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Ester Substituted Bithiophenes. Abnormally Low Dihedral Angle and Rotation Barrier Due to Dipolar Stabilization

Martin Pomerantz* and **Yang Cheng**

Department of Chemistry and Biochemistry, Box 19065,
The University of Texas at Arlington, Arlington, Texas 76019-0065 USA

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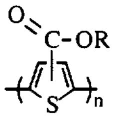
Abstract: Ab initio calculations [3-21G$^{(*)}$] on dimethyl 2,2'-bithiophene-4,4'-dicarboxylate (**3**), dimethyl 2,2'-bithiophene-3,4'-dicarboxylate (**4**) and dimethyl 2,2'-bithiophene-3,3'-dicarboxylate (**5**) have revealed that in **4** there is an abnormally small dihedral angle between the thiophene rings and an abnormally low barrier to rotation around the thiophene-thiophene single bond. This is due to a favorable coulombic interaction of the negative carbonyl oxygen and the positive sulfur of the adjacent ring which helps to flatten and bend the ground state and lower the rotation barrier.

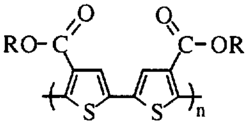
Keywords: Biaryls, Electrostatic effects, Theoretical studies, Thiophenes

In recent years there has been intense interest in polythiophenes both for their electrical[1] and electroluminescent properties.[2,3] Our studies of polythiophenes containing ester functionalities, with the carbonyl group directly attached to the ring, provided us with both regiorandom polymers, poly(hexyl thiophene-2,5-diyl-3-carboxylate) (**1a**) and poly(octyl thiophene-2,5-diyl-3-carboxylate) (**1b**) randomly containing head-to-head (HH), head-to-tail (HT) and tail-to-tail (TT) linkages, and with regioregular polymers, poly(dihexyl [2,2'-bithiophene]-5,5'-diyl-4,4'-dicarboxylate) (**2a**) and poly(dioctyl [2,2'-bithiophene]-5,5'-diyl-4,4'-dicarboxylate) (**2b**), containing alternating HH and TT linkages.[4-6] Examination of the properties, including UV-vis, fluorescence and electroluminescence spectra, suggested that the HH linkages provided considerable twisting around the thiophene-thiophene bonds, as a result of high rotational barriers and this gave rise to reduced conjugation along the chains. The HT and TT linkages did not seem to affect the properties much, suggesting smaller dihedral angles (less twisting), lower barriers and allowed greater conjugation along the chain. This has led us to perform ab initio calculations on dimeric systems, namely dimethyl 2,2'-bithiophene-4,4'-dicarboxylate (**3**), dimethyl 2,2'-bithiophene-3,4'-dicarboxylate (**4**) and dimethyl 2,2'-bithiophene-3,3'-dicarboxylate (**5**), to see if this was indeed the case. These bithiophenes are models for the TT, HT and HH polymer linkages respectively.

The geometries were optimized at the ab initio 3-21G$^{(*)}$ level and, in both **4** and **5** the carbonyl group of the ester (at the 3 and 3' positions) was pointing toward the adjacent ring sulfur. The barrier to rotation was obtained by forcing the two thiophene-thiophene dihedral angles to be 0° (planar structure) and then optimizing the remaining geometry. The energy difference between these two minima was taken as the rotation barrier.



1a: R = C_6H_{13}
b: R = C_8H_{17}



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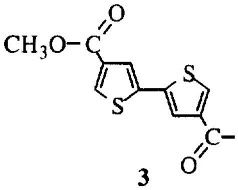

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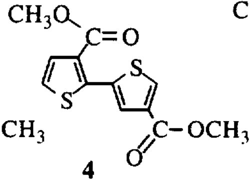

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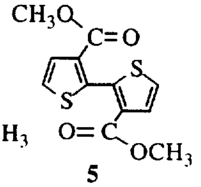

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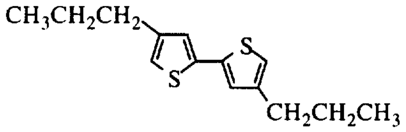
The values are presented in Table 1. The value of 35.1° for the TT conformation is close to the angle of 34° obtained for bithiophene itself in the gas phase.[7] It is also close to the angle calculated using a 6-31G** basis set.[8] The value of 77.4° for **5** appears to be a reasonable value when compared with 87.2° calculated for 3,3'-dimethyl-2,2'-bithiophene also using a 3-21G* basis set.[9] The dihedral angle in structure **4**, however, was clearly anomalously low. The values were 21.7° and 17.4°, there being two different values since the rings are slightly puckered. The calculated value for 3,4'-dimethyl-2,2'-bithiophene using a 3-21G* basis set was found to be much larger, namely 71.4°.[8]

The rotational barriers for **3** and **5** both seemed reasonable compared to the barriers calculated for 4,4'-dimethyl-2,2'-bithiophene and 3,3'-dimethyl-2,2'-bithiophene of 0.4 kcal/mol (1.7 kJ/mol) and 4.5 kcal/mol (19 kJ/mol) respectively at the 6-31G** level.[8] The barrier for **4**, however, was also clearly anomalously low. Indeed, the barrier was *less than the barrier in 3*, even though a larger ester group has replaced a smaller hydrogen atom. To see if the ester was the source of this anomaly we performed similar calculations on the dipropylbithiophenes **6**-**8** with the results shown in Table 1. The dihedral angles and the rotation barriers all appear reasonable and in particular the values for **7** which are intermediate between those for **6** and **8**.



