Nuclear Magnetic Resonance and *X*-Ray Diffraction Studies on Some Substituted Benzenesulphonamides

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Solid-state ^{13}C c.p.-m.a.s. and solution ^{13}C, ^{15}N, and ^{17}O n.m.r. spectra were measured for toluene-*p*-sulphonamide, *N*-methyltoluene-*p*-sulphonamide, *NN*-dimethyltoluene-*p*-sulphonamide, *p*-chlorobenzenesulphonamide, and *NN*-dimethyl-*p*-chlorobenzenesulphonamide. The ^{13}C c.p.-m.a.s. n.m.r. resonance lines of the carbon atoms bonded to nitrogen show characteristic line broadening with slightly asymmetric doublet patterns. Some differences are evident in the ^{13}C shielding of the carbon atoms between the solid-state and solution-state spectra. In the solution spectra the ^{15}N and ^{17}O chemical shifts increase in conformity with the polarity order of the amides. The n.m.r. relaxation times of the methyl groups of the compounds were measured as well. The crystal structures of *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide were determined by single-crystal *X*-ray diffraction technique and refined to final *R* values of 0.056 and 0.044, respectively. Except for some barely significant differences, the bond lengths and angles are similar in the two compounds. The most striking difference is the value of the C–C–S–N torsion angle.

As well as being medically important, benzenesulphonamide derivatives are also spectroscopically interesting. The discovery of an asymmetric doublet as the characteristic feature of the ^{13}C c.p.-m.a.s. n.m.r. spectra of organic solids containing a carbon atom bonded to nitrogen[1–13] encouraged us to investigate this property in toluene-*p*-sulphonamides. The observed lineshape is due to the perturbation of the ^{13}C–^{14}N dipolar interaction by the ^{14}N quadrupole interaction, since the ^{13}C–^{14}N dipolar energy is not necessarily averaged in one cyclic spinning. An orientation dependence may therefore yield a characteristic lineshape.

The polar properties of molecules are strongly determined by the molecular asymmetry, and the polarity of sulphonamides is relatively high.[14] The high dielectric permittivities of sulphonamides are mainly attributable to the permanent dipoles of the S=O bonds.[15] *N*-Methyl substituents slightly increase and *NN*-dimethyl substituents increase somewhat more, the values of dipole moments in sulphonamides.[16,17]

In this work we applied high-resolution solid-state ^{13}C c.p.-m.a.s. n.m.r. spectroscopy and solution multinuclear n.m.r. spectroscopy to the study of some *N*-unsubstituted, *N*-methyl-substituted, and *NN*-dimethyl-substituted sulphonamides. Solution spectroscopy was earlier used as a probe for investigating similar compounds.[18–21] In addition, crystallographic studies were made on *N*-methyl- and *NN*-dimethyltoluene-*p*-sulphonamides to get more accurate information about the molecular configurations and to obtain data useful for the interpretation of n.m.r. results.

Experimental

Sulphonamides were prepared from the corresponding sulphonyl chloride and ammonia or amine in dry ether at 263 K.[22] Crude products were crystallized several times from ethanol or ethanol–water and for the *X*-ray crystallographic study from heptane by slow evaporation of the solvent.

N.m.r. Spectroscopic Measurements.—For liquid-state n.m.r., samples were prepared in [$^2H_6$]acetone (Uvasol reagent; Merck AG), in molar ratio amide:[$^2H_6$]acetone 1:2. Measurements were made on a JEOL JNM FX-100 n.m.r. spectrometer with proton noise decoupling. An external ^7Li lock was used to stabilize the field frequency ratio. Typical spectral parameters were: operating frequency 13.46, 10.04, and 25.05 MHz; spectral width 10, 6, and 6 kHz; pulse width 30, 10, and 7 μs; and pulse repetition 0.05, 15, and 3 s for ^{17}O, ^{15}N, and ^{13}C, respectively. The chemical shifts of ^{17}O nuclei were measured relative to the external water, those of ^{15}N nuclei relative to nitromethane doped with Cr(acac)$_3$, and those of ^{13}C relative to internal tetramethylsilane.

