Conformational analysis of 3,3′-, 3,4′- and 4,4′-dimethoxy-2,2′-bithiophenes as models for related polymers

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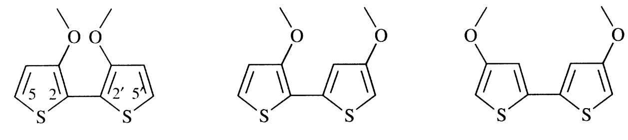
An analysis of ^{13}C chemical shifts of quaternary carbons of 3,3′-, 3,4′- and 4,4′-dimethoxy-2,2′-bithiophenes indicates they can be a useful tool for the identification of the inter-ring junction type. UV spectra and theoretical calculations are used to perform a conformational analysis of the compounds. The results show that the compounds prefer a non-planar conformation in non-condensated phases. The reasons for this non-planarity of the dimers and the effect on related polymers are discussed.

In the field of conducting polymers, β-alkoxy-substituted polythiophenes are the subject of current interest because of their low oxidation potential which renders their doped state very stable.[1]

Unfortunately, knowledge of the exact structure of such polymers is scarce, though the effect that the regiochemistry of the substitution has on the conformation of the polymer chain is of great importance in determining the physical properties of the material.[2] Only a few examples are reported in which the polymer has been characterized by its ^{1}H and ^{13}C NMR spectra,[1a,i] but no detailed structural information could be given.

An unambiguous way of establishing the regiochemistry of polymers is by comparison with model compounds.[3] We present in this paper ^{1}H, ^{13}C NMR and UV data for 3,3′-, 3,4′- and 4,4′-dimethoxy-2,2′-bithiophenes (**1**, **2** and **3**, respectively), that we consider models for the head-to-head, head-to-tail and tail-to-tail junctions present in the linear polymer (Scheme 1).



1 **2** **3**

Scheme 1 Head-to-head, head-to-tail and tail-to-tail junctions

The results of molecular mechanics and semiempirical quantum mechanical calculations on these compounds are also reported in order to determine their conformation and hence to have an insight into the conformational preferences of the corresponding polymer.

Results and discussion

NMR data

In Tables 1 and 2 ^{1}H and ^{13}C NMR data of the title compounds are reported.

Assignments are easily obtained by comparison with the values of 3-methoxythiophene.[4] It is evident that carbon chemical shifts are more sensitive to the regiochemistry of substitution than hydrogen ones. In particular, the negative mesomeric effect of the oxygen is mainly exerted on the β carbon of the formal double bond to which it is linked. As a consequence, quaternary carbons which are head in a junction have chemical shift values 20 ppm more shielded than their tail counterparts. Moreover, as carbons linked to oxygen are strongly deshielded, the three different quaternary types (head, tail and *ipso*) occupy three well separated regions of the spectrum (112, 135 and 155 ppm) and can be easily identified. For this reason, they can be considered useful probes to determine the nature of the inter-ring junctions present in a related polymer and to define its general regiochemistry.

UV data

In order to have an insight into the conformational preferences of inter-ring junctions in the polymer chain, UV absorption maxima of **1**–**3** were measured. As the overlap of π orbitals belonging to adjacent rings is related by a cosine law to the inter-ring twist angle, $\lambda_{\mathbf{max}}$ is expected to decrease if the molecules deviate from planarity. All the compounds show very similar absorption maxima ($\lambda_{\mathbf{max}} = 323$, 323 and 324 nm for **1**, **2** and **3**, respectively). These are the same values reported for 3,3′- and 4,4′-dipentoxy-2,2′-bithiophenes,[5] showing that the different length of the alkyl residue does not affect the conformational preferences of the alkoxy compounds. This is in contrast, however, with what is reported for alkyl thiophenes,[6] in which decreasing values are found going from 4,4′ to 3,4′ to 3,3′ isomers ($\lambda_{\mathbf{max}} = 311$, 299 and 268 nm, respectively), showing a neat increase in the torsion of the inter-ring junction on going from tail to head substitution. The UV data of alkoxy compounds would then signify that they have always the same conformation, irrespective of the regiochemistry of the substitution. This behaviour has been explained[5] by assuming that the alkoxy groups, having a reduced hindrance compared to alkyl groups, have a reduced tendency to distort the inter-ring junction. Moreover, in the case of *anti* head-to-head connectivity, the interaction of the S and the alkoxy substituent in the 3′ position would be not repulsive but rather attractive, further favouring an *anti* planar conformation. This would be in agreeement with X-ray determinations of the structures of 3,3′- and 4,4′-dimethoxy[7] and 3,3′- and 4,4′-dipentoxy-2,2′-bithiophenes,[5] which are all found to be *trans* planar.

