Nuclear Magnetic Resonance Spectra of Some Aromatic Sulphur Derivatives

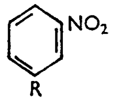
By **C. Brown** and **D. R. Hogg**, Department of Chemistry, University of Aberdeen, Aberdeen, AB9 2UE.

The n.m.r. spectra of series of 4-substituted-2-nitrophenyl acetonyl sulphides, ethyl sulphides, benzyl sulphides, and ethyl disulphides and of some ethyl 4-substituted-2-nitrobenzenesulphenates have been measured. The frequencies of the methyl and methylene protons give a good correlation with the Hammett σ-constant ($r > 0·990$). Transmission factors of 0·67 ± 0·07, 0·60 ± 0·09, and 0·69 ± 0·16 were obtained for –CH$_2$–, –S–, and –O– respectively. These values are discussed with respect to previously recorded values.

THE effect of substituents on the chemical shifts of various nuclei has been studied in detail.[1] In many cases [1,2] correlations between the chemical shifts of various nuclei (*e.g.* ^{13}C, ^{19}F, and ^{1}H) and the Hammett σ constants or similar substituent parameters have been reported. The precise nature of some of these correlations makes them potentially useful for studying the electronic effects of substituents and the transmission of these effects along side chains. The aim of the present study was to determine whether electronic effects relayed through longer side chains, especially those containing sulphur atoms, would measurably influence the chemical shifts of more distant atoms, and to explore the n.m.r. method as a means of obtaining transmission factors. In a preliminary communication [3] we reported that the chemical shifts of the methyl and methylene protons of a series of ethyl 4-substituted-2-nitrobenzenesulphenates bear a linear relationship to the Hammett σ constant, and calculated attenuation factors for –S·O– and –CH$_2$–. We now amplify and extend these observations to related series of sulphides and disulphides.

RESULTS AND DISCUSSION

The n.m.r. spectra of series of 4-substituted-2-nitrophenylacetonyl sulphides (I), ethyl sulphides (II), ethyl disulphides (III), and benzyl sulphides (IV) and of some ethyl 4-substituted-2-nitrobenzenesulphenates (V) were measured. The aromatic signals were generally complex and no correlation could be found between their chemical shifts or coupling constants and the substituent constants. The methylene protons in the five series become increasingly shielded in the order, ArS·CH$_2$Ph, ArS·OEt, ArS·CH$_2$·COMe, ArSEt, ArS·SEt, which, for the first four series, is in keeping with the combined effects of electronegativity differences, ring current, and anisotropy. The last two series are in the opposite order to that previously observed [4] for dimethyl sulphide and disulphide and we suggest that this small deshielding effect produced by increasing the sulphur chain length is less important, in the compounds studied, than the decrease in the ring current effect with increasing distance. The frequencies of the side-chain resonances (c./sec. relative to internal tetramethylsilane), the visually determined slopes of the graphs of frequency against σ, and the correlation coefficients (r) are given in the Table. A typical graph is shown in Figure 1.



(I) Y = CH$_2$·COMe
(II) Y = Et
(III) Y = SEt
(IV) Y = CH$_2$Ph
(V) Y = OEt

In agreement with previous observations, the value of ρ is decreased by the introduction of atoms between the ring and the protons studied, and for compounds of the type ArS·CH$_2$X [series (I), (II), and (IV)] the values of ρ found for the methylene frequencies are essentially independent of the group X. In cases [5] where ρ varies with substituents which are constant for each series, the constant substituent is conjugated with a reacting centre which develops a considerable demand for electrons.

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[3] C. Brown and D. R. Hogg, *Chem. Comm.*, 1965, 150.

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The transmission factor ε gives a measure of the ability of a group to attenuate the electronic effects of substituents during transmission. For a group X, the transmission factor has been defined[6] as the ratio of the ρ values for a given process undergone by the two series of compounds R–X–Y and R–Y, where R is the substituent-bearing portion of the molecule and Y the site which undergoes the process