The c.p.-m.a.s. ^{13}C n.m.r. spectra were measured with a JEOL FX-200 Fourier transform n.m.r. spectrometer operating at 50.10 MHz with proton noise decoupling. The spectral width was 10 kHz, the pulse width 7 μs, and repetition time 6 s. Single contact spin locked cross polarization was established under Hartman–Hahn conditions with contact time 2 ms. The spinning frequency estimated by the position of spinning side bands was 33 kHz. The ^{13}C n.m.r. signal of solid hexamethylbenzene was used as an external reference to determine the ^{13}C chemical shift values, which are shown converted to the scale of tetramethylsilane in Table 8. The ^{13}C relaxation times were measured by inversion recovery method with proton noise decoupling.

X-Ray Crystallographic Measurements.—Data pertaining to the crystallographic analysis of *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide are collected in Table 1. Cell parameters were determined by least-squares methods on the basis of 25 diffractometer-measured independent reflections for each compound. No significant intensity variations were observed for the standard reflections during the data collections. Both sets of data were corrected for Lorentz and polarization effects. ψ-Scans for several intense reflections of the compounds verified the absence of noteworthy variable absorption. The phase problems were solved by direct methods,[23] by calculating the molecular scattering factors in the normalization procedure from the expected geometry of the molecules. After anisotropic refinements with X-RAY 76 system

Table 1. Crystal data and details of data collection

	N-Methyltoluene-*p*-sulphonamide	*NN*-Dimethyltoluene-*p*-sulphonamide
Mol. formula	$C_8H_{11}NO_2S$	$C_9H_{13}NO_2S$
Mol. weight	185.25	199.27
Crystal system	Monoclinic	Monoclinic
a/Å	14.350(2)	9.509(1)
b/Å	7.020(2)	11.247(2)
c/Å	19.507(4)	10.066(2)
β/°	111.12(1)	106.42(1)
Space group	$P2_1$	$P2_1/n$
V/Å^3	1 833.1(7)	1 032.6(3)
D_c/g cm^{-3}	1.34	1.28
Z	8	4
Crystal dimensions (mm)	0.32 × 0.20 × 0.45	0.18 × 0.28 × 0.40
Diffractometer	Nicolet *P*3	Nicolet *P*3
Radiation	Mo-K_α (λ = 0.710 69 Å)	Mo-K_α (λ = 0.710 69 Å)
Absorption coefficient (cm^{-1})	3.0	2.8
Scan type	ω	ω
2θ Limits	$5° < 2\theta < 53°$	$5° < 2\theta < 55°$
Scan rate (°/min^{-1})	2—20	2—20
Number of collected reflections	4 247	2 376
Number of observed reflections	2 477	1 556
Criterion for observed reflections	$\lvert F_o\rvert > 6\sigma\lvert F_o\rvert$	$\lvert F_o\rvert > 6\sigma\lvert F_o\rvert$
Number of parameters	433	171
R	0.056	0.044
R_w	0.043	0.042

programs[24] the hydrogen atoms were positioned geometrically at 1.0 Å from the atoms to which they were bonded. The hydrogen atom parameters of *N*-methyltoluene-*p*-sulphonamide were not refined, but those of *NN*-dimethyltoluene-*p*-sulphonamide were. The functions minimized were $\Sigma w(\Delta F)^2$, where $w = 1/\sigma^2_{F_o}$. Atomic scattering factors were those included in the programs.

Results and Discussion

Crystallographic Studies.—Positional parameters for *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide are collected in Tables 2 and 3. Table 4 presents the bond lengths and angles of the four independent molecules of *N*-methyltoluene-*p*-sulphonamide including mean values of

Table 3. Positional parameters for the non-hydrogen atoms of *NN*-dimethyltoluene-*p*-sulphonamide

	x	*y*	*z*
S	0.288 5(1)	0.324 4(1)	0.442 4(1)
O(1)	0.238 5(3)	0.207 7(2)	0.397 3(2)
O(2)	0.433 2(2)	0.360 5(2)	0.443 7(2)
N	0.176 6(2)	0.416 7(2)	0.343 3(2)
C(1)	0.272 1(3)	0.342 0(2)	0.611 3(2)
C(2)	0.172 6(3)	0.274 5(2)	0.654 2(3)
C(3)	0.158 8(3)	0.288 0(3)	0.785 8(3)
C(4)	0.243 6(3)	0.368 8(2)	0.877 2(3)
C(5)	0.342 0(3)	0.436 3(2)	0.830 5(3)
C(6)	0.357 8(3)	0.423 9(2)	0.699 6(3)
C(7)	0.228 7(4)	0.384 9(3)	1.021 0(3)
C(8)	0.019 5(4)	0.389 3(3)	0.307 2(4)
C(9)	0.210 9(3)	0.543 1(3)	0.364 5(3)