In our opinion, as the methoxy group has a significant steric hindrance compared to the hydrogen atom, it cannot always be assumed that head-to-head and tail-to-tail connectivities lead to the same distortion, as could be inferred from the similarity of UV absorptions. On the other hand, conformational differences between the crystal and gas or solution state have already been reported for 2,2′-bithiophene[8] and for substituted oligothiophenes.[3b,9]

MM2 calculations

To gain a better insight into this subject, MM2 force-field calculations[10] were performed on compounds **1**–**3**. Force-field calculations have provided a better description of conformational preferences on substituted bithiophenes than semiempirical or *ab initio* calculations [see discussion in ref. 3(*b*)] and the results are reported in Table 3.

Table 1 ^{1}H chemical shifts (ppm) and coupling constants (*J*/Hz in parentheses) of the dimers **1**–**3**

Compound	Me	3-H	4-H	5-H	Me′	3′-H	4′-H	5′-H
1	3.96	—	6.87 (5.61)	7.11 (5.61)	3.96	—	6.87 (5.61)	7.11 (5.61)
2	3.94	—	6.86 (5.53)	7.07 (5.53)	3.81	6.91 (1.68)	—	6.13 (1.68)
3	3.81	6.82 (1.71)	—	6.15 (1.71)	3.81	6.82 (1.71)	—	6.15 (1.71)

Table 2 ^{13}C chemical shifts (ppm) of the dimers **1**–**3**

Compound	Me	C-2	C-3	C-4	C-5	Me′	C-2′	C-3′	C-4′	C-5′
1	58.3	113.9	152.9	115.8	121.9	58.3	113.9	152.9	115.8	121.9
2	58.8	112.1	153.7	116.8	121.7	57.2	134.0	114.7	157.9	95.0
3	57.3	136.2	115.7	158.3	96.1	57.3	136.2	115.7	158.3	96.1

Table 3 MM2 calculated inter-ring twist angles (ω/°), steric energies (E/kJ mol^{-1}) and relative populations (p%) of the dimers **1**–**3**

Compound	ω^{a}/°	E/kJ mol^{-1}	p(%)	ω/°	E/kJ mol^{-1}	p(%)
1	±10°	148.5	2	±135°	138.5	98
2	0°	131.0	22	±145°	129.7	78
3	0°	124.3	10	±155°	120.1	90

[a] $\omega = 0°$ corresponds to a *syn* planar conformation, $\omega = 180°$ to an *anti* planar conformation

Table 4 UV absorption maxima ($\lambda_{\max}$/nm) calculated for various inter-ring angles ω (°) of the dimers **1**–**3**

ω^{a}/°	1	2	3
180	355	343	332
165	353	342	329
150	348	336	324
135	337	325	312
120	321	310	297
105	301	294	282
90	279	275	265

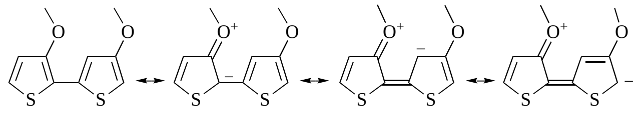
[a] $\omega = 0°$ corresponds to a *syn* planar conformation, $\omega = 180°$ to an *anti* planar conformation

For all three isomers the most stable conformation is the s-*trans* one. The s-*trans* forms are not planar but tilted by an angle $\pm\omega$. Deviation from planarity increases on going from tail-to-tail to head-to-head substitution, as found for methyl compounds.[6b]

The interconversion barrier for the s-*trans* forms from $-\omega$ to $+\omega$, which can be correlated with the steric hindrance of the substituent group, has then been calculated from the difference between the MM2 steric energy of a fixed *anti* planar form and the corresponding *anti* tilted minimum ($E_{180°} - E_{\omega}$) and is 10.9, 4.2 and 1.7 kJ mol^{-1} for **1**, **2** and **3**, respectively. These values compare well with those for 3,3′-, 3,4′- and 4,4′-dimethyl bithiophenes (14.6, 6.3 and 2.1, respectively).[6b] The S – – O′ distance in the head *anti* planar junctions is 2.94 Å, much less than the sum of the van der Waals radii (3.85 Å). As in the Buckingham type potential used in the MM2 force-field non-bonded interactions between two non-bonded atoms are repulsive when the interatomic distance is less than (sum of vdW radii)/1.136, then this distance gives rise to a repulsive interaction by 3.9 kJ mol^{-1}. The S – – H′ interactions in the tail *anti* planar junctions result in a repulsion of 1.4 kJ mol^{-1}. All these interactions force the system out of planarity. The greater steric hindrance of the alkoxy group with respect to hydrogen and the greater repulsive character of the S – – O′ interaction with respect to S – – H′ account for the increased distortion in going from **3** to **1**.