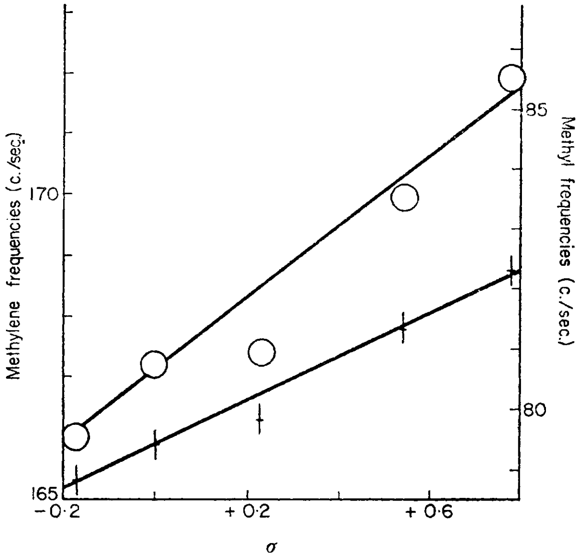

FIGURE 1 Plots of methylene frequencies (○) and methyl frequencies (†) against the Hammett σ constant for a series of 4-substituted-2-nitrophenyl ethyl disulphides

$$\varepsilon_X = \rho_{RXY}/\rho_{RY} \qquad (1)$$

From this equation

$$(\nu_R - \nu_H)_{RXY} = \varepsilon_X(\nu_R - \nu_H)_{RY}$$

The graph of $[\nu_R(CH_2) - \nu_H(CH_2)]$ against $[\nu_R(CH_3) - \nu_H(CH_3)]$ for series (II), (III), and (V) is shown in Figure 2; from a least-squares determination of the best straight line ε_{CH_2} is 0·67 (standard deviation 0·035). By combination of the data from series (II) with those from series (III), the data from series (II) with the published[1] values for substituted ethylbenzenes, and the data from series (V) with the limited data on 4-substituted phenetoles,[2c] $\varepsilon_S = 0{\cdot}60 \pm 0{\cdot}09$; similarly from series (II) and (V) $\varepsilon_O = 0{\cdot}69 \pm 0{\cdot}16$.

Methyl and methylene frequencies for series (I)—(V) measured for solutions in deuteriochloroform

4-Substituent (R)	ArS·CH$_2$·COMe (I)		ArSEt (II)		ArS·SEt (III)		ArS·CH$_2$Ph (IV)	ArSOEt (V)	
	ν(CH$_2$)	ν(CH$_3$)	ν(CH$_2$)	ν(CH$_3$)	ν(CH$_2$)	ν(CH$_3$)	ν(CH$_2$)	ν(CH$_2$)	ν(CH$_3$)
MeO	226·0	139·0					249·5		
Me	227·7	139·0	178·5	82·5	166·0	78·8	250·5	237·0	83·5
H	228·5	140·5	180·5	83·5	167·2	79·4	253·3	238·0	84·0
Cl	230·5	141·0	180·5	84·5	167·4	79·8	252·3	239·0	85·0
EtO$_2$C..............							256·0		
CF$_3$	233·7	143·0	185·3	87·1	170·0	81·3	257·3	241·0	87·0
NO$_2$	235·0	143·0	188·0	89·0	172·0	82·3	260·3	244·0	88·0
Slope (c./sec.) ...	9·4	4·3	10·0	7·0	6·0	4·0	10·1	7·2	4·8
r	0·995	0·990	0·991	0·994	0·992	0·991	0·991	0·991	0·996

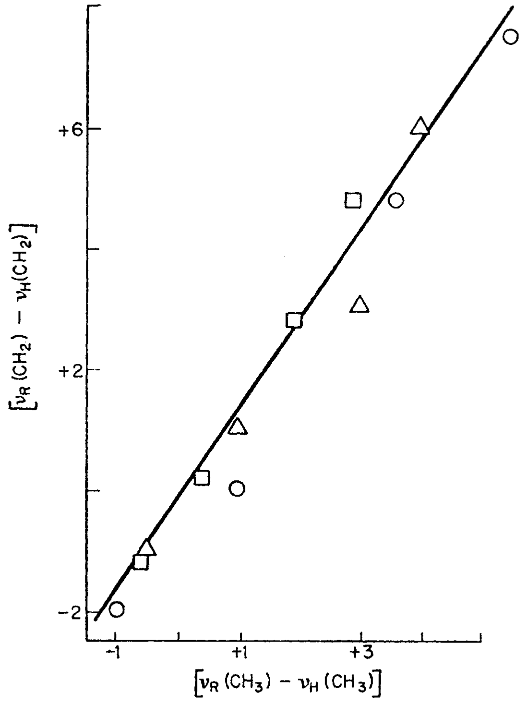

FIGURE 2 Plot of $[\nu_R(CH_2) - \nu_H(CH_2)]$ against $[\nu_R(CH_3) - \nu_H(CH_3)]$ for series (II) (○), series (III) (□), and series (V) (△)

