Molecular and Electronic Structures of Heteroaromatic Oligomers: Model Compounds of Polymers with Quantum-Well Structures

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Conformational preferences of 2,2′-bithiophene, 2-(2-thienyl)pyrrole, and *N*-methyl-2-(2-thienyl)-pyrrole have been investigated by means of computational methods. Calculations were performed at the ab initio HF/6-31G(d) and MP2/6-31G(d) levels and, additionally, with the density functional B3-LYP/6-31G(d). The results indicate that 2-(2-thienyl)pyrrole behaves similarly to the 2,2′-bithiophene. Thus, two minimum energy conformations were found for each compound, which correspond to *anti-gauche* and *syn-gauche*. Such minima are separated by barriers of about 1.7 and 1.3 kcal/mol at the HF and MP2 levels. On the contrary, the preferences found for *N*-methyl-2-(2-thienyl)pyrrole were different, giving an almost negligible energy barrier between the two minimum energy conformations. Furthermore, at the MP2 level the *anti-gauche* and *syn-gauche* minimum energy conformations present an inter-ring dihedral of 135° and 68°, respectively, displaying deviations greater than those found in 2,2′-bithiophene and 2-(2-thienyl)pyrrole. The conformational analysis was extended to the tricyclic compound *N*-methyl-2,5-di(2-thienyl)pyrrole. For this molecule, a contour map of the conformational energy as a function of the inter-ring dihedral angles was computed at the HF/6-31G(d) level. Minimum energy conformations were subsequently computed at the same level of theory. Results were in agreement with those obtained for the bicyclic compound *N*-methyl-2-(2-thienyl)pyrrole. Thus, the inter-ring dihedral angles of the minimum energy conformations present a large distortion with respect to the planarity, and such minimum energy conformations are separated by almost negligible energy barriers. Finally, *N*-hexyl-2,5-di-(2-thienyl)pyrrole radical cation was observed by EPR spectroscopy. This is the first time that a mixed trimer of thiophene and pyrrole is oxidized to its radical cation and detected by means of EPR spectroscopy. The spectrum seems to be symmetric, which is accounted for by a fast inter-conversion between conformers. This supports the small energy barrier calculated between minima for the bicyclic and tricyclic compounds. Overall, the results presented in this work indicate that *N*-methylpyrrole rings are able to induce large rotational deffects in [...-(pyrrole)$_n$-(thiophene)$_n$-...] block copolymers.

Introduction

Organic conducting polymers have been the subject of major research activity during the last years.[1,2] Among them, poly(thiophene) and its derivatives have been particularly investigated due to the fact that they exhibit interesting electric and nonlinear optical properties, as well as excellent environmental stability.[1,3] Thus, during the last years we have carried out a systematic effort

aimed at investigating the molecular and electronic structure of the poly(thiophene)'s constituent oligomers.[4–16]

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Semiconducting superlattices or quantum-well structures have been the object of great interest, since they have enhanced conducting and optical properties.[17] These structures have been extensively investigated in inorganic compounds and consist of alternating layers of two kinds of semiconductors with different bandgaps (ionization potentials and/or electron affinities).

Quantum-well structures have been introduced into polymer chemistry and physics, through block-conjugated copolymers. Thus, theoretical and experimental investigations on superlattice structures made of block-conjugated copolymers have been reported in the past few years.[18–22] Between such compounds, block copolymers of pyrrole and thiophene have displayed unique properties due to their excellent confinement characteristics of the π-conjugated electrons. Their large degree of confinement is because the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) reside largely on the pyrrole and thiophene units, respectively. Furthermore, it is considered that the degree of confinement of the π-electrons improves with an increase in the size of the blocks. This is explained in terms of raising the HOMO level and lowering the LUMO level.[23,24] Thus, [...-(pyrrole)$_n$-(thiophene)$_n$-...] regular block copolymers with n larger than 3 are promising tunable quantum-well structures.

On the other hand, conjugated polymers and particularly poly(thiophene) develop charged defects in the oxidized state, polarons (radical cations), and bipolarons (dications), which are responsible for the conducting properties of these systems.[25] Recent electrochemical studies[26,27] in mixed thiophene–pyrrole and thiophene–N-alkylpyrrole oligomers indicate that such compounds are also able to generate radical cations and dications by oxidization. Furthermore, in some cases the presence of a more easily oxidizable pyrrole units results in the formation of a radical trication species.[26] The knowledge of the spin density distribution in such small oligomers would be useful to understand the distribution of polarons over [...-(pyrrole)$_n$-(thiophene)$_n$-...] block copolymers.

In this work, we combined theoretical and experimental methodologies to study the molecular and electronic structures of small heterocycle oligomers containing pyrrole and thiophene units. We initiate our work with a systematic comparison between the molecular structures of 2,2′-bithiophene (**1**) and its monopyrrolic analogues 2-(2-thienyl)pyrrole (**2**) and N-methyl-2-(2-thienyl)-pyrrole (**3**). The geometries and relative energies of the

