Intramolecular Hydrogen Bonds involving Polar Carbon–Hydrogen Bonds: Infrared and ^{1}H Nuclear Magnetic Resonance Spectra of Some Cyanomethyl and Benzyl Sulphones

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Two series of sulphones, containing respectively the cyanomethylsulphonyl and the benzylsulphonyl groups, have been prepared, in which a polar methylene group is allowed on steric grounds to interact intramolecularly with a nearby donor atom. The i.r. and ^{1}H n.m.r. spectra of these sulphones are compared with spectra of reference compounds in which no such interaction is possible. No conclusive evidence for intramolecular hydrogen bonds is found: possible causes for the observed spectral shifts are discussed.

INTERMOLECULAR hydrogen bonds between a polar C–H and a suitable electron-donor group are now well established.[1] They are characterised in the i.r. by low-frequency shifts in ν_{C-H}, accompanied by line broadening and intensification;[2] in the ^{1}H n.m.r. by a shift of the C–H proton to lower field;[3] and by close C–H $\cdots$ X approaches in the solid state as revealed by *X*-ray crystallography.[4] The latter effect is however regarded as an insufficient criterion for a hydrogen bond, unless supported further by spectroscopic evidence.[5]

Few claims for intramolecular hydrogen bonds involving polar C–H have been supported by all the above criteria. Most have been based on close C–H $\cdots$ X approaches in crystals, in the absence of substantiating

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[1] R. D. Green, ' Hydrogen Bonding by C–H Groups,' Macmillan, London, 1974, and references cited therein.

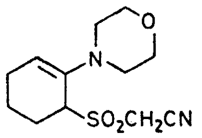
[2] A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 1715.

[3] H. J. Friedrich, *Z. Naturforsch.*, 1965, **20b**, 1021; J. V. Hatton and R. E. Richards, *Trans. Faraday Soc.*, 1961, **57**, 28.

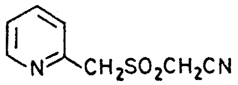
[4] (*a*) P. Anderson and T. Thurmann-Moe, *Acta Chem. Scand.*, 1964, **18**, 433; (*b*) J. C. Calabrese, A. T. McPhail, and G. A. Sim, *J. Chem. Soc.* (*B*), 1970, 282, and references cited therein.

[5] Ref. 4*b*, p. 284.

spectroscopic evidence,[6] or on a debatable interpretation of i.r. data.[7]



(1)



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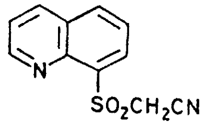

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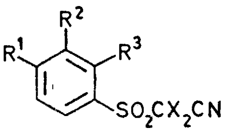

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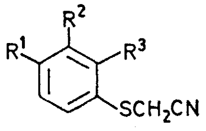
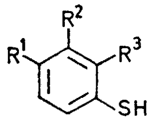
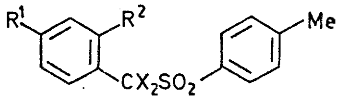


(9)

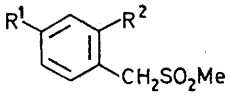


(10)

a; R^1=Me, R^2=R^3=H
b; R^1=R^3=H, R^2=F
c; R^1=R^2=H, R^3=F
d; R^1=Me, R^2=H, R^3=NO_2



(5) X = H
(8) X = D



(6)

a; R^1=R^2=H
b; R^1=H, R^2=F
c; R^1=NO_2, R^2=H
d; R^1=H, R^2=NO_2
e; R^1=R^2=NO_2

We recently reported compound (1) in which a close intramolecular C–H $\cdots$ N approach, detected by *X*-ray crystallography, was accompanied by a low-frequency shift in ν_{C-H} in the solid-phase i.r., thus providing very strong evidence for an intramolecular hydrogen bond in the solid state.[8] Evidence from the i.r. and ^1H n.m.r. spectra for the existence of the interaction in solution was strong but not conclusive.

The present work was carried out in the hope of identifying intramolecular hydrogen bonds, by both i.r. and ^1H n.m.r. spectroscopy, in a range of sulphones containing a polar methylene group.

