

## A Useful Method for Structure Determination of Symmetrically Substituted 3,3'-Bithienyls

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The  $\text{OCH}_3$ -resonance in 2- and 3-carbomethoxythiophenes and in 5,5'-dicarbomethoxy-3,3'-bithienyls occurred within the small interval of 6.10–6.20  $\tau$  but was shifted 0.2–0.3 ppm up-field in 2,2'- and 4,4'-dicarbomethoxy-3,3'-bithienyls. The shifts cannot be explained in terms of electronic effects by the aryl substituents. The various ways in which the  $\text{OCH}_3$ -resonance in the latter compounds may be affected by the magnetic anisotropy of the aromatic rings and the carbonyl groups in the molecule are discussed.

By the difference between the chemical shifts of the carbomethoxy groups in the 5,5'- and in the 2,2'- or 4,4'-positions of symmetrically substituted 3,3'-bithienyls, a useful method for assigning structures to this system is available through PMR-spectroscopy. Many products obtained by electrophilic aromatic substitution reactions in 3,3'-bithienyls are easily converted to carboxylic methyl esters whose structure can be determined by PMR-spectroscopy. This method might be valid also for other biaryl systems.

In connection with work on 3,3'-bithienyls,<sup>1</sup> it was found from the PMR-spectra of some dicarbomethoxy-3,3'-bithienyls and carbomethoxythiophenes that the  $\text{OCH}_3$  resonance occurred within the small interval of 6.10–6.20  $\tau$  in 2- and 3-carbomethoxythiophenes and in 5,5'-dicarbomethoxy-3,3'-bithienyls. When the carboxylic ester groups were situated at the 2,2'- or 4,4'-positions, *i.e.* *ortho* to the pivot bond of 3,3'-bithienyls, however, the resonance was shifted 0.2–0.3 ppm up-field (Table 1). For example, the  $\tau_{\text{OCH}_3}$ -values for the bromo compounds 3, 4, and 14 in Table 1 are approximately the same, but the value for 22 is 0.2 ppm higher. The same is found if the iodine compounds 5, 6, and 15 are compared with 23. The  $\text{OCH}_3$  resonance occurred at 6.11  $\tau$  in the nitro compound 2 and at 6.29  $\tau$  in 21. In this connection it would have been of greater interest to compare 21 and 17 with 2,2'- or 4,4'-dinitro-5,5'-dicarbomethoxy-3,3'-bithienyl, but these compounds have not yet been prepared. For compound 24 both  $\tau_{\text{OCH}_3}$ -values are 0.24 ppm higher than for compound 12.

Table 1. Chemical shifts of the OCH<sub>3</sub> protons of some carbomethoxythiophenes and dicarbomethoxy-3,3'-bithienyls in CS<sub>2</sub> (2 % TMS).

No.	Ester	$\tau$	Ref. <sup>a</sup>
1	2-Carbomethoxythiophene (neat 6.12)	6.18	9
2	—, 4-nitro-	6.11	10
3	—, 3,4-dibromo-	6.15	1
4	—, 3,4,5-tribromo-	6.15	
5	—, 3,4-diiodo-	6.13	
6	—, 3,4,5-triiodo-	6.15	
7	3-Carbomethoxythiophene	—	
8	—, 2-formyl-	6.11	11
9	—, 4,5-dibromo-	6.19	
10	—, 4-bromo-5-iodo-	6.19	
11	—, 4-bromo-2,5-diiodo-	6.15	
12	2,4-Dicarbomethoxy-3-bromothiophene	6.16; 6.19	
13	5,5'-Dicarbomethoxy-3,3'-bithienyl	—	
14	—, 2,2',4,4'-tetrabromo-	6.14	1
15	—, 2,2',4,4'-tetraiodo-	6.12	
16	4,4'-Dicarbomethoxy-3,3'-bithienyl	6.49	12
17	—, 2,2'-dinitro-	6.31	13
18	—, 2,2'-diiodo-	6.47	
19	—, 2,2',5-triiodo-	6.43; 6.51	
20	2,2'-Dicarbomethoxy-3,3'-bithienyl	—	
21	—, 4,4'-dinitro-	6.29	14
22	—, 4,4'-dibromo-	6.36	1
23	—, 4,4'-diiodo-	6.37	
24	2,2',4,4'-Tetracarbomethoxy-3,3'-bithienyl	6.40; 6.43	

<sup>a</sup> Refer to preparations.