minimum energy conformations, rotational profiles, and torsional barriers of three such simple model bicycles were determined at the ab initio Hartree–Fock (HF), post-Hartree–Fock, i.e., including electron correlation effects by second-order Møller–Plesset perturbation theory (MP2), and density functional theory (DFT) levels. The results permit an understanding of the rotational defects introduced by the pyrrole units along the block copolymers backbone, which interrupt and weaken the extent of π-conjugation between segments of thiophene rings. In a second stage, we extend the structural implications of the rotational defects to tricyclic compounds. Thus, conformational preferences of N-methyl-2,5-di(2-thienyl)-pyrrole (**4**) were computed using ab initio quantum mechanical methods. The results are compared with those recently reported for 2,2′,5′,2″-terthiophene[10,14] (**5**). Finally, we investigate the electronic structure of the monopyrrolic tricycle N-hexyl-2,5-di(2-thienyl)pyrrole radical cation (**6**[•+]) by electron paramagnetic resonance (EPR) spectroscopy. EPR is a powerful method to study the properties of semioccupied molecular orbitals. Thus, information on the HOMO of a molecule is obtained through formation of its radical cation. Furthermore, theoretical estimations of the atomic spin densities have been carried out using semiempirical quantum mechanical methods. Results are compared with those previously reported for homocyclic thiophene oligomers.[6,28–30]
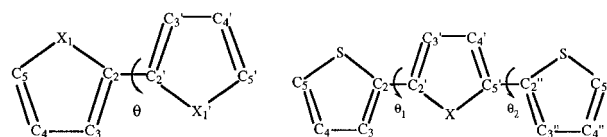
1 ; $X_1 = X_1' = S$

2 ; $X_1 = S$, $X_1' = N$-H

3 ; $X_1 = S$, $X_1' = N$-CH$_3$

4; $X = N$-CH$_3$

5; $X = S$

6; $X = N$-C$_6$H$_{13}$

Computational Methods

Compounds **1–3** were investigated using both ab initio quantum mechanical methods and DFT functionals. Quantum mechanical calculations were carried out at both HF and MP2 levels of theory. Becke's three-parameter hybrid functional with the nonlocal correlation provided by the Lee, Yang, and Parr functional (B3-LYP)[31] was used in DFT calculations. All the calculations were performed with the standard 6-31G(d)[32] (d-functions on S, N, and C atoms) basis set. Equilibrium structures for the bicyclic systems were optimized without any constraint. Minimum energy structures were characterized as such by calculating and diagonalizing the Hessian matrix and ensuring they do not have a negative value.

The rotational profiles of **1–3** were computed spanning the torsional angle between the planes of the two rings (θ) in steps of 30°. A flexible rotor approximation was used in all cases, the molecular geometry of each point of the rotational profile being optimized at a fixed θ value.

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A contour map of the conformational energy as a function of the dihedral angles θ_1 and θ_2 was generated for **4**. The potential energy surface was evaluated at the ab initio HF/6-31G(d) level using a grid of 30°. The interring dihedral angles were held fixed for each point of the potential energy surface, while all other geometrical parameters were fully relaxed. To find all the minimum energy conformations of **4**, structures located in the low-energy regions of the potential energy surface were used as starting points in full geometry optimizations.

The spin densities for **4**[.+] were computed at the semiempirical AM1[33] level, which is known to provide reasonable results.[34] For this purpose, molecular geometries obtained from geometry optimizations were used. Spin densities were computed using the keyword ESR.

Ab initio calculations were performed with the Gaussian-94[35] computer program. AM1 calculations were performed with the MOPAC93 Revision 2[36] program. All the calculations were run on a CONVEX C3480 of the Centre Europeu de Paral·lelisme de Barcelona (CEPBA) and on the Cluster of Digital Alpha Servers (21004/275) at the Computer Center of the University of Vienna and on local RISC 6000/550 and Silicon Graphics worstations at the Institute of Theoretical Chemistry and Radiation Chemistry of the University of Vienna.

Experimental Methods

EPR Experiments. EPR experiments were recorded using a Varian E/109 spectrometer working in the X-band and using a Varian E 257 temperature controller. The EPR simulations were carried out with the WinSIM program from the National Institute of Environmental Health Sciences (NIEHS). Diluted solutions of the oligomers in the appropiate solvent with or without oxidant were degassed by passing a stream of dry argon through the solution to remove oxygen before introducing into the cavity of the spectrometer. Photolysis into the cavity was performed by using an Oriel 500-W high-pressure mercury arc.

^{1}H and ^{13}C NMR spectra were determined at 200 MHz and 50 MHz, respectively, with a Varian Gemini 200 MC. 2,5-Di-(2-thienyl)pyrrole was synthesized as described in the literature.[37]

N-Hexyl-2,5-di(2-thienyl)pyrrole (4) was prepared according to a described procedure to prepare N-methyl-2,5-di-(2-thienyl)pyrrole.[38] A solution of 1,4-bis(2-thienyl)-1,4-butanedione (7.4 g; 30 mmol), hexylamine (3.31 g; 33 mmol), and propionic acid (4 mL) in benzene (90 mL) was refluxed under nitrogen in a flask equipped with a Dean−Stark trap for 2 days. The mixture was concentrated in vacuo, treated with saturated NaHCO$_3$ solution (30 mL) and water, and extracted with CH$_2$Cl$_2$ (30 mL). The organic layer was washed with HCl (30 mL), a saturated solution of NaHCO$_3$ (30 mL), and brine (30 mL) and dried (Na$_2$SO$_4$). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica (10:1; hexane/CH$_2$Cl$_2$) to give N-hexyl-2,5-bis(2-thienyl)pyrrole (7.7 g; 98%) as an oil: ^{1}H NMR (CDCl$_3$) δ (ppm) 0.8 (t, 3H, $J = 6.0$ Hz), 1.11 (m, 6H),