The value of ε_{CH_2} obtained in this study is considerably higher than the value of 0·37 usually[7] assigned to the methylene group and the values of 0·43 ± 0·05 and 0·51 obtained from n.m.r. studies on substituted ethylbenzenes.[1,2a] Deviations of this magnitude are not unusual: a value of 0·71 ± 0·07 has been obtained[1] for the additional methylene group in β-phenylpropionic acid, and from the ρ values for the alkaline hydrolysis of the ethyl esters of phenylacetic and β-phenylpropionic acids[8] a value of 0·72 may be calculated. The value for ε_S is somewhat lower than the value of 0·77 calculated from pK_a [8a,9] measurements for the series ArS·CH$_2$·CO$_2$H

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and $ArCH_2{\cdot}CO_2H$. In view of the conflicting influence of size and polarisability on the transmission of electronic effects[10] similar values for ε_S and ε_O seem reasonable. We suggest that in addition to the intrinsic factors controlling the transmission of electronic effects through atoms, field effects are important in these and in similar systems. In the compounds studied, conformations exist in which the methyl group is closer to the substituent and the aromatic ring than the methylene group. In such conformations the attenuation of the electronic effect of the substituent should be compensated for by the field effect of the substituent and the aromatic ring, and thus the magnitudes of ρ_{RXY} and ε_{CH_2} will be increased.

EXPERIMENTAL

The n.m.r. spectra were measured at room temperature (*ca.* 30°) for solutions in deuteriochloroform with a Varian model A60 analytical spectrometer at 60·005 Mc./sec. Frequencies are expressed as c./sec. downfield from internal tetramethylsilane, and each quoted value is the mean of at least six measurements on at least two solutions of different concentrations (*ca.* 3% w/w). With the acetonyl sulphides (I), the ethyl sulphides (II), and the ethyl disulphides (III) a three-fold dilution did not affect the resonance frequencies in any regular manner. The benzyl sulphides (IV) showed a concentration effect: the frequency decreased in a linear fashion with increasing concentration. Over the concentration range covered (20—250 mg. ml.$^{-1}$) the plots of methylene frequency against concentration were approximately parallel for all the benzyl sulphides studied (slope -9 c./sec. g.$^{-1}$ ml.). The frequencies recorded for the benzyl sulphides were obtained by extrapolation to infinite dilution, although the magnitude of the concentration effect was such that the error introduced by small differences in concentration would have been well within the estimated error ($\pm$0·5 c./sec.).

Materials.—All the compounds the spectra of which are recorded were synthesised by known methods or simple modifications thereof, and gave n.m.r. spectra in accord with their structures. In the case of known compounds the m.p.s were in agreement with the literature values.

Acetonyl Sulphides.—The acetonyl 4-substituted-2-nitrophenyl sulphides (I; R = MeO, Me, H, Cl, CF_3, or NO_2) were prepared by reaction of the appropriate sulphenyl chloride[11] with acetone in the dark for 2—3 days. Removal of the excess of acetone under reduced pressure left a nearly quantitative yield of the acetonyl sulphide. *Acetonyl 4-methoxy-2-nitrophenyl sulphide* gave orange needles, m.p. 90·5—91° [from benzene–light petroleum (b.p. 60—80°)], $\nu_{max.}$ (Nujol) 1725 cm.$^{-1}$, $\lambda_{max.}$ (ethanol) 242, 274sh, and 395 mμ (ε 17,900 and 3600) (Found: C, 50·1; H, 4·8; N, 5·5; S, 13·5. $C_{10}H_{11}NO_4S$ requires C, 49·7; H, 4·6; N, 5·8; S, 13·3%); *acetonyl 2-nitro-4-trifluoromethylphenyl sulphide* gave yellow needles, m.p. 130—132° (from aqueous acetone), $\nu_{max.}$ (Nujol) 1725 cm.$^{-1}$, $\lambda_{max.}$ (ethanol) 251, 272, and 364 mμ (ε 11,900, 7200, and 2980) (Found: * C, 45·4; H, 3·1; N, 5·0; S, 11·8. $C_{10}H_8F_3NO_3S$ requires C, 43·1; H, 2·9; N, 5·0; S, 11·5%).

