# Observations on the N.m.r. Spectra of Some Derivatives of 1,4-Oxathian *S*-Oxide. Anisotropy of the S→O Bond

By K. W. BUCK, A. B. FOSTER,* W. D. PARDOE, M. H. QADIR, and J. M. WEBBER
(*Chemistry Department, The University, Birmingham* 15)

IN the preceding Communication,[1] the major sulphoxide[2] (*A*) obtained by periodate oxidation of (2*S*,6*R*)-6-hydroxymethyl-2-methoxy-1,4-oxathian (derived[3] from methyl α-D-glucopyranoside)

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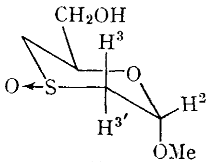
* Present address: Chester Beatty Research Institute, Institute of Cancer Research: Royal Cancer Hospital, Fulham Road, London, S.W.3.

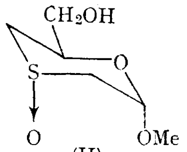
was shown to adopt essentially the chair conformation (I) in the crystal state. The n.m.r. spectrum† of sulphoxide (*A*) showed, *inter alia*, a triplet for H-2 (anomeric proton) at $\tau$ 4·87 ($J_{2,3} + J_{2,3'}$ *ca.* 5 c./sec.) typical[4] of an *eq* proton equally coupled to the protons of a vicinal methylene group and consistent with the chair conformation (I). Comparable signals ($\tau$ 5·16 and 5·24, $J_{2,3} + J_{2,3'}$ *ca.* 5 c./sec. in each case) were shown for H-2 in (2*S*,6*R*)-6-hydroxymethyl-2-methoxy-1,4-oxathian and its trityl derivative [*cf.* quartet, $\tau$ 5·43, $J_{2,3} + J_{2,3'}$ *ca.* 11 c./sec., for the (2*R*,6*R*)-isomer[5] of the latter compound]. The minor sulphoxide (*B*) showed a quartet ($\tau$ 4·93) for H-2 indicative[4] of unequal coupling with the vicinal methylene protons, but the low value (*ca.* 5·5 c./sec.) of the summated coupling constants, $J_{2,3} + J_{2,3'}$, was consistent with a conformation only slightly distorted from the chair form (II). Presumably, the nonbonded interaction between the sulphoxide and methoxyl oxygen atoms, which are in *syn*-axial positions, causes this distortion. The well established[6] (although as yet unexplained) preference of the sulphoxide oxygen atom in thian *S*-oxide derivatives for an *ax* position may be invoked to account for the tendency of sulphoxide (*B*) to adopt a conformation near to that of structure (II) rather than the alternative chair conformation with two *eq* groups.

The signal (complex multiplet, $\tau$ 5·29) for H-6 in sulphoxide (*B*) was at much lower field than that ($\tau$ 6·10) for the corresponding proton in isomer (*A*). The significant deshielding of H-6 in sulphoxide (*B*) may be rationalized by invoking acetylenic-type anisotropy for the $\text{S} \rightarrow \text{O}$ bond [*syn*-axial to H-6 in structure (II)] and/or the operation of a *syn*-axial proximity effect[7] due to van der Waals interactions.[8] Burg[9] considers that the $\text{S} \rightarrow \text{O}$ bond can be described as a single ($\sigma$) bond with partial triple bond character (*d,p*-$\pi$ overlap) with an overall bond order of 2. In contrast, Edmundson[10] assumed, but did not establish, that the anisotropy of the $\text{S} \rightarrow \text{O}$ bond is formally analogous to that of the C=O bond.

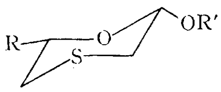
Results obtained with related sulphoxides may also be rationalized in terms of an acetylenic-type anisotropy coupled with a *syn*-axial proximity effect of the $\text{S} \rightarrow \text{O}$ bond. The signal for H-2 [quartet at $\tau$ 4·25 ($CCl_4$), $J_{2,3} + J_{2,3'}$ *ca.* 12 c./sec.] for (2*R*,6*S*)-2-acetoxy-6-methyl-1,4-oxathian (derived[3] from methyl α-L-rhamnopyranoside) is characteristic of an *ax* proton unequally coupled to the *ax* and *eq* protons of a vicinal methylene group and is consistent[4] with the di-*eq* conformation (III). Now periodate oxidation of 4-substituted thians results[11] in preferential *ax* oxygenation with the preponderating *cis*-sulphoxide assuming a chair conformation with an *ax* $\text{S} \rightarrow \text{O}$ group. *S*-Oxidation of the oxathian (III) gave *ca.* 70% of a sulphoxide {m.p. 153°, $[\alpha]_D$ + 110° (ethanol), structure (IV) expected by analogy} in which the H-2 signal was a quartet ($\tau$ 3·52, $J_{2,3} + J_{2,3'}$ *ca.* 10·5 c./sec.) at much lower field than that ($\tau$ 4·27, $J_{2,3} + J_{2,3'}$ *ca.* 10·5 c./sec.) for the minor sulphoxide (not isolated pure) presumably having structure (V). Similarly, racemic[12] 2-methoxy-1,4-oxathian, which showed a quartet ($\tau$ 6·15 (benzene), $J_{2,3} + J_{2,3'}$ *ca.* 9 c./sec.] for H-2 consistent with conformation (VI), gave, on *S*-oxidation, *ca.* 80% of a sulphoxide, m.p. 62—63°, of expected structure (VII) having an H-2 signal [quartet, $\tau$ 5·30 (benzene), $J_{2,3} + J_{2,3'}$ *ca.* 9 c./sec.] at much lower field than that (superimposed on the H-3 and H-3′ signals at $\tau$ 5·90—6·40) for the minor isomer (VIII), m.p. 38—40°.



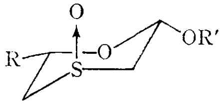
(I)



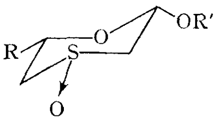
(II)



(III) R = Me, R′ = Ac
(VI) R = H, R′ = Me



(IV) R = Me, R′ = Ac
(VII) R = H, R′ = Me



(V) R = Me, R′ = Ac
(VIII) R = H, R′ = Me

Absolute configuration has been reliably assigned to stereoisomeric sulphoxides only by the *X*-ray method[13] and on the basis of intramolecular nucleophilic displacements[14] although asymmetric synthesis may have some value in certain cases.[15] Establishment of the anisotropic character fo the

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† All n.m.r. spectra were determined on *ca.* 20% solutions in $CDCl_3$ (unless otherwise stated) with internal tetramethylsilane.

S → O bond might allow configurational assignments to suitable compounds, such as the 1,4-oxathian *S*-oxide derivatives described above, to be based on n.m.r. spectroscopy.

(*Received, September 6th*, 1966; *Com.* 664.)

*Note:* Compound (I) in the preceding Communication should strictly be named as (2*R*,6*S*)-2-hydroxymethyl-6-methoxy-1,4-oxathian. However, since reference is made to 2-methoxy-1,4-oxathian, compound (I) is named here as a derivative of the latter system to facilitate comparison.—*Ed.*

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