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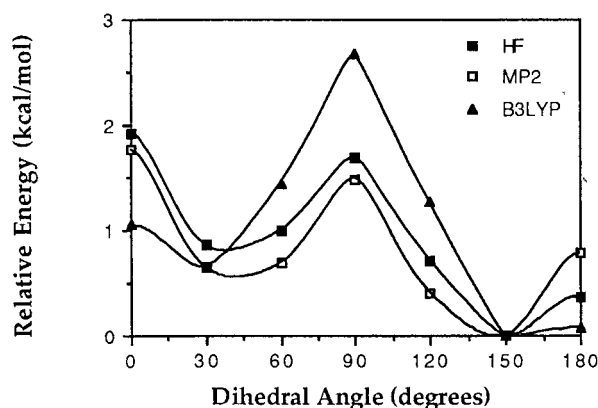(38) Niziurski-Mann, R. E.; Cava, M. P. *Adv. Mater.* **1993**, *5*, 547.

Figure 1. HF, MP2, and B3-LYP rotational barriers for **1**. All the calculations were performed with the 6-31G(d) basis set.
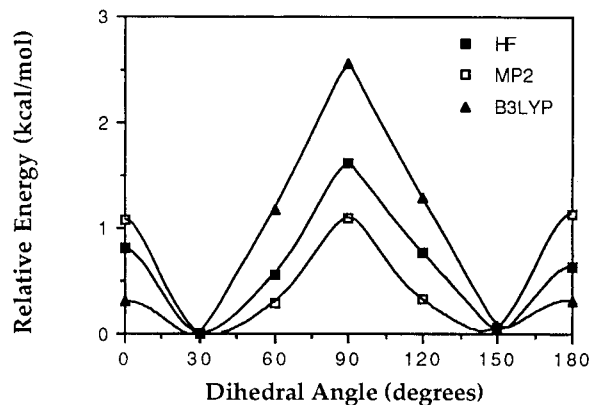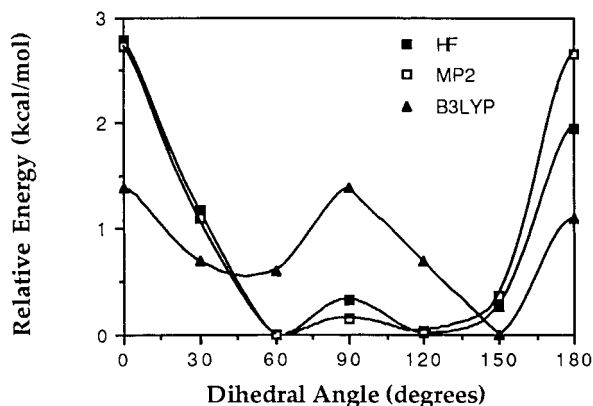

Figure 2. HF, MP2, and B3-LYP rotational barriers for **2**. All the calculations were performed with the 6-31G(d) basis set.

1.56 (m, 2H), 4.12 (t, 2H, $J = 8.0$ Hz), 6.33 (s, 2H), 7.06 (m, 4H), 7.28 (dd, 2H, $J = 2.0$ Hz, $J = 4.4$ Hz); ^{13}C NMR (CDCl$_3$) δ (ppm) 13.91, 22.39, 26.09, 31.14, 45.15, 110.72, 125.19, 125.91, 127.23, 128.28, 135.04. Anal. Calcd for C$_{18}$H$_{21}$NS$_2$: C, 68.5, H, 6.7, N, 4.4, S, 20.3. Found: C, 68.7, H, 6.8, N, 4.6, S, 20.3.

Results and Discussion

Molecular Structure of the Bicyclic Systems. The rotational profiles of **1**−**3** computed at the HF, MP2, and B3-LYP levels of theory are represented in Figures 1−3. Furthermore, the energies of the minima and saddle points are reported in Tables 1−3. A schematic picture of the most significant conformations: *anti, anti-gauche, gauche-gauche, syn-gauche,* and *syn,* is shown in Figure 4.

The most stable conformation for **1** corresponds to the *anti-gauche* conformation, which is located at $\theta = 142°$ at the MP2 level. A second minimum for such a compound is calculated to arise when the torsional angle θ is 43°. This *syn-gauche* structure is about 0.5 kcal/mol less favored than the *anti-gauche*. The two-well-defined minima are separated by a barrier that corresponds to the *gauche-gauche* ($\theta = 90°$) conformation. This is unfavored with respect to the *anti-gauche* by 1.5 kcal/mol. Results displayed in Figure 1 indicate that planar conformations are less stable than the twisted ones. Thus, the *syn* conformation is less favored than the *syn-gauche* one by 1.3 kcal/mol at the MP2 level, whereas

Figure 3. HF, MP2, and B3-LYP rotational barriers for **3**. All the calculations were performed with the 6-31G(d) basis set.
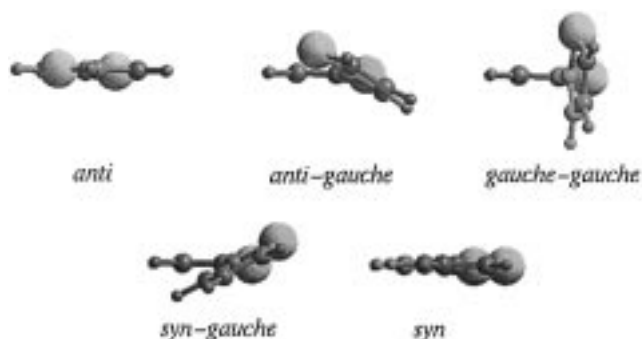

Figure 4. Schematic picture of the *anti, anti-gauche, gauche-gauche, syn-gauche,* and *syn* conformations for **1**. Conformations are displayed looking down the rotated bond from one thiophene ring to the other.