Table 2. Positional parameters for *N*-methyltoluene-*p*-sulphonamide. The *y*-co-ordinate of the sulphur atom of molecule 1 was fixed for fixing of the origin

	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
S	0.120 7(1)	0.1733	0.673 4(1)	0.451 1(1)	0.277 1(4)	−0.169 1(1)
O(1)	0.192 9(3)	0.254 5(8)	0.646 5(2)	0.546 8(3)	0.369 4(2)	−0.140 2(2)
O(2)	0.140 2(4)	−0.008 9(8)	0.709 8(3)	0.441 7(3)	0.096 1(8)	−0.204 8(3)
N	0.106 3(4)	0.321 2(10)	0.732 2(3)	0.375 9(3)	0.418 0(8)	−0.230 0(3)
C(1)	0.006 0(4)	0.158 5(11)	0.598 4(3)	0.405 4(4)	0.257 3(10)	−0.096 3(3)
C(2)	−0.005 6(5)	0.247 8(12)	0.532 7(4)	0.456 2(4)	0.348 4(10)	−0.029 9(3)
C(3)	−0.098 1(5)	0.241 8(11)	0.476 0(3)	0.418 4(5)	0.338 6(10)	0.025 9(3)
C(4)	−0.178 3(5)	0.153 2(12)	0.484 8(4)	0.330 9(5)	0.239 0(10)	0.016 4(4)
C(5)	−0.165 4(4)	0.071 8(12)	0.551 3(4)	0.282 0(4)	0.147 7(11)	−0.049 5(4)
C(6)	−0.074 0(5)	0.070 2(12)	0.607 9(4)	0.319 5(4)	0.158 3(11)	−0.106 0(3)
C(7)	−0.280 0(4)	0.154 2(13)	0.423 0(4)	0.288 3(5)	0.228 4(10)	0.076 2(4)
C(8)	0.076 2(5)	0.515 3(13)	0.708 6(4)	0.363 5(5)	0.612 3(12)	−0.208 3(4)

	Molecule 3			Molecule 4		
	x	*y*	*z*	*x*	*y*	*z*
S	0.597 5(1)	0.055 2(3)	0.671 9(1)	0.064 0(1)	0.637 6(4)	0.175 6(1)
O(1)	0.677 0(3)	−0.021 4(8)	0.651 0(2)	−0.039 7(3)	0.582 2(11)	0.150 4(3)
O(2)	0.607 9(3)	0.241 1(8)	0.705 5(3)	0.092 4(5)	0.813 6(10)	0.214 7(3)
N	0.579 6(4)	−0.092 5(9)	0.730 6(3)	0.127 4(4)	0.471 9(11)	0.229 3(3)
C(1)	0.489 0(4)	0.055 7(11)	0.591 2(3)	0.099 9(4)	0.641 2(12)	0.097 9(3)
C(2)	0.490 2(5)	−0.029 7(11)	0.529 2(4)	0.040 0(4)	0.563 9(13)	0.032 4(4)
C(3)	0.403 1(5)	−0.028 1(11)	0.466 2(4)	0.071 0(5)	0.565 6(13)	−0.026 1(4)
C(4)	0.316 0(5)	0.051 1(11)	0.468 1(4)	0.160 8(5)	0.641 8(11)	−0.022 1(4)
C(5)	0.316 5(4)	0.134 3(11)	0.533 0(4)	0.220 3(4)	0.719 0(11)	0.044 9(4)
C(6)	0.403 8(5)	0.136 1(11)	0.595 9(3)	0.191 8(4)	0.715 8(11)	0.105 0(3)
C(7)	0.220 7(5)	0.053 9(12)	0.400 6(4)	0.192 5(5)	0.641 1(12)	−0.088 2(4)
C(8)	0.566 6(5)	−0.294 5(12)	0.711 2(4)	0.117 2(5)	0.281 1(14)	0.202 5(4)