The first series of compounds, the cyanomethylsulphones (2c and d), (3), and (4) were designed to lack the chiral centre found in the enamine-sulphone (1). They are however closely related to that compound in that the methylene group of interest is polarised by the same two groups (SO_2 and CN), and is theoretically able to interact intramolecularly with a nearby donor atom (F:, NO_2, or $\geqslant$N:).† No such intramolecular interaction is possible in the sulphones (2a and b), which thus may be used for reference purposes in detecting shifts in the spectra.

In the second series [types (5) and (6)], the polar methylene of a benzylsulphonyl group is further activated by substituents R^1 and R^2. When R^2 = F or NO_2, an intramolecular interaction is theoretically possible,† but when R^2 = H, this is not the case, and compounds

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† Intramolecular hydrogen bonds involving respectively nitro-[9] and fluoro-groups [10] and a proton donor are well known, but are relatively weak when compared with those involving more traditional bases.

[6] (*a*) H. Pandraud, *Acta Cryst.*, 1961, **14**, 901; (*b*) C. J. Fritchie and J. L. Wells, *Chem. Comm.*, 1968, 917; T. M. Gorrie and N. F. Haley, *J.C.S. Chem. Comm.*, 1972, 1081; (*c*) D. J. Sutor, *J. Chem. Soc.*, 1963, 1105.

[7] S. Pinchas, *J. Phys. Chem.*, 1963, **67**, 1862, and references cited therein.

[8] M. P. Sammes, R. L. Harlow and S. H. Simonsen, preceding paper.

[9] W. F. Baitinger, P. von R. Schleyer, T. S. S. R. Murty, and L. Robinson, *Tetrahedron*, 1964, **20**, 1635; A. O. Diablo, *Spectrochim. Acta*, 1972, **28A**, 1765.

[10] (*a*) T. Kobayashi and M. Hirota, *Chem. Letters*, 1972, 975; (*b*) R. C. Griffith and J. D. Roberts, *Tetrahedron Letters*, 1974, 3499.

(5a and c) and (6a and c) may be used for reference purposes.

Partial and complete deuterium exchange of the polar methylene was carried out on several of the compounds [to give types (7) and (8)], in order to assist in the identification of ν_{C-H} modes in the i.r. The crystal structures of compounds (2c), (3), and (5e) are reported elsewhere.[11]

RESULTS AND DISCUSSION

The chemical shifts and ν_{C-H} i.r. modes for the polar CH_2 (or CD_2) of the compounds studied are presented in Table 1. Data for the enamine-sulphone (1) are included also for reference purposes.

TABLE 1

^1H N.m.r. and i.r. data for active CX_2 in compounds (1)—(8)

Compound	δ ($CDCl_3$)	HCB [a] ν_{as}	HCB [a] ν_s	$CDCl_3$ ν_{as}	$CDCl_3$ ν_s	CCl_4 ν_{as}	CCl_4 ν_s
(1) [i]	4.08, 4.68	2 971	2 910	2 969 [b]	2 918	2 970	2 917
(2a)	4.07	2 985	2 933	2 986 [b]	2 934	2 986	2 934
(2b)	4.15	2 971	2 920	2 978	2 928	2 979	2 930
(2c)	4.30	2 994	2 942	2 985	2 930	2 989	2 934
(2d)	4.68	2 994	2 925	2 997	2 931	2 999	2 936
(7a)		2 247	2 133	2 249 [b]	2 133	2 247	2 133
(7b)		2 236	2 129	2 241 [b]	2 137	2 242	2 136
(7c)		2 254	2 142	2 244 [b]	2 138	2 249	2 142
(3)	4.29 [d]	2 994 [e]	2 942	2 979 [f]	2 930	2 991 [e]	2 939
		2 975	2 923			2 972	2 922
(4)	5.05	2 971	2 906	2 972	2 927	2 981	2 931
(5a)	4.25	2 979	2 937	2 980	2 925	2 980	2 927
(5b)	4.37	2 992	2 936	2 992	2 930	~2 990 [c]	2 931
(5c)	4.36	2 997	2 947	2 980	2 927	2 980	2 929
(5d)	4.88	3 016	2 952	3 013	2 955	3 012	2 954
(5e)	4.95	3 026	2 955	3 027	2 953	3 028	2 956
(8a)		2 243	2 159	2 239 [b]	2 157	2 240	2 155
(8b)		2 249	2 164	2 246 [b]	2 160	2 423	2 160
(8c)		2 257	2 164	2 243 [b]	2 160	2 241	2 161
(8d)		2 264	2 167	2 270 [b]	2 169	*g*	2 164
(8e)		2 273	2 176	2 274	2 172	*g*	2 172
(6a)	4.22	2 978	2 935	2 978	2 932	2 977	2 929
(6b)	4.29	2 988	2 938	2 993	2 936	2 992	2 938
(6c)	4.30	*h*	*h*	*h*	*h*	*h*	*h*
(6d)	4.78	*h*	*h*	*h*	*h*	*h*	*h*
(6e)	4.86	3 010	2 960	*h*	*h*	3 009	2 960

