the choice of the zero-energy reference points for ab initio and MM2 calculations and is ignored in subsequent MM2 calculations.

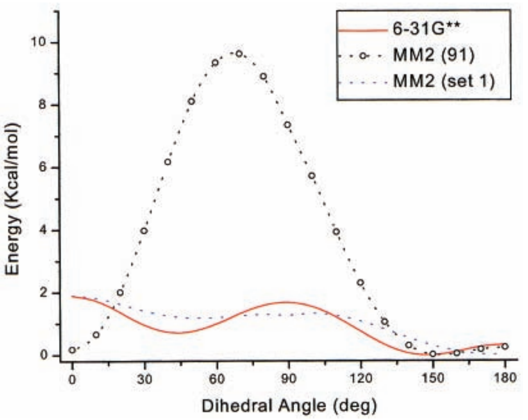


Figure 8. Ab initio 6-31G** (solid line) and two MM2 inter-ring torsional profiles for 2,2′-bithiophene (**1**). The dashed line with open circles represents an MM2 calculation with zero S−C−C−S torsional parameters. The dashed line represents an MM2 calculation with the adjusted (set 1) S−C−C−S parameters.

TABLE 3: S−C−C−X Torsional Parameters for the Parent Compounds (1) and (6) (Set 1)

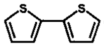
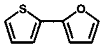
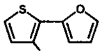
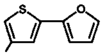
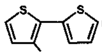
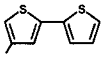
	V_1	V_2	V_3
 (1)	-0.274	-22.754	5.734
 (6)	-1.148	-11.952	2.963

TABLE 4: S−C−C−X Torsional Parameters for the Methyl-Substituted Compounds (7)−(10) (Set 2)

	V_1	V_2	V_3
 (7)	-2.564	-13.356	2.079
 (8)	-1.034	-12.041	3.020
 (9)	-1.603	-22.725	5.423
 (10)	-0.263	-22.168	5.742

The least squares procedure produces the $\mathbf{V_1}$, $\mathbf{CV_2}$, and $\mathbf{V_3}$ parameters directly. Parameter $\mathbf{V_2}$ is readily obtained from $\mathbf{CV_2}$ and the known value of the scaling factor **C** available from MM2.

Parametrization of MM2 for 2,2′-Bithiophene and 2-(2′-Thienyl)Furan. Parametrization of the MM2 torsional energy parameters for the inter-ring dihedral angles **S−C−C−X** in the unsubstituted 2,2′-bithiophene (**1**) and 2-(2′-thienyl)furan (**18**) was performed in accordance with the procedure outlined in the previous section. The parameters thus obtained are listed in Table 4. Figures 8 and 9 compare the ab initio profiles for 2,2′-bithiophene (**1**) and 2-(2′-thienyl)furan (**6**) with the MM2 profiles obtained with the old and new sets of torsional parameters. It is clear that a significant improvement is achieved both in barrier heights and the relative order of stabilities of cis and trans isomers.

Parametrization of MM2 for Substituted Derivatives of 2-(2′-Thienyl)Thiophenes and 2-(2′-Thienyl)Furans. Since there is a great deal of interest in alkyl substituted thiophenes, it is important to test whether the torsional parameters obtained in the previous section for the parent 2,2′-bithiophene (**1**) and 2-(2′-

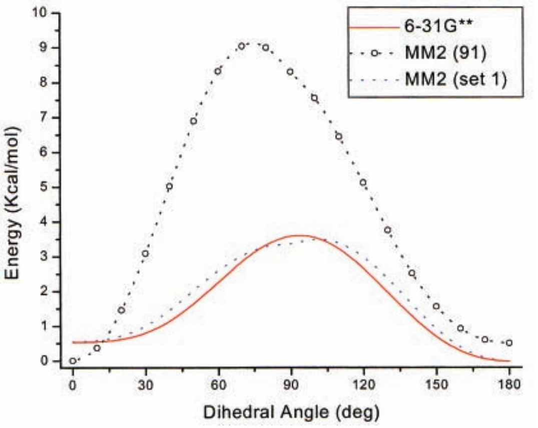


Figure 9. Ab initio 6-31G** (solid line) and two MM2 inter-ring torsional profiles for 2-(2′-thienyl)furan (**6**). The dashed line with open circles represents an MM2 calculation with zero S−C−C−O torsional parameters. The dashed line represents an MM2 calculation with the adjusted (set 1) S−C−C−O parameters.

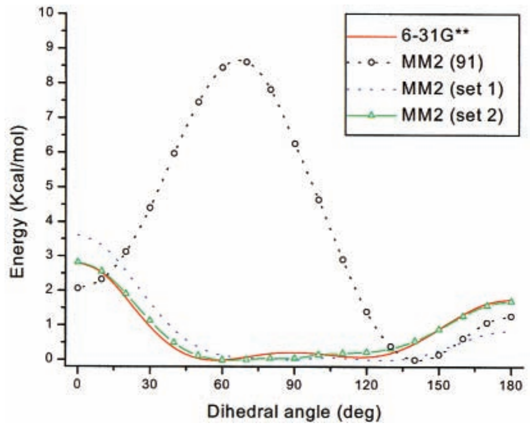


Figure 10. Ab initio 6-31G** and three MM2 inter-ring torsional profiles for 2-(3′-methyl-2′-thienyl)thiophene (**9**) with zero and adjusted (sets 1 and 2) S−C−C−S parameters.