Table 4. Selected bond lengths (Å) and angles (°) for the four independent molecules of *N*-methyltoluene-*p*-sulphon amide and for *NN*-dimethyltoluene-*p*-sulphonamide

	N-Methyltoluene-*p*-sulphonamide					*NN*-Dimethyltoluene *p*-sulphonamide
Molecule	*1*	*2*	*3*	*4*	Mean value	
S–O(1)	1.437(5)	1.437(5)	1.446(5)	1.442(5)	1.441(4)	1.426(3)
S–O(2)	1.441(6)	1.432(6)	1.444(6)	1.432(7)	1.437(6)	1.431(2)
S–N	1.615(7)	1.622(5)	1.632(7)	1.610(7)	1.620(9)	1.614(2)
S–C(1)	1.768(5)	1.771(7)	1.771(5)	1.768(7)	1.770(2)	1.762(2)
N–C(8)	1.453(11)	1.458(10)	1.462(12)	1.426(12)	1.450(16)	1.467(4)
N–C(9)						1.461(4)
C(4)–C(7)	1.522(8)	1.501(12)	1.519(9)	1.514(12)	1.514(9)	1.505(5)
O(1)–S–O(2)	119.6(3)	120.1(3)	120.0(3)	118.4(4)	119.5(8)	119.8(2)
O(1)–S–N	107.3(3)	107.6(3)	107.5(3)	107.4(4)	107.5(1)	107.0(1)
O(2)–S–N	105.8(4)	105.3(3)	105.8(3)	106.9(3)	106.0(7)	106.7(1)
O(1)–S–C(1)	107.5(3)	107.4(3)	106.3(3)	107.2(3)	107.1(5)	107.3(1)
O(2)–S–C(1)	108.3(3)	108.9(4)	108.4(3)	109.2(4)	108.7(4)	107.8(1)
N–S–C(1)	107.8(3)	107.1(3)	108.3(3)	107.3(4)	107.6(5)	107.5(1)
S–N–C(8)	118.5(5)	118.5(5)	118.2(5)	118.7(4)	118.5(2)	117.7(2)
S–N–C(9)						117.0(2)
C(8)–N–C(9)						114.2(2)
S–C(1)–C(2)	120.4(5)	119.3(5)	120.2(5)	121.0(5)	120.2(7)	119.9(2)
S–C(1)–C(6)	119.3(5)	120.3(4)	117.3(5)	118.9(4)	119.0(12)	120.1(2)

Table 5. The distances (Å) of the atoms from the best least-squares planes determined by the aromatic carbon atoms

	N-Methyltoluene-*p*-sulphonamide				*NN*-Dimethyltoluene-*p*-sulphonamide
Molecule	*1*	*2*	*3*	*4*	
S	0.100(10)	0.063(9)	−0.027(10)	−0.021(11)	0.004(4)
O(1)	−0.054(13)	−0.099(12)	0.109(12)	0.229(15)	−0.583(4)
O(2)	−0.784(13)	−0.815(12)	0.908(13)	0.836(14)	−0.549(5)
N	1.591(14)	1.553(12)	−1.501(14)	−1.519(15)	1.545(5)
C(7)	0.021(13)	0.020(11)	0.021(12)	−0.003(13)	0.005(5)
C(8)	2.719(14)	2.671(13)	−2.662(14)	−2.599(15)	2.324(6)
C(9)					2.302(5)

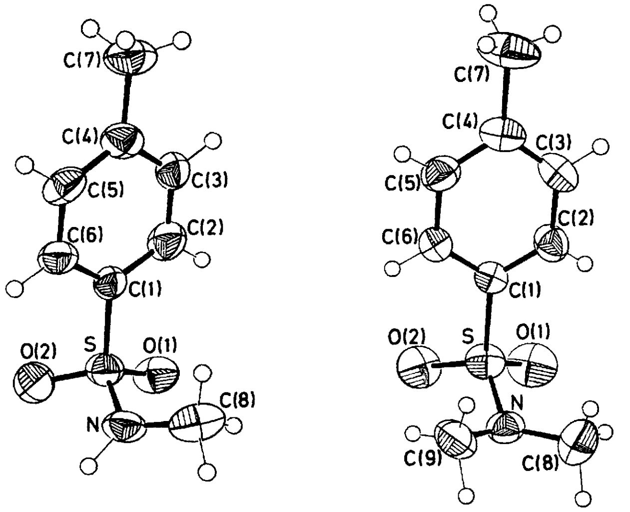


Figure 1. Molecular drawings of *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide

the four sets of bonds, and the bond lengths and angles of *NN*-dimethyltoluene-*p*-sulphonamide. All bond parameters of *N*-methyltoluene-*p*-sulphonamide discussed below are mean values. Figure 1 shows the numbering systems of the compounds and Figure 2 the diagrams of *N*-methyltoluene-*p*-sulphonamide (molecule 1) and *NN*-dimethyltoluene-*p*-sulphonamide in the direction of the S–C(1) bond.

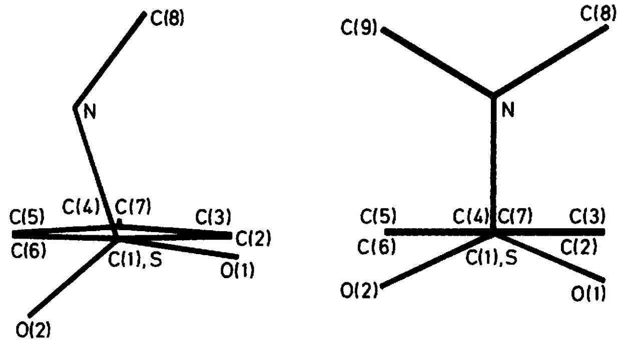


Figure 2. Diagram of molecule (1) of *N*-methyltoluene-*p*-sulphonamide and diagram of *NN*-dimethyltoluene-*p*-sulphonamide viewed in the direction of the S–C(1) bond

Molecules 1 and 4 of *N*-methyltoluene-*p*-sulphonamide are approximately mirror images of molecules 2 and 3. Although almost all the individual bond lengths and angles of the four molecules are essentially the same, some significant differences in the deviations of the atoms from the planes determined by the benzene rings (Table 5) and in the torsion angle values (Table 6) indicate minor differences in the configurations of the four molecules.

The asymmetric unit of *NN*-dimethyltoluene-*p*-sulphonamide consists of a single molecule with approximately δ symmetry. The pseudo-mirror plane bisects the molecule through the atoms S, N, C(1), C(4), and C(7).

Table 6. Selected torsion angles (°) for *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide

	N-Methyltoluene-*p*-sulphonamide				
Molecule	*1*	*2*	*3*	*4*	*NN*-Dimethyltoluene-*p*-sulphonamide
O(1)–S–C(1)–C(2)	−10.7(7)	8.2(6)	8.1(7)	−12.0(8)	−24.4(3)
O(1)–S–C(1)–C(6)	174.5(6)	−173.7(6)	−175.4(6)	170.9(6)	156.2(3)
O(2)–S–C(1)–C(2)	−141.2(7)	139.6(5)	138.4(7)	−141.3(7)	−154.8(2)
O(2)–S–C(1)–C(6)	43.9(7)	−42.4(6)	−45.1(7)	41.6(7)	25.8(2)
O(1)–S–N–C(8)	56.8(5)	−55.0(6)	−50.4(5)	55.1(7)	41.6(3)
O(1)–S–N–C(9)					−176.4(2)
O(2)–S–N–C(8)	−174.3(5)	175.9(5)	−179.9(5)	−176.9(6)	171.0(2)
O(2)–S–N–C(9)					−46.9(2)
C(1)–S–N–C(8)	−58.7(6)	60.1(6)	64.1(6)	−59.8(7)	−73.5(2)
C(1)–S–N–C(9)					68.6(2)

In both *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide the oxygen atoms are on the same side of the plane determined by the benzene rings. The benzene rings are essentially co-planar, the greatest deviation of an individual aromatic carbon atom from the plane being only 0.016(8) Å. The individual aromatic C–C bond lengths range between 1.356(11) and 1.402(9) Å in *N*-methyltoluene-*p*-sulphonamide and 1.374(4) and 1.386(4) Å in *NN*-dimethyltoluene-*p*-sulphonamide, and the bond angles between 116.9(8) and 122.6(7)° in *N*-methyltoluene-*p*-sulphonamide, and 117.3(3) and 122.5(2)° in *NN*-dimethyltoluene-*p*-sulphonamide. These values could be assumed normal. Comparison of the bond lengths and angles of *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide reveals the expected close similarity. The most striking difference lies in the configurations of the molecules, as is evident from the C–C–S–N and C–C–S–O torsion angle values and the views presented in Figure 2. Slight differences in other features are observed as well.