In 5,5'- and 2,2'-dicarbomethoxy-4,4'-dimethyl-3,3'-bithienyl, the OCH<sub>3</sub> resonance occurred at 6.20  $\tau$  and 6.40  $\tau$ , respectively, as recorded by Gronowitz and Hagen.<sup>2</sup>

It is seen from the  $\tau$ -values given in Table 1 that the OCH<sub>3</sub> resonance is only little affected by substituents and that there is no shielding by an aryl group *meta* to the carboxylic ester group. The deviating  $\tau$ -value for a carbomethoxy group *ortho* to the pivot bond in symmetrically substituted 3,3'-bithienyls cannot therefore be explained in terms of electronic effects. Long-range shielding effects caused by the magnetic anisotropy of the aromatic rings and the carbomethoxy group in the adjacent \* ring have to be considered.

In a twisted 3,3'-bithienyl with *cis-skew* conformation the carbomethoxy groups at the 2,2'- or 4,4'-positions come close to each other. Models show that the OCH<sub>3</sub> protons of the carboxylic ester group in one ring may be shielded by the carbonyl part of the carbomethoxy group in the other and *vice versa*. Further investigations of 2- or 4-carbomethoxy-3,3'-bithienyls not having carboxylic ester groups or other strongly shielding substituents in the *ortho*

\* The aromatic ring situated at the *ortho* position to the carbomethoxy group in question will henceforth be referred to as the adjacent ring.

positions of the other ring would show what importance long-range effects by these groups have.

Long-range shielding effects by the aromatic nuclei in biaryl systems have been observed in symmetrically bridged biphenyls<sup>3</sup> and the shielding of *ortho* hydrogens in twisted biphenyls has long been known.<sup>4</sup> Scale models show that the methyl protons of a 2- or 4-carbomethoxy group in a twisted 3,3'-bithienyl may be situated above the adjacent thiophene nucleus. If it is assumed that the carboxylic ester group (in *cis* conformation<sup>5</sup>) is arranged in the plane of the ring to which it is attached (max. conjugation), as in Fig. 1, the OCH<sub>3</sub> protons are situated approximately 5 Å above the pivot

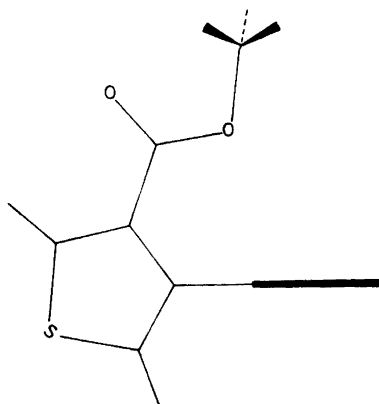


Fig. 1. Geometry of 4-carbomethoxy-3,3'-bithienyl.

atom in the adjacent thienyl group. Further, if it is assumed that the shielding by a thiophene nucleus is the same as that by a benzene ring, a graph by Johnson and Bovey<sup>6</sup> predicts an up-field shift of 0.3–0.4 ppm for the OCH<sub>3</sub> resonance when the angle of twist is 90°. In fact the shielding by thiophene is somewhat smaller than by benzene which is evident from an investigation by de Jongh and Wynberg.<sup>7</sup> Thus the magnitudes of the observed shifts exhibited by the OCH<sub>3</sub> protons in 2,2'- and 4,4'-dicarbomethoxy-3,3'-bithienyls might be explained in terms of anisotropy effects by the aromatic rings.

At angles of twist of about 45°, however, the ester protons are very little shielded by the adjacent ring<sup>6</sup> unless the conformation of the carbomethoxy group is changed. Rotation about the bonds within this substituent will also have other consequences. If the carboxylic ester group and the ring to which it is attached are arranged as in Fig. 1, the OCH<sub>3</sub> protons are *deshielded* both by the carbonyl group and the ring.<sup>4</sup> Deviations from this conformation, especially if caused by rotation around the C—OCH<sub>3</sub> bond, should result in an up-field shift of the proton resonance because of *less deshielding*. Such deviations might be brought about in various ways by interaction between the carbomethoxy group and the adjacent ring or substituents in the *ortho* positions of the adjacent ring.