Table 1. Energies (in kcal/mol) and Torsional Angles[a] **(θ (Deg)) of the Three Bicyclic Compounds Computed at the HF Level with the 6-31G(d) Basis Set**

compd	syn	syn-gauche	gauche-gauche	anti-gauche	anti
1	1.9	0.7 ($\theta = 42$)	1.7	0.0 ($\theta = 148$)	0.4
2	0.9	0.0 ($\theta = 37$)	1.7	0.1 ($\theta = 146$)	0.7
3	2.9	0.1 ($\theta = 57$)	0.4	0.0 ($\theta = 132$)	2.1

[a] Torsional angle between the planes of the two rings. *Syn,* $\theta = 0°$; *gauche-gauche* barrier, $\theta = 90°$; *anti,* $\theta = 180°$.

Table 2. Energies (in kcal/mol) and Torsional Angles[a] **(θ (Deg)) of the Three Bicyclic Compounds Computed at the MP2 Level with the 6-31G(d) Basis Set**

compd	syn	syn-gauche	gauche-gauche	anti-gauche	anti
1	1.8	0.5 ($\theta = 43$)	1.5	0.0 ($\theta = 142$)	0.8
2	1.3	0.0 ($\theta = 41$)	1.3	0.1 ($\theta = 139$)	1.3
3	2.9	0.2 ($\theta = 68$)	0.4	0.0 ($\theta = 135$)	2.9

[a] Torsional angle between the planes of the two rings. *Syn,* $\theta = 0°$; *gauche-gauche* barrier, $\theta = 90°$; *anti,* $\theta = 180°$.

the energy difference between the *anti* and *anti-gauche* conformations decreases to 0.8 kcal/mol. These results are in agreement with experimental data since an *anti-gauche* conformation with $\theta = 146°$ was found for **1** in the vapor phase.[39]

It should be noted that HF and MP2 methods (Tables 1 and 2) provide very similar results, which are quite different from those obtained from DFT calculations

Table 3. Energies (in kcal/mol) and Torsional Angles[a] **(θ Deg)) of the Three Bicyclic Compounds Computed at the B3-LYP Level with the 6-31G(d) Basis Set**

compd	syn	syn-gauche	gauche-gauche	anti-gauche	anti
1	1.1	0.7 ($\theta = 34$)	2.7	0.0 ($\theta = 157$)	0.1
2	0.6	0.0 ($\theta = 28$)	2.5	0.0 ($\theta = 155$)	1.3
3	1.6	0.5 ($\theta = 46$)	1.5	0.0 ($\theta = 143$)	1.2

[a] Torsional angle between the planes of the two rings. *Syn,* $\theta = 0°$; *gauche-gauche* barrier, $\theta = 90°$; *anti,* $\theta = 180°$.

(Table 3). Thus, the most important drawbacks of the DFT results with respect to the HF and MP2 ones are as follows: (i) the minimum energy conformations obtained from DFT calculations appear less twisted than the MP2 ones; (ii) the energy difference between the planar conformations (*syn* and *anti*) and the corresponding twisted ones (*syn-gauche* and *anti-gauche*) is considerably understimated; and (iii) the energy barrier is overestimated by 1.0 and 1.2 kcal/mol with respect to the HF and MP2 energy barriers, respectively. Thus, DFT calculations tend to underestimate the interactions associated with the planar structures leading to their stabilization.[16,40]

Results for **2** are similar to those obtained for **1** from a qualitative point of view. At the MP2 level the *anti-gauche* and *syn-gauche* occur around a torsional angle of 139° and 41°, respectively. However, relative energies between the different conformations differ considerably from those obtained for **1**. For **2**, the *syn-gauche* and *anti-gauche* conformations are almost isoenergetic, indicating that in the former conformation the interactions between the heteroatoms are less repulsive for **2** than for **1**. The perpendicular conformation is 1.3 kcal/mol higher than the global minimum at the MP2 level, which is fully consistent with that of **1**. Comparison between results obtained at the HF, MP2, and DFT levels of theory reveals trends similar to that for **1**. Thus, the DFT calculations tend to destabilize the twisted conformations, which determine an increase of both the torsional energy barrier and the planarity of the inter-ring dihedral angle θ for the minimum energy conformations.

The case of **3** appears to be very different. The *anti-gauche* and *syn-gauche* conformations present a torsional angle θ of 135° and 68°, respectively, displaying deviations greater than those of **1** and **2**. Both minima turn out to be almost isoenergetic. Thus, the low energy of the *syn-gauche* conformation in **2** and **3** should be explained in terms of attractive electrostatic interactions between the groups attached to the nitrogen atom, which have a positive charge distribution, and the lone pairs of the sulfur atom. Minimum energy conformations are separated by a small barrier of 0.4 kcal/mol, which correspond to the *gauche-gauche* conformation. However, the *anti* and *syn* planar conformations are destabilized by 2.9 kcal/mol, revealing the repulsive contacts generated by the bulky methyl group. These interactions are removed when the inter-ring dihedral angle θ deviates about 50°−70° from the planarity. The large distortions in the θ dihedral angle induced by the alkyl group attached to the nitrogen atom could be responsible for the rotational defects introduced by pyrrole units along [...-(pyrrole)$_n$-(thiophene)$_n$-...] block copolymer backbones.