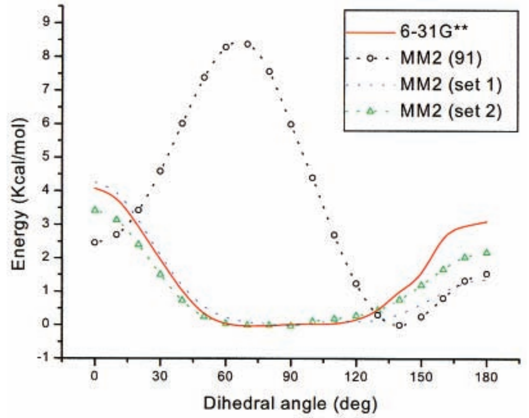


Figure 11. Ab initio 6-31G** and three MM2 inter-ring torsional profiles for 2-(3′-ethyl-2′-thienyl)thiophene (**14**) with zero and adjusted (sets 1 and 2) S−C−C−S parameters.

thienyl)furan (**6**) predict correctly the inter-ring torsional profiles for the substituted systems. Figures 10−15 compare ab initio torsion profiles with the MM2 profiles obtained with the old and new sets of torsional parameters, one fitted for a nonsubstituted system (Table 3, set 1) and another fitted for a 3- or 4-methyl-substituted system (Table 4, set 2). The MM2 force field (91) does not have the torsional parameters for an alkane type of carbon atom directly attached to a thiophene ring. The

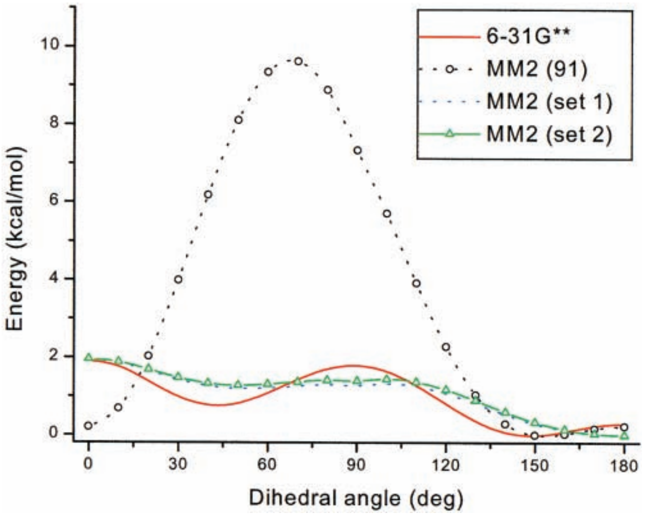


Figure 12. Ab initio 6-31G** and three MM2 inter-ring torsional profiles for 2-(4′-methyl-2′-thienyl)thiophene (**10**) with zero and adjusted (sets 1 and 2) S−C−C−S parameters.

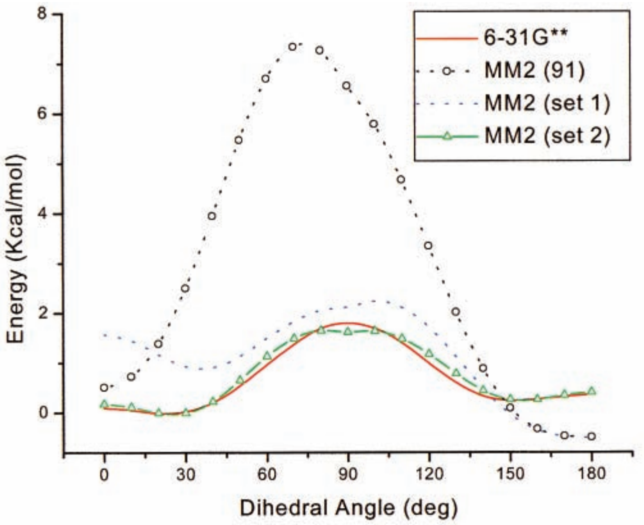


Figure 13. Ab initio 6-31G** and three MM2 inter-ring torsional profiles for 2-(3′-methyl-2′-thienyl)furan (**7**) with zero and adjusted (sets 1 and 2) S−C−C−O parameters.

missing 42−2−2−1 torsional parameters were approximated by the set of parameters for an alkene type of carbon bonded to the thiophene ring ($\mathbf{V_1} = 0.000$, $\mathbf{V_2} = 15.000$, and $\mathbf{V_3} = 2.600$). It can be seen from Figures 10−15 that the set of the “unsubstituted” S−C−C−X torsional parameters (set 1) improves substantially the quality of the MM2 inter-ring torsion profiles in the substituted systems. It is also clear that the “methyl-substituted” parameters (set 2) give only a marginal improvement. Taken together, the evidence confirms the transferability of the new set of parameters and suggests that the parameters can be used for other 3- and 4-alkyl-substituted thiophene systems as well.