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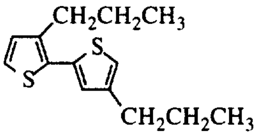

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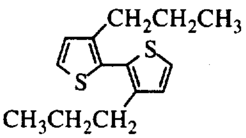

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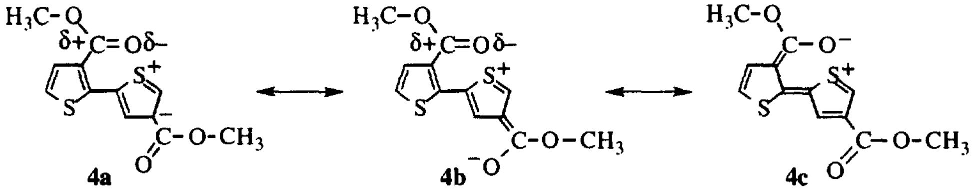
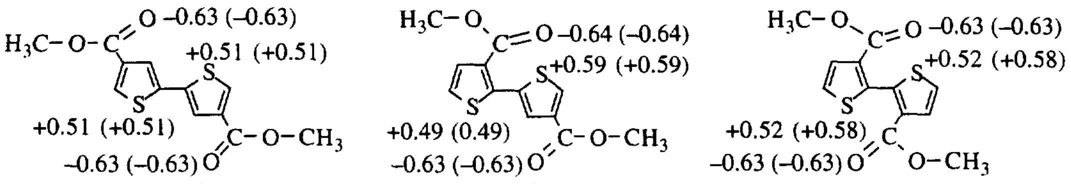
Upon closer inspection of **4** it became clear that both the twisted ground state and the planar structure were being stabilized by attractive interactions between the rather negative carbonyl oxygen and the relatively positive sulfur atom in the adjacent ring and this was giving rise to a considerably reduced rotation barrier and a small dihedral angle. This means that resonance forms with a positive charge on sulfur, such as the ones shown in structures **4a-c**, are being stabilized by this interaction. That this is indeed the situation can be seen from the calculated Mulliken charge densities for the twisted ground states for **3**-**5** and the flat structures $\mathbf{3}^{\ddagger}$-$\mathbf{5}^{\ddagger}$shown in Figure 1. Note that the values for the flat structures $\mathbf{3}^{\ddagger}$-$\mathbf{5}^{\ddagger}$ are given in parentheses. As expected in **3** and $\mathbf{3}^{\ddagger}$, where there are no O–S interactions possible, the sulfur and oxygen atoms are +0.51 and –0.63 respectively in both structures. In **4** and $\mathbf{4}^{\ddagger}$, however, the sulfur atom close to the carbonyl oxygen has over 20% more positive charge than the other sulfur (+0.59 vs +0.49) in both the twisted and flat forms. Also, the oxygen atom facing the sulfur is slightly more negative than the other carbonyl oxygen. This suggests a

Table 1. Thiophene-thiophene dihedral angle and rotation barrier in **3**-**8**

Bithiophene	Dihedral Angle	Rotation Barrier
3	35.1°	0.37 kcal/mol (1.5 kJ/mol)
4	21.7° and 17.4°	0.084 kcal/mol (0.35 kJ/mol)
5	77.4°	8.55 kcal/mol (36 kJ/mol)
6	32.6°	0.34 kcal/mol (1.4 kJ/mol)
7	58.7° and 62.1°	2.27 kcal/mol (9.5 kJ/mol)
8	86.6°	7.84 kcal/mol (33 kJ/mol)