The results displayed in Figure 3 and Tables 1−3 indicate that B3-LYP calculations clearly fail in describ-

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Table 4. Torsional Potentials (in kcal/mol) of the Three Bicyclic Compounds Obtained by Fitting the Energies Computed at the MP2/6-31G(d) to a Six-Term Fourier Expansion

compd	V_1	V_2	V_3	V_4	V_5	V_6
1	0.79	0.30	0.14	−1.26	0.04	−0.08
2	−0.05	0.18	0.00	−1.26	−0.00	−0.19
3	0.43	−2.16	0.05	−1.41	−0.41	−0.38

ing the conformational behavior of **3**. Thus, the DFT method localizes the minimum energy conformations in the neighborhood of the "*standard*" *anti-gauche* and *syn-gauche* conformations, i.e., 46° and 143°, respectively. Furthermore, the torsional energy barrier is predicted to be very high. Thus, B3-LYP calculations predict a barrier of 1.5 kcal/mol, whereas that computed from the HF and MP2 methods is about 0.4 kcal/mol. The results provided by B3-LYP calculations for the three compounds **1–3**, together with those recently reported by different authors,[16,40] suggest that the use of DFT methods to investigate conformational properties of conjugated systems should be restricted to cases for which their applicability has been previously tested.

Barriers in compounds of this type are frequently examined by their decomposition into a truncated Fourier expansion:

$$V_\varphi = \sum V_n/2[1 + \cos(n\varphi - \gamma_n)] \qquad (1)$$

where V_φ is the torsional energy barrier of the n-Fourier expansion term for the rotation around the bond, γ_n is the phase angle of the n-Fourier term, which determines the torsional angle of maximum energy, and φ is the torsion angle. To simplify the analysis, it is customary to consider all the phase angles equal to 0 and perform the fitting between quantum mechanics and torsional energies. The sign of each V_φ parameter indicates the phase angle of the n-Fourier term. If V_φ is positive the phase angle is 0°, and 180° if it is negative. This method of deriving the potential function for the internal rotation has proven to provide an accurate way to obtain the locations and relative energies of the critical points in the torsional potential when these points cannot be determined by direct geometry optimization. Table 4 shows the six-term Fourier-fitted MP2 torsional potentials for **1–3**.

Tables 5 and 6 display the HF- and MP2-optimized geometries of the minimum energy conformations for compounds **2** and **3**, respectively. Molecular geometries for the *anti-gauche* and *syn-gauche* minimum energy conformations of **1** have been previously reported at different levels of theory.[8,10,41] It should be noted that within each method geometric parameters are very similar for the two minima, the largest variations in bond length and bond angles being of 0.005 Å and 1°, respectively. A comparison of the molecular geometries between the different compounds reveals that thiophene rings have almost an identical structure in all cases. On the other hand, the substitution of a sulfur atom by a nitrogen atom introduces some important changes in the geometric parameters of the five-membered ring. The most important change occurs in the C5′–X1′ bond

(41) (a) Ortí, E.; Viruela, P. M.; Sanchez-Marín, J.; Tomas, F. *J. Phys. Chem.* **1995**, *99*, 4955. (b) Hernández, V.; López Navarrete, J. T. *J. Chem. Phys.* **1994**, *101*, 1369. (c) Hernández, V.; López Navarrete, J. T. *Synth. Met.* **1996**, *76*, 221.

Table 5. HF/6-31G(d) and MP2/6-31G(d) Optimized Geometries[a] for the Minimum Energy Conformations of 2

parameter	syn-gauche		anti-gauche	
	HF	MP2	HF	MP2
C2−C3	1.352	1.383	1.352	1.385
C3−C4	1.434	1.417	1.434	1.417
C4−C5	1.344	1.377	1.344	1.377
C5−X1	1.726	1.720	1.726	1.719
C2−C2′	1.461	1.449	1.461	1.449
C2′−C3′	1.364	1.392	1.364	1.392
C3′−C4′	1.423	1.414	1.423	1.414
C4′−C5′	1.358	1.385	1.358	1.385
C5′−X1′	1.361	1.371	1.361	1.371
∠C2−C3−C4	113.2	113.1	113.2	113.0
∠C3−C4−C5	112.6	112.7	112.6	112.6
∠C4−C5−X1	111.8	111.5	111.8	111.6
∠X1−C2−C2′	121.6	121.7	121.0	121.7
∠C2−C2′−X1′	122.1	122.0	121.3	122.0
∠C2′−C3′−C4′	107.4	107.8	107.4	107.8
∠C3′−C4′−C5′	107.1	107.6	107.1	107.6
∠C4′−C5′−X1′	108.2	107.4	108.2	107.4
θ	37	41	146	139

[a] Distances in Å. Angles and θ in deg.

