

CARBON-13 NMR OF 6A-THIATHIOPHTHENS

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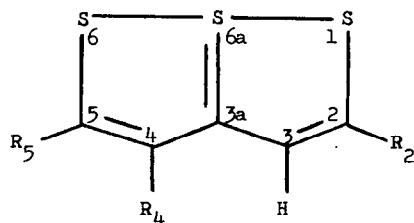
(Received in UK 31 May 1974; accepted for publication 26 June 1974)

A considerable quantity of work¹⁻³ has been carried out in recent years into the nature of the bonding and structure of 6a-thiathiophthens⁴. The exact nature of the electronic distribution in such molecules has also been the subject of controversy, but it is now generally accepted that such a distribution involves a delocalized ten π -electron system analogous to naphthalene. We have chosen to investigate some 6a-thiathiophthens by carbon-13 nmr as a direct means of studying the carbon skeleton of such molecules and their electron distributions.

Carbon-13 nmr spectral information has been reported for monocyclic five-membered heterocycles⁵⁻¹⁰. The information available in this regard indicates that as far as substituent chemical shift (SCS) effects are concerned the behaviour of these heterocycles is more akin to that of olefins than aromatic systems despite the fact that their chemical reactivities reflect aromatic-like behaviour. We now report some carbon-13 SCS effects for 6a-thiathiophthens.

The assignment of Carbon-13 nmr resonances to specific carbons was carried out as follows. With the aid of proton single-frequency off-resonance decoupling, quaternary carbon signals could be distinguished from those arising from carbons with attached protons. In the parent compound, 6a-thiathiophthen (I), the resonance at 176.8 ppm could thus be assigned to C-3a. The C-2/C-5 resonance in this compound would also be expected to be to low field of the C-3/C-4 resonance owing to the deshielding effect of the neighbouring sulphur atom.

Assignment of the resonances in derivatives (II) and (IV) and in (III) and (V) were made by comparing the chemical shifts with those of (I) and assuming additivity of the SCS effects of methyl and phenyl substitution, a procedure which



- (I) $R_2 = R_4 = R_5 = H$
 (II) $R_2 = CH_3, R_4 = R_5 = H$
 (III) $R_2 = C_6H_5, R_4 = R_5 = H$
 (IV) $R_2 = R_5 = CH_3, R_4 = H$
 (V) $R_2 = R_5 = C_6H_5, R_4 = H$
 (VI) $R_2 = CH_3, R_4 = H, R_5 = C_6H_5$
 (VII) $R_2 = CH_3, R_4 = C_6H_5, R_5 = H$
 (VIII) $R_2 = C_6H_5, R_4 = H, R_5 = SCH_3$
 (IX) $R_2 = R_5 = SC_2H_5, R_4 = H$

Table I

Carbon-13 Chemical Shifts* of some 6a-Thiathiophthens

	C-2	C-3	C-3a	C-4	C-5	CH ₃	C ₆ H ₅				SCH ₃	SCH ₂
							C-1	o	m	p		
I	161.1	128.2	176.8	128.2	161.1	-	-	-	-	-	-	-
II	176.6	126.4	177.9	128.9	161.5	24.2	-	-	-	-	-	-
III	176.1	125.5	177.9	127.4	160.9	-	136.9	127.1	128.4	129.9	-	-
IV	176.7	126.9	178.9	126.9	176.7	24.6	-	-	-	-	-	-
V	175.7	124.6	178.9	124.6	175.7	-	137.2	127.0	128.4	129.9	-	-
VI	176.2	127.9	178.9	123.6	176.2	24.4	137.4	127.0	128.3	129.7	-	-
VII	176.3	127.6	178.6	141.4	158.7	25.3	137.7	129.0	128.3	129.2	-	-
VIII	165.6	122.1 [†]	174.0	124.2 [†]	190.9	-	134.2	126.7	128.5	129.9	17.7	-
IX	177.6	122.4	174.0	122.4	177.6	14.1	-	-	-	-	-	29.2

* In ppm downfield from internal TMS. Solutions were about 0.1 M in CDCl₃ and spectra were obtained on a Varian XL-100-15FT spectrometer.

† Assignments may be reversed.

has precedence from work on aromatic, olefinic and heterocyclic compounds⁹⁻¹⁰.

Confirmation of this process was provided by the fact that the chemical shifts calculated for 2-methyl, 5-phenyl, 6a-thiathiophthen (VI) using the SCS effects corresponded almost exactly with the observed shifts. A computer analysis on the chemical shifts of compounds (II) to (VI) relative to those of (I) to find the best-fit

Table II

Substituent Chemical Shift Effects* for the 6a-Thiathiophthen Ring System

Substituent	C-2	C-3	C-3a	C-4	C-5
2-CH ₃	+ 15.4	+ 0.6	+ 1.1	-1.9	+ 0.3
2-C ₆ H ₅	+ 14.9	-2.7	+ 1.1	-0.9	-0.3
2-SCH ₃	+ 30.1	-3.1	-3.9	-3.4	-10.4
3-C ₆ H ₅	-2.7	+ 15.1	+ 0.7	-1.2	-0.2

* In ppm ; positive indicates a downfield shift.

2-methyl and 2-phenyl SCS effects possessed an r.m.s. error of 0.06 ppm which is within experimental error (± 0.1 ppm). The assignments in the remaining molecules were made similarly. The chemical shifts are given in Table I and the SCS effects in Table II.

The initial observation made from the results was that in the case where 6a-thiathiophthen was symmetrically substituted (compounds I, IV, V, and IX) the molecules were totally symmetric within the nmr time-scale as indicated by the equivalence of the carbon-13 chemical shifts for C-2 and C-5 and for C-3 and C-4. Similar results have been found from proton nmr^{11,12}, but such a result is not indicated from X-ray crystallographic data¹⁵ for the 2,5-diphenyl derivative (V). Hence it is clear that the information gained from the solid state must be used with caution when investigations are made in solution. Also the excellent fit of the additivity scheme for the 2-methyl and 2-phenyl SCS effects clearly indicates that the electronic and conformational effects influencing the carbon-13 chemical shifts are a constant for a particular substituent and suggests that the degree of substitution in these limited cases does not affect the time-averaged geometry of the ring system in any significant way in solution unlike the results indicated for the solid state.

The SCS effects given in Table II are similar to those for thiophene⁸ derivatives and in common with the effects found for pyrroles⁵⁻⁸ and furans⁶, where comparison with literature values is possible, are different to those found for benzenoid⁹⁻¹⁰ and naphthalenic¹⁴ derivatives. The difference is most noticeable in the case of the 2-SCH₃ effects which are strikingly different to those found for thio-

anisole [$+10.1$ (C_{att}), -1.9 (ortho), $+0.2$ (meta), and -3.7 ppm (para)]. The large long-range SCS effect at C-5 due to this substituent is unexpected and the size and extent of all the effects indicate a large perturbation of the electron distribution with more charge present on C-3, C-3a, C-4, and C-5 than in 6a-thiathiophthen itself. This may be due to geometrical distortions, large degrees of which are observed in the solid state for 2-methylthio-6a-thiathiophthen derivatives¹⁵.

Acknowledgements: We wish to thank Dr. R.J.S. Beer (University of Liverpool) and Dr. D.H. Reid (University of St. Andrews) for providing the compounds and also Dr. R.J.S. Beer for helpful discussions throughout this work.

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