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Planar 2,2′-bithiophenes with 3,3′- and 3,3′,4,4′-substituents. A computational study

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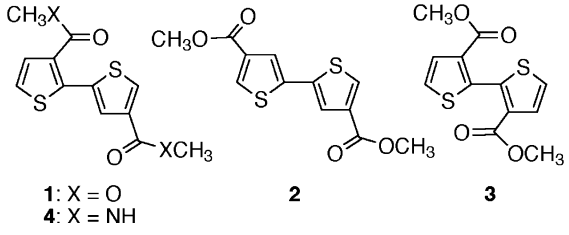
Abstract—Ab initio calculations have shown that when carbonyl groups are incorporated into the 3- and 3′-positions of bithiophenes, as part of five-membered rings, the bithiophene system is planar. This is due to electrostatic attraction between the carbonyl oxygen and the sulfur atom in the adjacent ring. In the analogous systems containing a CH_2 group in place of the carbonyl, or containing six-membered rather than five-membered rings, the bithiophenes are twisted. This has implications for preparing planar polythiophenes.

We recently reported on a new, interesting phenomenon, based upon ab initio quantum mechanical calculations of bithiophene esters, involving an electrostatic stabilization of resonance forms which caused significant steric distortions of the system. In particular we showed that in dimethyl 2,2′-bithiophene-3,4′-dicarboxylate (**1**) the oxygen of the ester group in the 3-position was pulled toward the sulfur atom in the adjacent ring. This had the effect of significantly reducing the dihedral angle between the rings and causing the barrier to rotation around the thiophene–thiophene bond to be extremely low.[1] Furthermore, the two thiophene rings were splayed out in order for the carbonyl group oxygen to be able to get as close to the sulfur atom in the other thiophene ring as possible. In addition, the sulfur atom (in the other ring) which was close to the carbonyl oxygen (proximal sulfur) had significantly more positive charge than the sulfur atom which was further away (distal sulfur). This requires that the resonance forms containing a positive charge on the proximal sulfur atom make a greater contribution to the resonance hybrid than they would if the carbonyl oxygen was not close to that sulfur atom.[1]

In a very recent paper[2] we reported on the preparation of the three isomeric bithiophene esters, dimethyl 2,2′-bithiophene-3,4′-dicarboxylate (**1**), dimethyl 2,2′-bithiophene-4,4′-dicarboxylate (**2**) and dimethyl 2,2′-bithiophene-3,3′-dicarboxylate (**3**) and on the X-ray crystal structures of each. Compounds **1** and **2** were both planar in the solid state and these planar structures were in excellent agreement with the reported ab initio calculated structures, confirming the low rotational barriers.[1] The 3,3′-isomer **3** was also extremely interesting in that it showed a large dihedral angle between the thiophene rings (74.8°) and, more significantly, this was the first bithiophene shown to have the two thiophene ring sulfur atoms exclusively *syn*.[2] All other 2,2′-bithiophenes whose structures have been determined have their sulfur atoms *anti*.



1: X = O
4: X = NH

2 **3**

With the observation that the calculated thiophene–thiophene dihedral angle was approximately 19° and the rotational barrier was extremely low (0.084 kcal/mol; 0.35 kJ/mol) in **1**, we reasoned that with judicious choice of substituents we should be able to produce planar bithiophenes containing substituents, particularly carbonyl groups, in the 3- and 3,3′-positions.

This would be particularly important in the area of conjugated polymers where a reduction in band gap (as the result of greater conjugation in completely planar

Keywords: planar bithiophenes; ab initio calculations; 3,3′,4,4′-tetra-substituted-bithiophenes; electrostatic attraction.

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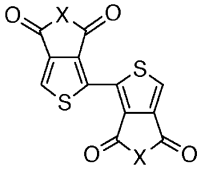
systems) would give rise to altered optical and electronic characteristics.[3,4]

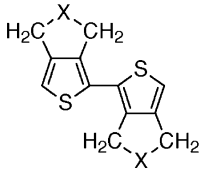
It was hoped that by placing a greater amount of negative charge on the carbonyl oxygen atom there would be a greater attraction to the proximal sulfur atom. This might force the bithiophene to become planar. A substituent with a greater negative charge on the carbonyl oxygen than an ester is an amide. An ab initio calculation [3-21G(*) basis set] on the *N*-methyl amide **4** with geometry optimization showed that rather than the dihedral angles getting smaller they got somewhat larger and were calculated to be 34.7 and 28.0°.† This in spite of the slightly more negative proximal carbonyl oxygen (Mulliken charge density = −0.65 versus −0.64 in **1**). Apparently the increase in dihedral angle is due to the greater C–O bond distance in **4** (more single bond character in the C=O bond; 1.225 Å in **4** versus 1.210 Å in **1**) resulting in greater steric interaction.