The bond lengths and angles of the sulphonamide groups are typical for compounds containing the S^{VI} atom. The sulphonyl sulphur atoms have distorted octahedral co-ordination, as the O–S–O angles are opened to 119.5(8)° in *N*-methyltoluene-*p*-sulphonamide and 119.8(2)° in *NN*-dimethyltoluene-*p*-sulphonamide, and the other angles around the sulphur atoms, 106.0(7)—108.7(4)° for *N*-methyltoluene-*p*-sulphonamide and 106.7(1)—107.8(1)° for *NN*-dimethyltoluene-*p*-sulphonamide, are slightly smaller than the ideal tetrahedral angle (109.5°).

The averaged S–O bond length, 1.43 Å, of the compounds corresponds to a double-bond order of *ca.* 0.67 as presented by Cruickshank,[25] and the S–N bond lengths of 1.620(9) Å for *N*-methyltoluene-*p*-sulphonamide and 1.614(2) Å for *NN*-dimethyltoluene-*p*-sulphonamide are comparable with the value of 1.61 Å obtained for sulphamide (double-bond order 0.25). Also, the S–C(1) bond lengths of 1.770(2) Å for *N*-methyltoluene-*p*-sulphonamide and 1.762(3) Å for *NN*-dimethyltoluene-*p*-sulphonamide are typical for sulphonamides.[26]

Steric reasons may be responsible for the slight differences in S–N–C angles [118.5(2)° in *N*-methyltoluene-*p*-sulphonamide and 117.7(2)° and 117.0(2)° in *NN*-dimethyltoluene-*p*-sulphonamide]; for *N*-methyltoluene-*p*-sulphonamide contains one and *NN*-dimethyltoluene-*p*-sulphonamide two methyl groups bonded to the nitrogen atom.

The crystallographic data further reveal relatively short intermolecular N • • • O distances in *N*-methyltoluene-*p*-sulphonamide: N(molecule 1) • • • O(1) (molecule 4) 3.248(10) Å, N(molecule 2) • • • O(1) (molecule 1) 3.075(6) Å, N(molecule 3) • • • O(2) (molecule 2) 3.010(8) Å, N(molecule 4) • • • O(1) (molecule 3) 2.934(6) Å. At least the shortest of these contacts indicate hydrogen bonds. Earlier i.r. spectroscopic studies in solution revealed hydrogen bond formation ability for this kind of compound.[27]

Table 7. ^{17}O And ^{15}N n.m.r. chemical shifts [δ(p.p.m.)] in acetone and dipole moments in 1,4-dioxane for some sulphonamides

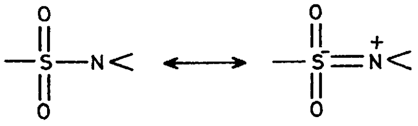
Compound	δ(^{17}O)	δ(^{15}N)	μ/D[b]
Toluene-*p*-sulphonamide	158.7	−287.6	5.39
N-Methyltoluene-*p*-sulphonamide	149.8	−295.5[a]	5.51
NN-Dimethyltoluene-*p*-sulphonamide	139.0	−298.7	5.60
p-Chlorobenzenesulphonamide	160.8	−287.8	4.33
NN-Dimethyl-*p*-chlorobenzene-sulphonamide		−298.6	4.38

[a] $^{1}J_{NH}$ 84.5 Hz. [b] Ref. 4.

N.m.r. Spectroscopic Studies.—The ^{15}N and ^{17}O chemical shifts of the solution spectra of the five sulphonamides are given in Table 7, and the ^{13}C n.m.r. chemical shifts of the solution spectra and the ^{13}C c.p.-m.a.s. chemical shifts of the solid-state spectra in Table 8. The ^{15}N and ^{17}O chemical shifts of sulphur amides have earlier been found to be sensitive to the electronic environment around the sulphur atom, in particular to the oxidation state of the sulphur atom.[18–20] The changes due to *N*-methyl substitution (Table 7) are smaller but still notable.