Table 6. HF/6-31G(d) and MP2/6-31G(d) Optimized Geometries[a] for the Minimum Energy Conformations of 3

parameter	syn-gauche		anti-gauche	
	HF	MP2	HF	MP2
C2−C3	1.352	1.385	1.350	1.387
C3−C4	1.434	1.416	1.435	1.416
C4−C5	1.345	1.377	1.344	1.377
C5−X1	1.724	1.718	1.725	1.718
C2−C2′	1.465	1.454	1.470	1.450
C2′−C3′	1.365	1.394	1.364	1.395
C3′−C4′	1.418	1.411	1.419	1.410
C4′−C5′	1.358	1.386	1.359	1.385
C5′−X1′	1.362	1.372	1.361	1.373
∠C2−C3−C4	113.3	113.3	113.5	113.3
∠C3−C4−C5	112.6	112.6	112.5	112.6
∠C4−C5−X1	111.7	111.5	111.8	111.5
∠X1−C2−C2′		122.9		119.6
∠C2−C2′−X1′		123.3		123.1
∠C2′−C3′−C4′	107.5	107.8	107.4	107.8
∠C3′−C4′−C5′	106.7	107.2	106.6	107.3
∠C4′−C5′−X1′	109.2	108.3	109.2	108.4
θ	57	68	131	135

[a] Distances in Å. Angles and θ in deg.

length, which adopts a value of 1.72–1.73 Å in **1**[8,41] and decreases to 1.36–1.37 Å in **2** and **3**. Furthermore, bond angles change from 112 to 113° in thiophene rings to 107−109° in pyrrole rings.

The dependence of the bond length between the rings computed at the HF level and the torsional angle θ for **1–3** is shown in Figure 5. The results are similar for the three compounds and they do not depend on the level of theory (data not shown). Note that the shortest distances correspond to values of θ around 150° and 30°, i.e., those of the *anti-gauche* and *syn-gauche* minimum energy structures for **1** and **2**, and slightly deviated from the minimum energy structures for **3**. The inter-ring bonds elongate by only 0.012, 0.013, and 0.009 Å in **1**, **2**, and **3**, respectively, indicating that the C2−C2′ bond has a small double character. Bredas and co-workers[42]

(42) Bredas, J. L.; Street, G. B.; Themans, B.; Andre, J. M. *J. Chem. Phys.* **1985**, *83*, 1323.

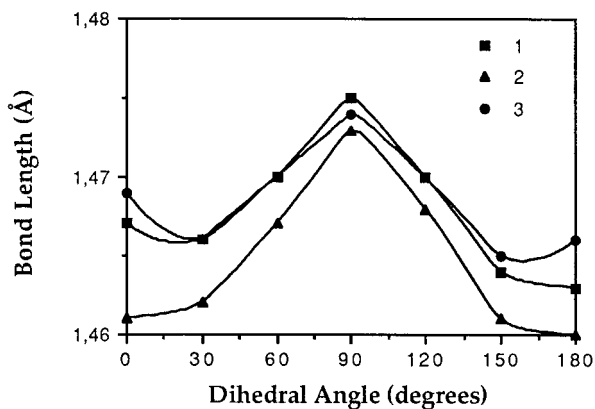**Figure 5.** Evolution of the inter-ring bond length for **1**, **2**, and **3** as a function of the torsional angle between the rings (θ).
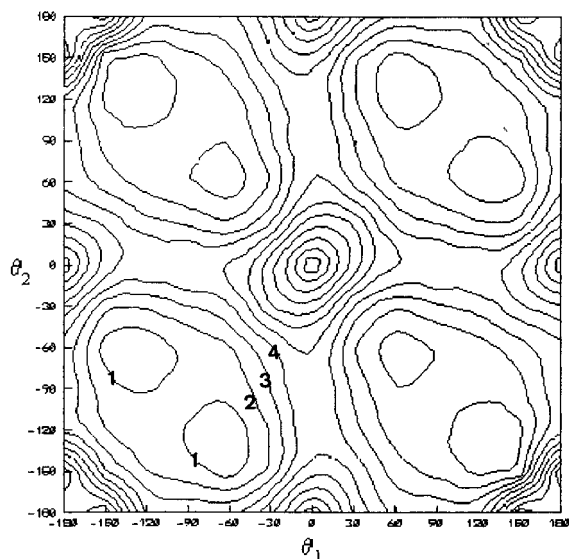

Figure 6. Conformational energy map of **4** computed at the ab initio HF/6-31G(d) level. Contour lines are drawn in increments of 1 kcal/mol.

Table 7. Inter-ring Dihedral Angles (Deg) and Relative Energies (kcal/mol) for the Minimum Energy Conformations of *N*-Methyl-2,5-di(2-thienyl)pyrrole (4) Computed at the HF/6-31G(d) Level

conformation	θ_1	θ_2	ΔE
anti-gauche⁺-anti-gauche⁻	134.7	−134.7	0.0
anti-gauche⁺-syn-gauche⁺	134.7	60.9	0.0
syn-gauche⁺-syn-gauche⁻	60.9	−60.9	0.2

anti-gauche⁻ minimum is 2-fold degenerated ($\theta_1, \theta_2 = -\theta_1, -\theta_2$), whereas the *anti-gauche⁺-syn-gauche⁺* one is 4-fold degenerated ($\theta_1, \theta_2 = \theta_2, \theta_1 = -\theta_1, -\theta_2 = -\theta_2, -\theta_1$). The third minimum corresponds to the *syn-gauche⁺-syn-gauche⁻* conformation and is also 2-fold degenerated. This structure is 0.2 kcal/mol less stable than the *anti-gauche⁺-anti-gauche⁻* one, which is in excellent agreement with the low relative energies previously obtained for the biciclyc compound **3**. Inspection of Figure 5 reveals that *anti-gauche⁺-anti-gauche⁻* and *syn-gauche⁺-syn-gauche⁻* minimum energy conformations are separated by a small barrier, in agreement with the results obtained in the previous section for **3**. Similarly, the energy barrier between the *anti-gauche⁺-syn-gauche⁺* and *syn-gauche⁺-anti-gauche⁺* degenerated minima is quite low.

