Magnetic Non-equivalence of Protons in a Sulphinyl Carbanion

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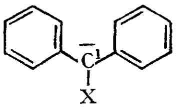
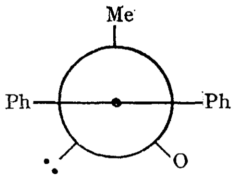
THE n.m.r. spectrum of the diphenylmethanide anion (Ia), obtained by abstraction of a proton from diphenylmethane with potassium amide in liquid ammonia, is temperature-dependent. Whereas the two *para*-protons appear as one triplet at all temperatures, the four *ortho*-protons appear as one signal at −20°, but as two doublets at −60°: rotation around the C(1)–C(aryl) bonds has become restricted on the n.m.r. time scale.

Compared with (Ia) the barrier for rotation will be lower for (Ib), (Ic), and (Id) by virtue of the electron-attracting properties of the methylthio-, methylsulphinyl, and methylsulphonyl-groups.[1] The spectra of (Ib) and (Id) are indeed temperature-independent (−20 to −60°), the ring protons in each case giving rise to a doublet (four *ortho*-protons), a triplet (four *meta*-protons), and a triplet (two *para*-protons).



(Ia) X=H
(Ib) X=MeS
(Ic) X=MeSO
(Id) X=$MeSO_2$



(II)

The anion (Ic) constitutes a different case. At high temperatures its spectrum shows the 4 : 4 : 2 pattern. When the temperature is lowered, all signals broaden and subsequently sharpen again (Figure). The most salient feature of the low-temperature spectrum is the non-equivalence of the two *para*-protons: one triplet (*J* 7·2 c./sec.) of triplets (*J* 1·2 c./sec.) at δ 6·34 and one at 6·62.

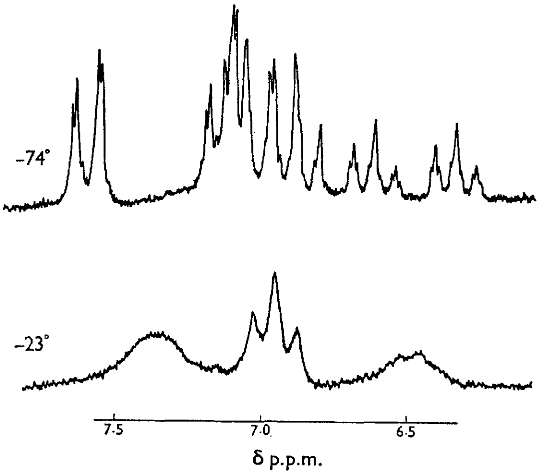


FIGURE. *Part of the* 100 *Mc. spectrum of the anion of diphenylmethyl methyl sulphoxide in liquid ammonia.*

Known cases of magnetic non-equivalence in molecules containing the pyramidal sulphiny-group are of the "ethane type".[2] This possibility can be excluded for the anion (Ic): for it would require a pyramidal configuration at C-1 and a temperature-independent 1 : 1 ratio of two conformers, and it might give rise to two methyl signals (which is not observed). The non-equivalence of the two rings is caused by restricted rotation around the C(1)–S bond. A probable configuration is (II).[3]

The different δ values for the *para*-protons point to different amounts of negative charge in the two rings. It might be caused by different electrostatic interactions with the sulphinyl group or by different torsions around the two C(1)–C(aryl) bonds.[4]

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[1] H. Kloosterziel, 3rd Organic Sulphur Symposium, Caen, May 1968, Abstracts, p. 22.
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[3] S. Wolfe, A. Rauk, and I. G. Csizmadio, *J. Amer. Chem. Soc.*, 1967, **89**, 5710.
[4] G. J. Heiszwolf and H. Kloosterziel, *Rec. Trav. chim.*, 1967, **86**, 1345.