In order to reduce the steric effect somewhat we incorporated the C=O into a five-membered ring. Calculations [3-21G(*) basis set with full geometry optimization] on the anhydride **5**, thioanhydride **6**, *N*-methylimide **7** and diketone **8** showed that they were all *planar* in spite of there being carbonyl groups in *both* the 3- and 3′-positions.‡ This should be contrasted with the head-to-head isomer **3** which has a dihedral angle of 74.8° and a very large calculated rotation barrier of 8.9 kcal/mol (37 kJ/mol).[1]

In order to demonstrate that these molecules are planar because of the electrostatic oxygen–sulfur interactions, we replaced the carbonyl groups with CH_2 groups and repeated the 3-21G(*) calculations on bithiophenes **9**–**12**. The dihedral angles for the four molecules were 14.6, 62.3, 36.1 and 34.8°, respectively, clearly considerably twisted.



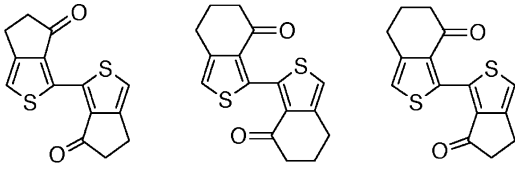
5: X = O
6: X = S
7: X = NCH_3
8: X = CH_2



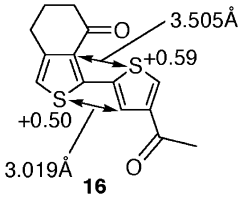
9: X = O
10: X = S
11: X = NCH_3
12: X = CH_2

Furthermore, and even more significantly, the carbonyl oxygen to proximal sulfur distances were 2.896 , 2.709, 2.876 and 2.792 Å in **5**–**8**, respectively, while the hydrogen to sulfur distances were 3.117 and 3.190 Å in **9**, 3.404 and 3.696 Å in **10**, 3.110 and 3.223 Å in **11** and 3.219 and 3.354 Å in **12**. *Thus, the larger oxygen atoms force themselves closer to the sulfur atom, at distances significantly smaller than the sum of the oxygen and sulfur van der Waals radii (3.32 Å)*[5] *than the smaller hydrogen atoms*. The sum of the hydrogen and oxygen van der Waals radii is 3.00 Å.[5] This extremely short sulfur–oxygen distance is the result of the electrostatic attraction between these two atoms.[1]

Another system we have examined at the 3-21G(*) level is the five-membered ring diketone **13** which is also completely planar. However, when we convert the five-membered rings to six-membered rings, a seemingly small perturbation, the dihedral angle then becomes 80.2° in molecule **14**. Even when one ring is five-membered and the other is six-membered as in **15** the molecule is considerably twisted with dihedral angles of 68.5 and 71.7°.§ When the five-membered ring carbonyl interaction is removed as in molecule **16** the molecule is still twisted although the dihedral angles are rather small, 11.3 and 8.8°.§ Furthermore, there is a short oxygen–proximal-sulfur distance of 2.625 Å and a larger positive charge on the proximal sulfur, +0.59, compared to the distal sulfur, +0.50. This, coupled with the approximately 0.5 Å greater sulfur to carbon-3-of-the-other-ring distance (on the carbonyl side of the molecule; see structure **16**) compared to the other sulfur to C-3′ distance, supports the idea of the molecule distorting considerably in order to gain the Coulombic stabilization as described previously.[1]



13 **14** **15**



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Thus, with the appropriate substituents it should be quite possible to prepare planar polythiophenes containing carbonyl substituents in head-to-head arrangements.

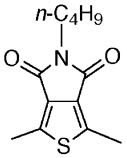
Several years ago a paper appeared in which the monomeric units **17**, **18** and **19** were incorporated into polymers.[6] These polymers were of two types. The first were donor–acceptor polymers containing units of **17**–**19** alternating with thiophenes containing electron donating substituents and the second were homopolymers of **18** and **19**. It was noted that the donor–acceptor polymers had lower band gaps than the

† The rings are slightly puckered giving two different dihedral angles.

‡ In all cases where the dihedral angles are said to be 0° or the molecule is said to be planar the dihedral angles are all calculated to be less than 0.3°.

§ The rings are slightly puckered giving two different dihedral angles with the larger one being on the side of the six-membered carbonyl ring.

homopolymers as is known for these types of systems.[6] Based on our calculations we can say that it is possible that part of the higher band gap in the homopolymers is due to the considerable twisting around the thiophene–thiophene bonds giving rise to much less effective conjugation. In addition a comparison of the absorption maxima of the two donor–acceptor polymers **20** and **21** shows that the one containing the five-membered ring imide **20** is red shifted relative to the molecule containing the six-membered ring quinone **21**. This could be due, at least in part, to the ability of the five-membered ring to allow for greater planarity of the polymer backbone relative to the six-membered ring which would cause much greater twisting.



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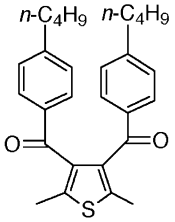

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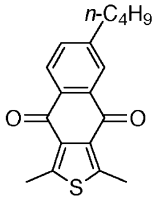

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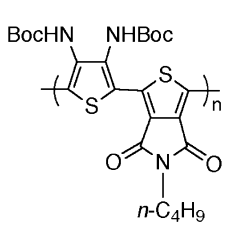

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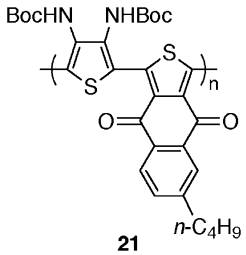

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