The conformational preferences of **5** were recently investigated using ab initio calculations.[14] For **5**, the ranges of distortion with respect to the planarity of the inter-ring dihedral angles are about 35° for both the *anti-gauche* and *syn-gauche* conformations. Such values are in good agreement with those obtained for the *anti-gauche* and *syn-gauche* conformations of 2,2'-bithiophene.[10,14,41]

Inspection of Table 7 reveals that the rotational defects are larger for **4** than for **5**. The distortion with respect to the planarity of the dihedral angles θ_1 and θ_2 in **4** are 45° and 61° for the *anti-gauche* and *syn-gauche* conformations, respectively. The distortions obtained for **4** are in good agreement with those obtained for **3** (see Table 1). Both the low energy barriers between minimum energy conformations and the large distortions with respect to the planarity of the inter-ring dihedral angles suggest that *N*-methylpyrrole rings are able to induce large rotational deffects in [...-(pyrrole)$_n$-(thiophene)$_n$-...] block copolymers.

EPR Experiments of the Tricyclic Systems. When a solution of *N*-hexyl-2,5-di(2-thienyl)pyrrole (**6**) in trifluoroacetic acid (TFA) at −10 °C was irradiated, the symmetric spectrum of Figure 7a was observed. A computer simulation of the spectrum, shown in Figure 7b, was carried out by using the following hyperfine coupling constants (hfc): $a(2H) = 6.69$ G, $a(2H) = 3.69$ G, $a(1N) = 3.05$ (G), $a(2H) = 2.45$ G, $a(2H) = 1.38$ G, $a(2H) = 0.69$ G, the line-width, $\Delta H_{pp} \approx 0.25$ G, and $g = 2.0023$. When deuteriotrifluoroacetic acid was used as solvent, all aromatic protons were rapidly exchanged by deuterium and the spectrum in Figure 8a was observed. In Figure 8b, a simulation using only the hfc's due to the nitrogen ($a = 3.05$ G) and the two *N*-methylene protons [$a(2H) = 2.45$ G], with a linewidth of $\Delta H_{pp} \approx 2.5$ G is displayed. The poorly resolved spectrum is ascribed to the small couplings with the aromatic deuteria in the molecule, whose coupling values only contribute to the width of the line, corresponding to the largest one to the 5 and 5″ position [$a(2D) = a(2H) \cdot \gamma_D/\gamma_H = 6.69/6.51 \approx 1.0$ G]. The structural assignment of the other hfc has been
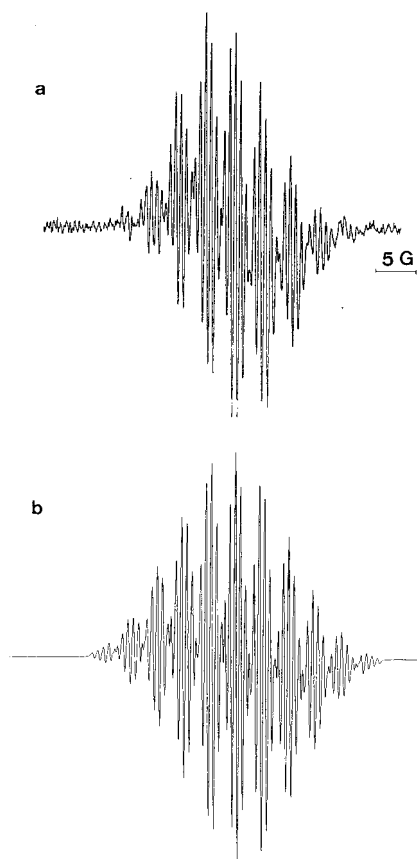
estimated that the π contribution represents only about 6.4% of the total inter-ring bond order in the case of **1**. The present results indicate that the π contribution also remains small for **2** and **3**.

Molecular Structure of the Tricyclic Systems. To obtain a better characterization of the large rotational deffects induced by the *N*-methylpyrrole rings in block copolymers of pyrrole and thiophene, the conformational preferences of the tricyclic compound **4** were investigated. Figure 6 shows the potential energy surface $E = E(\theta_1, \theta_2)$ computed at the ab initio HF level. Contour lines are drawn in increments of 1 kcal/mol. It should be noted that for the low-energy regions of the conformational space the inter-ring dihedral angles, θ_1 and θ_2, deviate from the planarity.