Ethyl Sulphides.—The ethyl 4-substituted-2-nitrophenyl sulphides (II; R = Me, H, Cl, CF_3, or NO_2) were prepared by reaction of the corresponding 1-chloro-4-substituted 2-nitrobenzenes under reflux with ethanethiol and an equivalent amount of sodium hydroxide in aqueous ethanol. *Ethyl 2-nitro-4-trifluoromethylphenyl sulphide* (30%) gave yellow needles, m.p. 68—69° (from aqueous methanol), (Found: * C, 43·6; H, 3·5; N, 5·9; S, 12·9. $C_9H_8F_3NO_2S$ requires C, 43·0; H, 3·2; N, 5·6; S, 12·75%).

Ethyl Disulphides.—The ethyl 4-substituted-2-nitrophenyl disulphides (III; R = Me, H, Cl, CF_3, or NO_2) were prepared by reaction of the corresponding 4-substituted-2-nitrobenzenesulphenyl chlorides with ethanethiol under reflux in acetic acid. *Ethyl 4-methyl-2-nitrophenyl disulphide* (89%) gave yellow needles, m.p. 46—47° (from ethanol) (Found: C, 47·4; H, 5·1; N, 6·4; S, 27·8. $C_9H_{11}NO_2S_2$ requires C, 47·1; H, 4·8; N, 6·1; S, 27·95%); and *ethyl 4-trifluoromethylphenyl disulphide* (91%) was a low melting yellow solid, b.p. 90—93°/0·5 mm. (Found: C, 38·2; H, 3·1; S, 22·9. $C_9H_8F_3NO_2S_2$ requires C, 38·2; H, 2·8; S, 22·65%).

Benzyl Sulphides.—The benzyl 4-substituted-2-nitrophenyl sulphides (IV; R = MeO, Me, H, Cl, CO_2Et, CF_3, or NO_2) were prepared by heating the corresponding 1-chloro-4-substituted-2-nitrobenzenes under reflux with toluene-α-thiol and an equivalent amount of potassium hydroxide in methanol. *Benzyl 4-ethoxycarbonyl-2-nitrophenyl sulphide* (92%) gave light yellow plates, m.p. 143—144° [from benzene–light petroleum (b.p. 60—80°)] (Found: C, 60·5; H, 5·0; N, 4·3; S, 10·5. $C_{16}H_{15}NO_4S$ requires C, 60·7; H, 4·7; N, 4·4; S, 10·1%); *benzyl 2-nitro-4-trifluoromethylphenyl sulphide* (82%) gave lemon-yellow needles, m.p. 137—138° [from benzene–light petroleum (b.p. 60—80°)] (Found: C, 54·6; H, 3·2; N, 4·2; S, 10·0. $C_{14}H_{10}F_3NO_2S$ requires C, 53·75; H, 3·2; N, 4·5; S, 10·2%).

Ethyl Sulphenates.—The ethyl 4-substituted-2-nitrobenzenesulphenates (*V*; R = Me, H, Cl, CF_3, or NO_2) were prepared by leaving the corresponding 4-substituted-2-nitrobenzenesulphenyl chloride overnight in anhydrous ethanol. Removal of the solvent under reduced pressure left a virtually quantitative yield of ester. The i.r. spectra of all these esters showed strong absorption at *ca.* 1010 and 880 cm.$^{-1}$; the assignment of these bands will be the subject of a later communication. *Ethyl 4-methyl-2-nitrobenzenesulphenate* gave an orange oil purified by short path distillation at 0·1 mm. (Found: C, 50·1; H, 5·0; S, 14·9. $C_9H_{11}NO_3S$ requires C, 50·7; H, 5·2; S, 15·0%); *ethyl 2-nitro-4-trifluoromethylbenzenesulphenate* gave a golden-yellow oil, m.p. 20°, purified by short path distillation at 0·4 mm. (Found: N, 5·5; S, 12·2. $C_9H_8F_3NO_3S$ requires N, 5·25; S, 12·0%). The compounds, (V; R = H or NO_2) were prepared by a modification of the method of Kharasch, McQuarrie, and Buess.[12]

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* Considerable difficulty was experienced in obtaining satisfactory analyses for fluorine-containing compounds.

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