Influence of *para*-Substituents on Chemical Shifts of 2-Nitrobenzenesulphenate Esters

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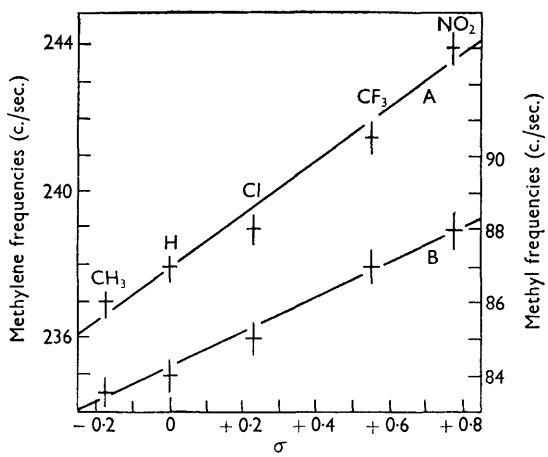
IN connection with another study we have prepared the ethyl esters of a series of 4-substituted 2-nitrobenzenesulphenic acids by reaction of the sulphenyl chlorides with anhydrous ethanol.[1] The n.m.r. spectra of these esters, 4-X-2-NO_2·C_6H_3·SOEt (X = NO_2, CF_3, Cl, H, Me), measured in deuterochloroform (using a Varian model A-60 analytical n.m.r. spectrometer; frequency 60·005 Mc./sec.), show a triplet at around τ 8·6, and a quartet at around τ 6·1, characteristic of the ethyl group. The frequencies of the mid-point of each of these resonances give a linear relationship with the Hammett σ-constant of the 4-substituent as shown. The slope of the line is 7·20 c./sec. (r = 0·991) for the methylene protons, and 4·84 c./sec. (r = 0·996) for the methyl protons, both correlation coefficients being well within the limits advocated by Jaffé.[2]

Correlations have recently been reported[3] between the Hammett σ-constant and the n.m.r. chemical shifts of protons bonded to atoms alpha and beta to the aromatic ring, but such effects have not hitherto been reported for more distant protons. In all cases these atoms were adjacent to the conjugated system associated with the ring, or formed a part of this system. From a consideration of the stereochemistry of disulphides and peroxides, it seems unlikely that the oxygen atom in these esters can be conjugated with the ring without participation by the *d*-orbitals of the sulphur. Alternatively the effect could be transmitted through the σ-bonds, the unusual range being explained by the polarisability of the sulphur atom.[2]

The observed slopes of the lines, in conjunction with the value of 13·74 c./sec. found for the methylene protons in a series of *para*-substituted ethylbenzenes,[3] gives attenuation factors,[2] ϵ, of 0·52 for –S·O–, and 0·67 for $-CH_2-$. Although the latter value is somewhat higher than the average value obtained,[4] transmission by the –S·O– linkage still seems significantly high for a two-atom group.



Plot of methylene frequencies (line A, left-hand scale) and methyl frequencies (line B, right-hand scale) against the Hammett σ-constant for the 4-substituent.

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[1] K. Fries, *Ber.*, 1912, **45**, 2965; N. Kharasch, D. P. McQuarrie, and C. M. Buess, *J. Amer. Chem. Soc.*, 1953, **75**, 2658.
[2] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.
[3] K. L. Williamson, N. C. Jacobus, and K. T. Soucy, *J. Amer. Chem. Soc.*, 1964, **86**, 4021, and references cited therein.
[4] R. A. More O'Ferrall and S. I. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 4016; Jaffé, ref. 2.