Starting from different low-energy points of the conformational map, geometry optimizations led to three minimum energy conformations, which in turn are several times degenerated. Relative energies and conformational angles are listed in Table 7. The two lowest energy conformations correspond to *anti-gauche⁺-anti-gauche⁻* and *anti-gauche⁺-syn-gauche⁺*, being isoenergetic. Due to the molecular symmetry, the *anti-gauche⁺-*

Figure 7. (a) EPR spectrum of an irradiated solution of *N*-hexyl-2,5-di(2-thienyl)pyrrole (**6**[•+]) in trifluoroacetic acid at −10 °C. (b) Computer simulation using the parameters given in the text.
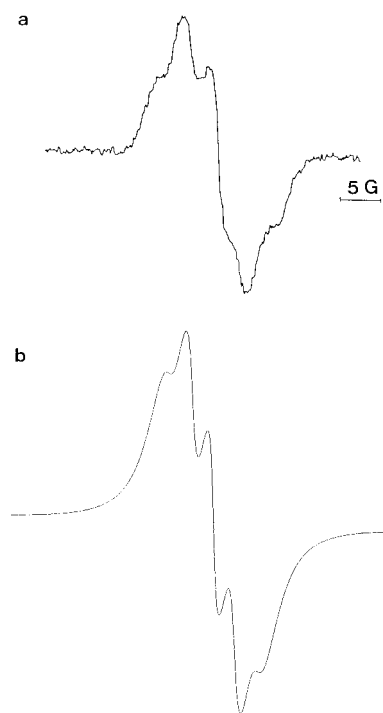

Figure 8. (a) EPR spectrum of an irradiated solution of *N*-hexyl-2,5-di(2-thienyl)pyrrole (**6**[•+]) in deuteriotrifluoroacetic acid at room temperature. (b) Computer simulation using the parameters given in the text.

Table 8. Ratios of the Experimental Hyperfine Coupling Constants (hfc) and Computed Spin Densities (ρ) for 6[•+]

ratio[a]	hfc	ρ
[C3,C3″]/[C5,C5″]	0.55	0.28
[C3′,C4′]/[C5,C5″]	0.24	0.19
[C4,C4″]/[C5,C5″]	0.10	0.00

[a] All the ratios are computed with respect to the protons attached to the C5 and C5″ atoms.

achieved by semiempirical calculations. Thus, spin densities computed for **4**[•+] with the AM1 semiempirical Hamiltonian provide the following relative order: ρ[C5,C5″] > ρ[C3,C3″] > ρ[C3′,C4′] > ρ[C4,C4″]. Then, as an estimation, we can assign the hfc values as follows, a(H5,H5″) = 6.69 G, a(H3,H3″) = 3.69 G, a(H3′,H4′) = 1.38 G and a(H4,H4″) = 0.69 G. These values are similar, although slightly different from, to those recently reported by Engelman *et al.*[30] for 5,5″-dimethyl-2,2′,5′,2″-terthiophene, which were unambiguously assigned by partial deuteration of the aromatic positions. Table 8 shows a comparison between the observed hfc values for **6**[•+] and the computed spin densities for **4**[•+], where the ratios with respect to the largest values, i.e., those corresponding to the protons attached to C5 and C5″, are displayed.

A variety of conditions were investigated to generate the 2,5-di(2-thienyl)pyrrole radical cation without much success. Thus, photolysis of a solution of the substrate in TFA or in CH_2Cl_2 in the presence of $AlCl_3$ showed only a singlet spectrum with unresolved splittings that corresponded to high oligomeric fractions. When the substrate was dissolved in CH_2Cl_2 with a small portion of TFA at low temperatures (210 K), a very weak and more resolved spectrum was observed but still difficult to interpret.

Conclusions

The barriers to internal rotation about the bond between the planes of the two rings have been computed for **1**−**3** using ab initio and DFT quantum mechanical calculations. Both HF and MP2 proved to be superior to the B3-LYP functional used here. The conformational preferences of **2** were very similar to that of **1**. Two minima were found for each compound, the *anti-gauche* and *syn-gauche* conformations, the latter being less favored than the former. Furthermore, the energy barrier of **2** appears also to be very similar to that of **1**, being about 1.5 kcal/mol. On the contrary, calculations on **3** indicate that the two minimum energy conformations are almost isoenergetic, and the energy barrier between them is lower than 0.5 kcal/mol. Thus, the presence of a methyl group attached to the nitrogen atom seems to provide a greater rotational freedom around the bond between the rings.

The conformational preferences of the tricyclic compound **4** have been investigated at the HF level. The results were quite consistent with those obtained for the bicyclic related compound **3**. Thus, minimum energy conformations, which are very similar in energies, are separated by a low energy barrier. Furthermore, a large deviation with respect to the planarity was predicted for the inter-ring dihedral angles of the minimum energy conformations of both **3** and **4**.

This is the first time that a mixed trimer of thiophene and pyrrole was oxidized to its radical cation and

observed by means of EPR spectroscopy. Despite the very short lifetime of **6**[•+] due to oligomerization through the very reactive 5,5″ positions, its EPR spectrum in fluid solution has been observed in TFA due to the good properties of this acid[43] either as a solvent of very low nucleophilicity to stabilize cationic species or as a mild oxidant of substrates with relative low oxidation potentials. An increasing stability of these radical cation species is afforded when the extreme positions are blocked by alkyl groups.[4,5] Some more stable and better characterized radical cation spectra are now in progress. Two other observations were made in regard to the mixed radical cation **6**[•+] in comparison with the terthiophene radical cation **5**[•+]:[28] (i) the hfc values in the pairs H3,H3″, H4,H4″, and H5,H5″ are slightly higher, and in the pair H3′,H4′ slightly lower, which is in agreement with the larger degree of confinement of the HOMO in the thiophene rings of **6**[•+] with regard to the extreme thiophene in **5**[•+], and (ii) the EPR spectrum of **6**[•+] seems to be symmetric, unlike **5**[•+], which is accounted for by a fast interconversion between conformers. This supports the small energy barrier calculated between minima for the bicyclic and tricyclic compounds.

(43) Eberson, L.; Radner, F. *Acta Chem. Scand.* **1992**, *46*, 630.

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