[a] Hexachlorobutadiene mull. [b] In $CHCl_3$. [c] Overlaps peak at 2 985 cm^{-1}. [d] Other CH_2 at δ 4.64. [e] Assignment to specific methylenes uncertain. [f] Peaks broad and unresolved. [g] Broad, ill-defined peak. [h] Assignments unclear. [i] See ref. 8.

N.m.r. Spectra.—Shifts in the CH_2 absorption relative to reference compounds may be due to inductive–mesomeric effects of other substituents, or in the presence of a hydrogen bond to the diamagnetic anisotropy and the electrostatic polarising effect of the donor atom or group. The first two factors may cause a shift either to high or to low field, though the anisotropic effect of the nitro-group is reported[12] to cause protons in the same plane to shift to low field. The third factor, the polarising effect, always causes a shift to low field, and is dominant in strong hydrogen bonds. However, with weak hydrogen bonds, the anisotropic effect may dominate.[13]

Cyanomethyl-sulphones. Compounds (2b—d), (3), and (4) all show a low-field shift in the CH_2 protons relative to the reference compound (2a). That of the fluoro-derivative (2b) cannot be due to an intramolecular hydrogen bond, and neither (2c)[11a] nor (3)[11c] contain such an interaction in the crystalline state, so are unlikely to do so in solution. The shifts in the nitro-sulphone (2d) and especially in the quinoline (4) are however significant [$\Delta\delta$ 0.61 and 0.98, respectively; *cf.* compound (1)], and indicate an interaction of some kind between the donor atom and the CH_2 protons.

Benzyl-sulphones. Compounds (5b—e) and (6b—e) likewise show a low-field shift in the CH_2 protons when compared with the reference compounds (5a) and (6a). The largest shifts occur when an *o*-nitro-group is present, and are much larger than would be predicted by comparison with a series of similarly substituted toluenes.[11d] This indicates that the polarising effect is probably dominating in the *o*-nitrobenzyl-sulphones, whereas inductive and anisotropic effects are probably dominating in the *o*-nitrotoluenes. Further evidence for this suggestion comes from *o*-fluorotoluene, where the methyl group absorbs at *higher* field (σ 2.25) than that in toluene itself (σ 2.33), the shift relative to the reference compounds being in the opposite direction with the fluoro-sulphones (5b) and (6b). Thus, an intramolecular dipole–dipole interaction seems to exist when a donor group is *ortho* to the CH_2.

I.r. Spectra.—The position of the ν_{C-H} modes for the

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[11] (*a*) R. Loghry and S. H. Simonsen, *Acta Cryst.*, in the press; (*b*) R. L. Harlow, M. P. Sammes, and S. H. Simonsen, *ibid.*, 1974, **B30**, 2903; (*c*) R. L. Harlow, S. H. Simonsen, C. E. Pfluger, and M. P. Sammes, *ibid.*, 1974, **B30**, 2264; (*d*) R. L. Harlow, S. H. Simonsen, R. L. Hitterman, M. H. Mueller, and M. P. Sammes, *ibid.*, in the press.