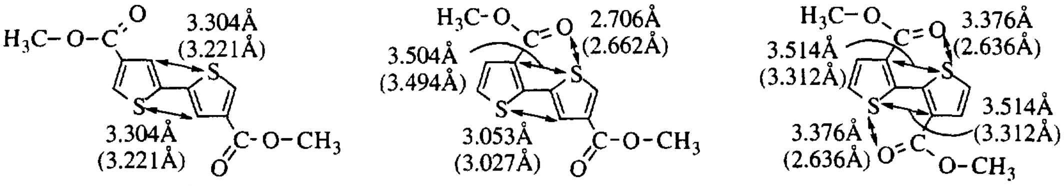


coulombic stabilization of the positive charge on the sulfur atom closest to the oxygen. In spite of this coulombic stabilization there is still a steric component to the barrier and the manifestation of this is shown in Figure 2 which gives some atom-atom distances in both the twisted and flat structures **3**-**5** and **3**‡-**5**‡ (in parentheses). As can be seen in **4**, the molecule bends in order to accommodate the carbonyl oxygen as close as possible to the sulfur atom to maximize the stabilization. This results in nearly a 0.5 Å difference in the distance between the sulfur atom near the oxygen and the carbon α to the ester in the other ring (carbon-3) compared with the other analogous sulfur-carbon (carbon-3') distance. In **4**‡ when the carbonyl oxygen passes the sulfur atom the molecule is already bent and can accommodate the steric strain and so this results in a very small rotation barrier. In the symmetric case of **3** and **3**‡ the corresponding sulfur-carbon distances are intermediate between the two distances in **4** and **4**‡.



3 (**3**‡) **4** (**4**‡) **5** (**5**‡)

Figure 1. Calculated [3-21G$^{(*)}$] Mullikan charges on selected atoms in twisted ground state **3**-**5** and flat **3**‡-**5**‡ (in parentheses).



3 (**3**‡) **4** (**4**‡) **5** (**5**‡)

Figure 2. Calculated [3-21G$^{(*)}$] distances in twisted ground state **3**-**5** and flat **3**‡-**5**‡ (in parentheses).

In the 3,3'-substituted diester there is clearly some dipolar stabilization as shown by the charges on the sulfur atoms in **5**‡ (Figure 1) but the steric barrier is much too large to be overcome by the coulombic stabilization and so the overall rotation barrier is large. In addition, in the ground state the molecule can not bend the way **4** does to accommodate the oxygen close to the sulfur so the molecule is severely twisted and there is considerably less positive charge on the sulfur atoms. Figure 3 presents several bond angles which also show the distortions. Of particular interest are the observations that the angles in twisted **4** and flat **4**‡ are nearly the same, that the ester group is pushed considerably when it has to pass a sulfur atom and the internal thiophene angles are quite distorted in **5**‡.

Finally, it should be pointed out that the conformation of **4** where the carbonyl is pointing away from the adjacent sulfur is a local minimum, 1.6 kcal (6.6 kJ) above the conformation shown in **4**. Significantly, however, the optimized geometry for this conformation showed the two C–C–C–S inter-ring dihedral angles to be 56.7° and 49.0°, values which are similar to those in **7**. This clearly demonstrates that the carbonyl group in **4** is the cause of the anomalously low dihedral angle and rotational barrier.

A search of the literature reveals examples where positively and negatively charged portions of the molecules will attract and the molecule will adopt a conformation minimizing the charge separation. Reference 10 provides a recent example.[10] The situation described here is unique in that the unlike charges in **4** not only attract one another to provide a particular conformation, but that attraction *also* results in the stabilization of resonance forms with a positive charge on the sulfur and this stabilization is so powerful that it results in a rather significant distortion of the molecule.

It is thus clear that certain polar groups, such as an ester group, can help stabilize distorted structures provided the distortions are not too great. Further theoretical and experimental work is in progress.

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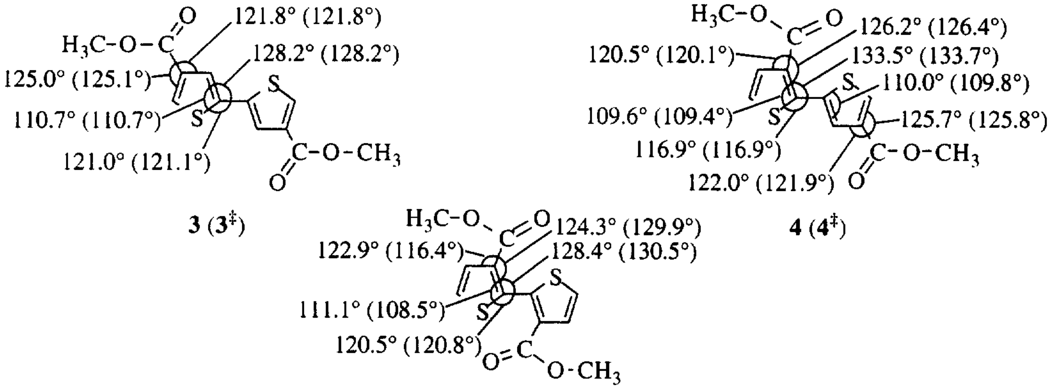

3 (**3**‡)

4 (**4**‡)

5 (**5**‡)

Figure 3. Selected calculated bond angles in the twisted and flat structures **3**-**5** and **3**‡-**5**‡ (in parentheses).

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