Conclusions

Dynamic NMR spectra of several substituted trithiophenes were consistent with the presence of systems in the fast exchange regime even at temperatures as low as 140 K. Thus, for example, the conformational exchange of 2,5-bis(2′-thienyl)-3,4-dihexylthiophene (**5**) proved to be fast even on the ^{13}C NMR time scale at temperatures as low as 164 K. We conclude, therefore, that this system possesses low rotational barriers which lie

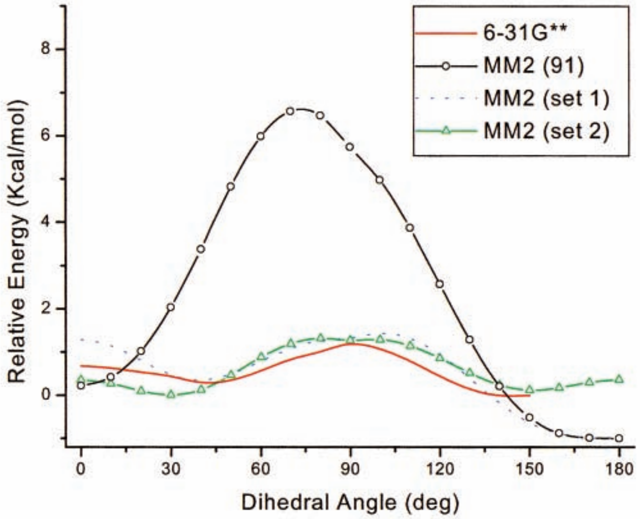


Figure 14. Ab initio 6-31G** and three MM2 inter-ring torsional profiles for 2-(3′-ethyl-2′-thienyl)furan (**15**) with zero and adjusted (sets 1 and 2) S−C−C−O parameters.

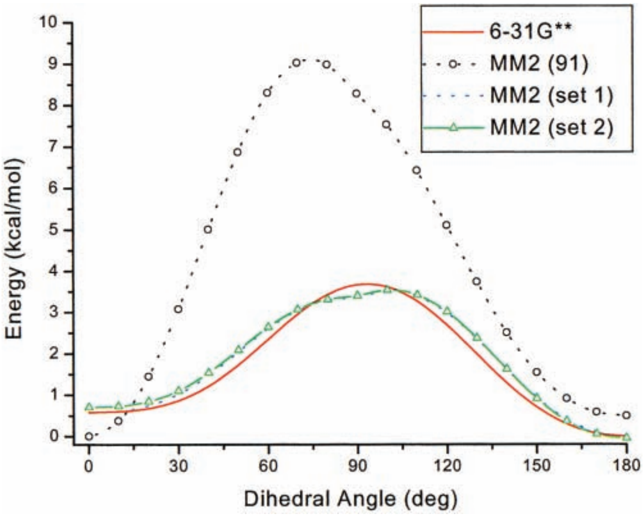


Figure 15. Ab initio 6-31G** and three MM2 inter-ring torsional profiles for 2-(4′-methyl-2′-thienyl)furan (**8**) with zero and adjusted (sets 1 and 2) S−C−C−O parameters.

outside the practical limits for measurement via DNMR spectroscopy. Reexamination of the 2,5-bis(2′-thienyl)-3,4-dibutylthiophene system (**2**) showed no evidence of coalescence in the temperature range of 85 to 90 °C, as described previously by Blanchard et al.[49,50] In fact, the ^{1}H NMR spectrum at much lower temperatures was consistent with the presence of a conformationally averaged spectrum. The low values of the ab initio inter-ring torsional energy barriers in the thiophene systems are in agreement with the observations from DNMR spectroscopy.

The MM2 (91) force field was parametrized to reproduce ab initio inter-ring torsional energy curves obtained at the 6-31G** level for 2,2′-bithiophene (**1**), 2-(2′-thienyl)furan (**6**), and their 3-methyl, 4-methyl-, and 3-ethyl- substituted thiophene derivatives (**7**−**10**, **14**, and **15**). This reparametrized MM2 force field has been used in our molecular dynamics conformational studies of oligothiophenes and oligo(thienyl)furans.[55]

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Supporting Information Available: Experimental details for the syntheses of the oligothiophene derivatives, variable-temperature ^{1}H NMR spectra for 2,5-bis(2′-thienyl)-3,4-dihexylthiophene (**5**) and 2,5-bis(2′-thienyl)-3,4-dibutylthiophene (**2**), and ab initio torsional profiles for *ter*-thiophene (**11**), 2,5-bis-(2′-thienyl)furan (**12**) and 2,5-bis(3′-methyl-2′-thienyl)furan (**13**). This material is available free of charge via the Internet at http://pubs.acs.org.

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