[12] I. Yamaguchi, *Mol. Phys.*, 1963, **6**, 105.

[13] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, 1958, **28**, 601.

polar CH_2 can be influenced by a number of factors, more than one of which are likely to be operating simultaneously.

Electron-withdrawing substituents attached to the CH_2 will shift ν_{as} and ν_s from their unperturbed positions (2 926 and 2 853 cm^{-1} respectively) to higher frequencies and cause their intensities to be reduced.[14] Likewise, steric compression between the CH_2 and a nearby group may also cause a shift to higher frequency.[15] Both inter- and intra-molecular hydrogen bonds will cause a shift to lower frequency, with ν_s changing more than ν_{as}.[2] Intramolecular hydrogen bonds involving polar C–H will however be difficult to detect, since the line half-widths and intensities for ν_{C-H} are not expected to change very much, and the shift in ν_{C-H} should be small for a weak, non-linear hydrogen bond.[2,8,16] Finally, if the interaction is very weak, a solvent such as $CHCl_3$ may compete successfully with the polar C–H for the proton acceptor, and thus uncouple any hydrogen bond present. Spectra were run in the solid phase, and in solution both in $CHCl_3$ and in CCl_4, in an attempt to distinguish some of these factors.

Cyanomethyl-sulphones. The behaviour of ν_{C-H} modes in compounds (2a—c) is fully paralleled by ν_{C-D} modes in the deuterio-derivatives (7a—c).* Meaningful trends in behaviour are however difficult to detect, due probably to the interplay of a number of the above factors. Shifts of ν_{C-H} to *higher* frequency (the opposite direction to that sought) roughly parallel changes in δ to lower field in the ^1H n.m.r. Notable exceptions are the fluoro-compound (2b) and the quinoline (4).† The former is hard to rationalise since concentration independence ($CHCl_3$, CCl_4) of ν_{C-H} rules out significant intermolecular interaction in solution, though this may be the cause in the solid state. I.r. and ^1H n.m.r. evidence indicates that the quinoline (4) may contain an intramolecular hydrogen bond, and an *X*-ray structure determination is currently underway. Also of note is the decrease in ν_{C-H} in the *o*-fluoro-compound (2c) in passing from the solid to the solution phase, when the *meta*-derivative (2b) shows the opposite trend. Intermolecular C–H $\cdots$ O distances slightly less than the normal van der Waals distance of 2.60 Å are observed[11a] between the CH_2 and SO_2 groups in (2c). Removal of possible interactions when the compound dissolves may help to account for the shift in ν_{C-H} to lower frequency. The high frequency of ν_{as} in the nitro-compound (2d) is also of interest, and is discussed in the next section.

Benzyl-sulphones. Once again, the behaviour of ν_{C-H} [in compounds (5a—e)] is paralleled by the ν_{C-D} modes in the dideuterio-derivatives (8a—e). Likewise, shifts of δ to lower field in the ^1H n.m.r. parallel shifts in ν_{C-H} to *higher* frequency, contrary to the behaviour expected from hydrogen bonds.‡ However, both *X*-ray[11c] and neutron diffraction[11d] studies on the dinitro-compound (5e) show a close (2.22 Å) approach between the methylene C–H and one of the oxygen atoms of the *o*-nitro-group. This interaction is also shown to be present in solution, both by the low field shift of the CH_2 in the ^1H n.m.r., and by the constancy of ν_{C-H} modes in the i.r. on passing from solid to solution phase.

Pinchas[7] uses high frequency shifts both in ν_{C-H} and ν_{NO_2} modes as evidence for an intramolecular hydrogen bond in *o*-nitrobenzaldehydes, but Forbes[15] interprets these data purely in terms of steric interactions. Interestingly, Kobayashi and Hirota[10a] observe a shift to higher frequency in ν_{SH} in both *o*-fluoro- and *o*-nitrothiophenol relative to thiophenol, and their conclusion that intramolecular hydrogen bonds exist in these molecules is supported by dipole moment measurements.[19]

It is more likely, however, that the high frequency shift in ν_{C-H} in the *o*-nitro-compounds (2d) and (5d and e) arise from steric compression between the CH_2 and NO_2 groups, due to the tendency of the latter to become coplanar with the aromatic ring. The low field shifts in the methylene groups in the ^1H n.m.r. relative to the methyl groups in similarly substituted toluenes[11d] probably arises from the greater polarity of the former (due to the SO_2 group). This would allow a greater dipole–dipole interaction with the *o*-nitro-group.