UV calculations

The behaviour suggested by MM2 calculations is nevertheless in contrast with the behaviour suggested by UV data. As already found for methylsulfanylbithiophenes,[3b] this contrast is resolved in analysing the resonance structures of the molecules (Scheme 2).



Scheme 2 Mesomeric effect of head methoxy on compound **2**

We can see that the methoxy group in a head position can extend its conjugation to the adjacent ring; as a consequence, head systems are more delocalized, and should therefore have, for the same torsion angle, a greater $\lambda_{\max}$ than tail ones. To study this hypothesis, we have calculated the $\lambda_{\max}$ of compounds **1**–**3** at different inter-ring angles ω by the use of a semiempirical program which calculates electronic transitions including singly excited configurations and d orbitals.[11] Calculations were performed on optimized PM3[12] geometries and the reliability was tested by comparing the value obtained for 3-methoxythiophene (247 nm) with the experimental one (243 nm). The results are reported in Table 4.

For the same inter-ring angle **1** always shows the greater $\lambda_{\max}$ followed by **2** and **3**, indicating that the inter-ring mesomeric effect of the alkoxy group follows, in fact, the order of head substitution. The experimental value at 323 nm found for all three isomers is not significant for the same torsional angle, but corresponds to different angles, 120°, 135° and 150° for **1**, **2** and **3**, respectively. Compound **1** results in the most tilted compound, followed by **2** and **3**, in perfect agreement with the results from the independent MM2 calculations.

Conclusions

Alkoxy groups have in effect a reduced steric hindrance compared to alkyl groups, but exert a similar regiosteric control of the junction conformation, the greater the head character of the junction, the more non-planar the substance becomes. This applies to the molecules in solution. Interconversion barriers are not high, so it is understandable that in the solid state the packing energy forces the dimers to planarity. It is questionable however how information arising from dimers in the solid state may be transmissible to polymers. To the best of our knowledge, bithiophenic systems have always been found to be *trans* planar in the solid state, but, considering only tetramers, dimethyl head-to-head junctions have been found to be both planar[9a] and non-planar;[9b] poly(3-alkyl thiophenes) exhibit the highest conjugation when head-to-head junctions are absent.[2c,6b] The situation is different in polyalkoxythiophenes, in which a different substitution pattern does not affect significantly the electrical and optical properties of the polymer. In particular, polymers derived from trimers from which only head-to-head linkages can be formed show almost the same λ_{max}(555 nm) as polymers in which only tail-to-tail linkages are present (560 nm).[1*k*] As *trans* planar head-to-head junctions have a greater λ_{max} than tail-to-tail ones, the equality of these values leads us to conclude that, also in the polymer case, the alkoxy head-to-head junction can be considered a source of steric hindrance, but that this 'defect' effect is counterbalanced by the strong mesomeric effect of the oxygen atom in the head position, giving rise to the same 'effective conjugation' of less tilted systems.

Experimental

3,3′-Dimethoxy-2,2′-bithiophene was prepared by oxidative coupling of 2-lithio-3-methoxythiophene.[13] 4,4′-Dimethoxy-2,2′-bithiophene was prepared by oxidative coupling of 5-lithio-2-trimethylsilyl-3-methoxythiophene and subsequent desilylation.[14] 3,4′-Dimethoxy-2,2′-bithiophene was prepared by coupling of the 2-triisopropylsilyl-5-bromo-3-methoxythiophene and 2-trimethyltin-3-methoxythiophene in the presence of tetrakistriphenylphosphinepalladium(0) and subsequent desilylation.[15]

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C in $CDCl_3$ solution, with $SiMe_4$ as internal standard. UV spectra were recorded on a λ6 Perkin-Elmer instrument in $CHCl_3$ solution.

Theoretical calculations were carried out on a Vax 3500 computer. All minima were checked by frequency analysis.

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