Benzene-induced Solvent Shifts in the Nuclear Magnetic Resonance Spectra of Sulphoxides

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THE n.m.r. spectra of a variety of unsymmetrical sulphoxides[1,2] confirms that methylene protons α to the sulphoxide group are magnetically non-equivalent. It has been briefly noted that the α-protons of thian 1-oxide give an AB spectrum at temperature above −20°[3] and that the methylene protons of diethyl sulphoxide are non-equivalent.[4]

Benzene solvent-shifts in the high resolution n.m.r. spectra of carbonyl compounds[5] have been found to be useful in elucidating their proton geometry. Sizeable shifts are also found for compounds containing other polar groups.[6] We have found that the magnetic non-equivalence of methylene protons in sulphoxides is enhanced in C_6D_6. Particularly interesting results are obtained with tetrahydrothiophen *S*-oxide and isobutyl sulphoxide: n.m.r. spectrum of tetrahydrothiophen *S*-oxide δ (CCl_4) *ca.* 2·73,† [t (with traces of line doubling), 4H], 2·41 (complex, 2H), 2·01 p.p.m. (complex, 2H): (C_6D_6), 2·37 (complex, 2H),

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† All δ values, in p.p.m. downfield from Me_4Si in the particular solvent. The values are for dilute solutions (<2%) and were unchanged by further dilutions. Spectra were recorded on a Varian HR-100 spectrometer.

1·95 (complex, 4H), and 1·20 p.p.m. (complex, 2H). The resonances at 2·73 and 2·01 p.p.m. did not shift to 1·95 and 1·20 p.p.m. in C_6D_6, and that at 2·41 remained essentially unchanged, as shown by the n.m.r. spectrum of α-[$2H_4$]tetrahydrothiophen *S*-oxide in CCl_4 of two separate bands *ca.* 2·4 and 2·0 p.p.m., integrating to 2H each, general appearance of an AA^{1}BB^1 spectrum. This confirms that the four nearly equivalent protons at 2·73 p.p.m. are indeed the α-protons: the two bands in C_6D_6 appear at *ca.* 1·95 and 1·20 p.p.m. The effect of the benzene is to shift the α-protons by unequal amounts to *ca.* 2·37 and 1·95 p.p.m.

Models of the origin of benzene solvent shifts predict that the benzene molecule will position itself as far as possible from the negative end of a dipole.[6a] Hence, benzene will preferentially solvate the tetrahydrothiophen *S*-oxide molecule *trans* to the oxygen. The signals which are shifted most in benzene will be due to *trans*-protons. The two β-protons giving a signal *ca.* 2·01 p.p.m. (CCl_4 *ca.* 0·8 p.p.m. shift in C_6D_6) must be *trans* to the oxygen. The sulphoxide oxygen has deshielded the β-protons *cis* to it, as expected.[2,7] The resonances for the protons of tetrahydrothiophen *S*-oxide (C_6D_6) are centred approximately as follows: *cis*-α, 2·37; *trans*-α, 1·95; *cis*-β, 1·95; *trans*-β, 1·20 p.p.m.

Noticeable solvent shifts are also found for aliphatic sulphoxides. The methylene protons of diethyl sulphoxide in CCl_4 give an apparent first-order quartet centred at 2·56 p.p.m. The low-field lines show some tendency toward splitting under conditions of highest resolution. In C_6D_6 the methylene band gives a well-resolved spectrum, at 2·01 p.p.m. corresponding to the AB part of an ABX_3 spectrum. The n.m.r. spectra of di-n-propyl and di-n-butyl sulphoxides (CCl_4) clearly indicate that the methylene protons are non-equivalent. The chemical-shift difference between the A and B protons are even more pronounced in C_6D_6. The methyl groups of di-isopropyl sulphoxide are non-equivalent δ (CCl_4) 1·24 and 1·21 p.p.m. In C_6D_6 the chemical shifts are separated to 1·06 and 0·86 p.p.m. Hence, signals due to the protons *trans* to the sulphoxide oxygen for the greatest part of the time will be the most shifted by benzene (*cf.* ref. 2).

An exception was dibenzyl sulphoxide. The methylene protons give an AB spectrum in CCl_4, δ_A 3·72, δ_B 3·71 p.p.m., J_{AB} 13·0 ± 0·5 c./sec.: in C_6D_6 3·42, singlet only: but in [$^2H_6$]dimethyl sulphoxide an AB spectrum was again recorded, δ_A 4·18, δ_B 3·90, J_{AB} 13 c./sec.

With di-isobutyl sulphoxide, not only are the chemical shift differences between the methylene proton-signals enhanced in C_6D_6, but the methyl protons, (1·09 p.p.m., CCl_4), are non-equivalent in C_6D_6, (0·90 and 0·85 p.p.m.). This apparently stems from the asymmetric solvation of the sulphoxide function.

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