Thus, genuine physical interactions seem to exist in these compounds, but due to unfavourable bond angles, and the poor donor properties of the nitro-group, they should not be classed as hydrogen bonds. This work re-emphasises the importance of combining i.r., ^1H n.m.r., and crystal data before drawing conclusions about the existence of weak hydrogen bonds.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer model 577 spectrophotometer for hexachlorobutadiene (HCB) mulls in the solid phase, and for $CDCl_3$ (0.5 mm cell) and CCl_4 (0.5 or 10 mm cell depending on solubility) in the solution phase. Polystyrene was used in calibration. ^1H N.m.r. spectra were recorded on a Varian A60 D spectrometer for solutions in $CDCl_3$, with Me_4Si as internal reference. Spectroscopic data are recorded in Table 1.

Preparation of Sulphones.—Cyanomethyl-sulphones (2)

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* Only partial deuteriation was carried out in this series. In all three cases and in all three phases the monodeuterio-derivative present gave rise to *two* bands each in the ν_{C-H} and the ν_{C-D} regions. This is surprising since monodeuteriomalononitrile[17] shows only *one* band in each of the regions.

† The anomolous values for the quinoline in CCl_4 probably arise from its very low solubility in that solvent. At the concentration used (10 mm cell; × 5 abcissa scale expansion) interaction between traces of acid and the quinoline nitrogen was probably significant.

‡ The ν_{NO_2} modes in compounds with an *o*-nitro-group [(5d and e), (6d and e)] all show a small shift to *higher* frequency relative to the *p*-nitro-compounds (5c) and (6c). This probably arises from rotation of the nitro-group out of the plane of the aromatic ring,[18] and not from a hydrogen bond which should cause a shift in the opposite direction.

[14] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Chapman and Hall, London, 1975, 3rd edn., vol. 1, p. 16.

[15] W. F. Forbes, *Canad. J. Chem.*, 1962, **40**, 1891.

[16] G. C. Pimental and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Francisco, 1960, ch. 5.

[17] Y. Yamadera and S. Krimm, *Spectrochim. Acta*, 1968, **24A**, 1677.

[18] Ref. 14, p. 335.

[19] V. Baliah and M. Uma, *Indian J. Chem.*, 1972, **10**, 395.

were prepared by oxidation (H_2O_2–AcOH) of the corresponding sulphides (9) which in turn were prepared from the appropriate thiols (10) by treatment of a solution in aqueous KOH with chloroacetonitrile; the nitro-sulphide (9d) was, however, prepared by nitration of (9a). A similar sequence, starting from 2-mercaptomethylpyridine [20] led to the sulphone (3), only here the final oxidation was carried out by $KMnO_4$–AcOH to avoid formation of the *N*-oxide. Reduction (Na_2SO_3–$NaHCO_3$) of quinoline-8-sulphonyl chloride [21] gave the corresponding sodium sulphinate, which on treatment under reflux in ethanol with chloroacetonitrile yielded the quinoline (4). Deuterium exchange of compounds (2a—c) and (5a—e) was carried out at 100° with pyridine-D_2O (99.7%) (1 : 1). Products usually crystallised on cooling.