It is obvious that *ortho* substituents in an aromatic ring adjacent to a carbomethoxy group may be of importance for the chemical shifts of the

OCH<sub>3</sub> protons. This will be further investigated when suitable compounds have been prepared. Until then, the discussion below has to be limited to symmetrically substituted 3,3'-bithienyls.

By the difference between the chemical shifts of carbomethoxy groups in the 5,5'-positions and in the 2,2'- or 4,4'-positions of 3,3'-bithienyls, a useful method for assigning structures to this system is available in PMR-spectroscopy. The method should also be applicable to other biaryls. In 3,3'-bithienyl chemistry, there is seldom any doubt as to whether substituents are situated in the 2,2'- or in the 4,4'-positions, but often there is a choice between the 2,2'- and 5,5'-positions as they are the most reactive ones. It is clearly shown in Table 1, and it is also apparent from the observation of Gronowitz and Hagen, that it can be decided by PMR-spectroscopy if carbomethoxy groups are situated in the 5,5'-positions or not, *i.e.* the structures of most dicarbomethoxy-3,3'-bithienyls can be determined in this way.

Carboxylic methyl esters are conveniently prepared from carboxylic acids with diazomethane. Except for nitration and sulphonation products, the compounds obtained in most electrophilic aromatic substitution reactions in the 3,3'-bithienyl system are easily converted to carboxylic acids. From the PMR-spectra of their methyl esters, the structures of all compounds in the reaction series can be deduced. Thus metalation products afford carboxylic acids upon carbonation. Halogen derivatives obtained on bromination and iodination react smoothly with aliphatic lithium compounds and the products yield carboxylic acids on carbonation. Halogen compounds are very useful in thiophene<sup>8</sup> and in 3,3'-bithienyl<sup>1</sup> chemistry, as the intermediate lithium derivatives obtained from them are very reactive and can be converted to a great variety of products. The structures of these products are apparent from the structures of the carboxylic acids obtained from the common lithium intermediate. In most cases, even the structures of the halogen compounds used as starting material are apparent from the structures of the carboxylic acids, though under certain conditions rearrangements may take place in the halogen-metal exchange reaction.<sup>8</sup> Formylation yields aldehydes, which can be smoothly oxidized to carboxylic acids, and methyl ketones obtained on acetylation are easily converted to carboxylic acids by the haloform reaction.

Disubstituted 3,3'-bithienyls and tetrasubstituted ones which have methyl or formyl groups in the rings may be assigned structures on the bases of coupling constants.<sup>8</sup> This new very useful method of structure determination is especially recommendable for tetra- and hexasubstituted 3,3'-bithienyls. It is also invaluable in disubstituted compounds as a complement to existing methods, or when the observation of coupling constants is made difficult by strong couplings in the system.

*Materials.* All the esters, except those of the aldehyde and nitro compounds, were prepared by the author and co-workers by methods which will be published later.

The bithienyl *14* (Table 1) was prepared from hexabromo-3,3'-bithienyl and compound *22* from 3,4-dibromo-2-carbomethoxythiophene (*3*).<sup>1</sup> By a similar method, the iodine analogues *15* and *23* were prepared from hexaiodo-3,3'-bithienyl and 3,4-diiodo-2-carbomethoxythiophene (*5*), respectively. The structures of the bithienyls *15* and *23* were deduced in the same way as the structures of the compounds *14* and *22*.<sup>1</sup> The structures of the bithienyls *18*, *19*, and *24* are apparent from their mode of preparation; compound *24* was obtained from *12* by an Ullmann reaction and *18* and *19* were obtained

through iodination of 16. Compounds 14, 16, 17, 21, and 22 are described in the literature. The bithienyls 13 and 20 have not yet been prepared.

The PMR-spectra were recorded on a Varian Associated A-60 spectrometer using CS<sub>2</sub> solutions saturated with the test compound or containing 15 % of sample. Diluting the solutions to double volume caused a shift of less than 0.01 ppm.

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