TABLE 2

Physical and analytical data for new compounds (2)—(6), (8), and (9)

Compound	Yield (%) from precursor	M.p. (°C) [B.p. (°C/Torr)]	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
(9a)	86	[162/18] [d]	66.35	5.6	8.4	C_9H_9NS	66.2	5.55	8.6
(9b)	78	[128/5] [e]	57.6	3.9	8.4	C_8H_5FNS	57.5	3.6	8.4
(9c)	76	[128/5] [f]	57.5	3.7	8.2	C_8H_6FNS	57.5	3.6	8.4
(9d)	8	135 [a]	51.6	3.9	13.35	$C_9H_8N_2O_2S$	51.9	3.9	13.45
(2b)	30	137 [a]	44.7	3.3	11.7	$C_9H_8N_2O_4S$	45.0	3.35	11.65
(2c)	77	68 [a]	47.95	3.3	7.05	$C_8H_6FNO_2S$	48.25	3.05	7.0
(2d)	86	76 [a]	48.1	3.25	7.0	$C_8H_6FNO_2S$	48.25	3.05	7.0
(3)	63	110 [a]	49.1	4.4	14.05	$C_8H_8N_2O_2S$	49.0	4.1	14.3
(4)	48	150 [a]	56.5	3.5	12.1	$C_{11}H_8N_2O_2S$	56.9	3.5	12.1
(5b)	70	126 [a]	63.2	5.15	12.2 [g]	$C_{14}H_{13}FO_2S$	63.6	5.0	12.1 [g]
(6e)	75	138 [c]	37.1	3.1	10.8	$C_8H_8N_2O_6S$	36.9	3.1	10.8
(8a)	85	146 [b]	67.0	6.3	12.8 [g]	$C_{14}H_{12}D_2O_2S$	67.7	6.5	12.9 [g]
(8b)	90	125 [b]	63.1	5.6	12.1 [g]	$C_{14}H_{11}D_2FO_2S$	63.1	5.7	12.05 [g]
(8c)	95	190 [b]	57.1	5.3	4.9	$C_{14}H_{11}D_2NO_4S$	57.3	5.15	4.8
(8d)	80	132 [b]	57.3	5.1	4.75	$C_{14}H_{11}D_2NO_4S$	57.3	5.15	4.8
(8e)	92	161 [b]	49.7	3.95	8.3	$C_{14}H_{10}D_2N_2O_6S$	49.7	4.2	8.3

[a] From ethanol. [b] From anhydrous acetone. [c] From acetone–ethanol (1 : 1). [d] n_D^{20} 1.570 0. [e] n_D^{25} 1.554 2. [f] n_D^{25} 1.554 0. [g] %S.

Representative experimental conditions follow, where appropriate. Physical and analytical data for all new compounds are presented in Table 2.

Thiophenols (10b *and* c).—Although the preparation of *m*- and *o*-fluorothiophenols is both difficult and potentially hazardous,* only scanty experimental details appear in the literature.[19,22] Full details of the preparation *via* the xanthate ester (based on ref. 23) are given here.

A mixture of *o*-fluoroaniline (22.2 g, 0.2 mol), concentrated hydrochloric acid (40 cm^3), and ice (40 g) was treated (0 °C) with a solution of sodium nitrite (14.7 g, 0.21 mol) in water (35 cm^3), the temperature being maintained below 4 °C. The diazonium salt solution was added during 2 h to a vigorously stirred solution of potassium ethyl xanthate [24] (37.3 g, 0.23 mol) in water (50 cm^3) at 40—45 °C. *Very* careful control of the rate of addition, and of the temperature (addition of pieces of ice as necessary) was essential to prevent the evolution of N_2 from becoming too violent. After stirring for a further 10 h, the mixture was extracted with ether (2 × 100 cm^3), the extracts washed with NaOH (40 cm^3; 10%) and water (3 × 100 cm^3), dried ($CaCl_2$), and the ether removed. The crude xanthate (43 g, essentially quantitative) was dissolved in boiling ethanol (125 cm^3; 95%), and KOH pellets (40 g) added with shaking. The resulting cloudy suspension was heated under reflux (steam-bath) overnight; then the condenser was removed and *ca.* 80% of the solvent was allowed to distill off. Water (100 cm^3) was added, the solution cooled, and then extracted with ether (3 × 50 cm^3). The aqueous layer was acidified with aqueous H_2SO_4 (100 cm^3; 1 : 1), this resulting in a vigorous evolution of COS, and the separation of the thiol. Zinc dust (10 g) was added, and the mixture steam-distilled until no more oil came over. The distillate was extracted with ether (3 × 50 cm^3), dried ($MgSO_4,3H_2O$), the solvent removed, and the residue distilled. The yield of *o*-fluorothio phenol (10c) was 14.7 g (57%), b.p. 158° at 662 Torr, n_D^{22} 1.549 5 (lit. 57%, 65° at 15 Torr, n_D^{26} 1.539 5,[22a] n_D^{30} 1.551 9 [19]). Similarly, *m*-fluoroaniline yielded *m*-fluorothiophenol (10b) (15.1 g, 59%), b.p. 159—161° at 662 Torr, n_D^{25} 1.548 4 (lit. 54%, 53° at 11 Torr, n_D^{27} 1.548 1,[22a] n_D^{30} 1.567 5 [19]).

Nitro-sulphide (9d).—The sulphide (9a) was nitrated under conditions similar to those described for the preparation of 2-amino-3-nitrotoluene.[25] The crude, dark, oily product was extracted ($CHCl_3$), dried (Na_2SO_4), and the solvent removed under reduced pressure. The resulting light red oil evolved oxides of nitrogen and HCN over several days, and slowly deposited the nitro-derivative (9d) as yellow crystals, $\nu_{max.}$ (Nujol) 2 258, 2 248, 1 520, and 1 338 cm^{-1}; δ($CDCl_3$) 8.13 (1 H, s), 7.72—7.40 (2 H, dd, *J* 8 Hz), 3.77 (2 H, s), and 2.48 (3 H, s).

Sulphones (2a—d).—The appropriate sulphide (9) (0.033

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* Treatment of the Grignard reagent derived from the appropriate bromofluorobenzene with sulphur under a variety of conditions [22c] failed to give the desired thiols. Addition of a solution of *m*-fluorobenzenediazonium chloride to an aqueous solution of sodium disulphide (both solutions < −2 °C) resulted in the precipitation of the diazonium disulphide. This exploded violently after 20 min stirring at −5 °C.

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mol) was stirred (25 °C, 2 h) with a solution of H_2O_2 (9 cm^3; 30%) in glacial acetic acid (40 cm^3). After heating on a steam-bath (1 h), the mixture was poured into water (1 000 cm^3) and the product separated by filtration.

Cyanomethyl 2-*Picolyl Sulphone* (3).—2-Mercaptomethylpyridine [20] was treated in aqueous KOH with the equivalent amount of chloroacetonitrile to give 2-(cyanomethylthiomethyl)pyridine (60%), b.p. 132 °C at 0.05 Torr, $\nu_{max.}$ 2 255 cm^{-1}, $\delta(CDCl_3)$ 8.8—7.1 (4 H, m), 4.05 (2 H, s), and 3.40 (2 H, s). The sulphide (4 g, 0.025 mol) in glacial acetic acid (90 cm^3) was heated to 45 °C, and a solution of $KMnO_4$ (5.4 g, 0.034 mol) in water (160 cm^3) added with vigorous stirring over 10 min. The mixture was cooled, neutralised with solid $NaHCO_3$, and extracted continuously ($CHCl_3$) for 24 h. After drying (Na_2SO_4) removal of the solvent yielded the sulphone (3).

Sulphones (5) *and* (6).—These were prepared from the corresponding benzyl bromide or chloride (0.01 mol) by heating under reflux (2 h) with the appropriate sodium sulphinate (0.011 mol) in ethanol (25 cm^3). The yield, m.p. and literature m.p. respectively are given for benzyl sulphones recorded previously: (5a), 81%, 145°, 144°; [26] (5c), 76%, 189—190°, 188—189°; [27] (5d), 70%, 131—132°, 131—132°, 131—132°; [27] (5e), 80%, 160—161°, 159—160°; [27] (6a), 47%, 125—126°, 125—126°; [28] (6b), 40%, 91—92°, 91—93°; [29] (6c), 79%, 170—171°, 169—170°; [30] (6d) 66%, 86—87°, 85—87°.[31]

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