Comparison of the chemical shifts shows the shielding order of the nitrogen-15 nucleus in the toluene-*p*-sulphonamides to be as follows: $NH_2 < NHCH_3 < N(CH_3)_2$. This order is in conformity with the polarity order of the amides, as the dipole moments in 1,4-dioxane are 5.39 D for toluene-*p*-sulphonamide, 5.51 D for *N*-methyltoluene-*p*-sulphonamide, and 5.60 D for *NN*-dimethyltoluene-*p*-sulphonamide.[17] The shielding of the nitrogen nucleus in the *p*-chlorobenzenesulphonamides is similar to that in the toluene-*p*-sulphonamides (Table 7), *viz.* larger in the dimethyl-substituted compounds. The variation in the shielding of the oxygen-17 nuclei is clear and in the same direction as the shielding of the nitrogen-15 nuclei.

The trends in the ^{15}N and ^{17}O n.m.r. chemical shifts become evident if one looks at the resonance possibilities for the sulphur amides (Scheme).[16] These resonance possibilities are also in conformity with the polarity measurements and with the slight shortening of the bond lengths around the sulphur atom in *NN*-dimethyltoluene-*p*-sulphonamide relative to *N*-methyltoluene-*p*-sulphonamide, found in the crystallographic study (Table 4).



Scheme.

A methyl substituent increases the electron density of the N

Table 8. ^{13}C N.m.r. chemical shifts [δ (p.p.m.)] in acetone and in solid state for some sulphonamides

Compound	Solvent	C-1	C-2,6	C-3,5	C-4	N-CH_3	C-CH_3
Toluene-*p*-sulphonamide	Acetone	143.1	126.7	129.9	141.8		21.3
	Solid	145.5	126.5	130.3	138.3		21.1
N-Methyltoluene-*p*-sulphonamide	Acetone	137.1	127.5	130.0	143.4	29.3	21.2
	Solid	133.7	128.2	128.2	143.8	31.3; 30.2	22.0
NN-Dimethyltoluene-*p*-sulphonamide	Acetone	133.4	128.4	130.2	144.0	38.0	21.3
	Solid	140.5	125.8	128.6	143.1	33.8; 30.8	16.9
p-Chlorobenzenesulphonamide	Acetone	143.2	128.7	129.7	138.3		
	Solid	147	129	130	140		
NN-Dimethyl-*p*-chlorobenzenesulphonamide	Acetone	133.7	129.2	129.7	138.1	37.4	
	Solid	130.7	127.3	127.3	141.2	34.0	

atom and favours double-bond character in the S–N bond. Further, the change in electron density around the nitrogen atom may be reflected in the S–O and S–C(1) bond lengths, since the S atom can utilize its vacant *d*-orbitals. Given the only slight differences between the bond lengths of *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide, and the fairly large standard deviations in the bond lengths of *N*-methyltoluene-*p*-sulphonamide, conclusions can only be tentative.

The chemical shifts of the ^{13}C nuclei are characteristic for the type of sulphonamide and different for the *N*-methyl- and *NN*-dimethyl-substituted compounds (Table 8).[18–21] Some differences are seen in the ^{13}C chemical shifts of the c.p.-m.a.s. spectra and the corresponding solution spectra. In the solution spectra, the signals of the *N*-methyl carbon atoms of *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide have chemical shifts of δ 29.3 and 38.0 p.p.m., respectively. In the solid state, the corresponding signals have chemical shifts of δ 30.9 (31.3; 30.2) and 32.8 (33.8; 30.8) p.p.m. The chemical shift of the *N*-methyl carbon of *NN*-dimethyl-*p*-chlorobenzenesulphonamide is δ 34.0 p.p.m. The differences in the chemical shifts in the solid-state and solution spectra are somewhat greater than the differences due to solvent effects.

Packing effects are assumed to be weak, since in addition to the hydrogen bond distances mentioned above, there are no short intermolecular contacts: the shortest non-bonding distances are 3.32 Å in *N*-methyltoluene-*p*-sulphonamide and 3.36 Å in *NN*-dimethyltoluene-*p*-sulphonamide. The bond lengths and angles are nearly the same in the four independent molecules of *N*-methyltoluene-*p*-sulphonamide and their effect on the ^{13}C n.m.r. spectra in solid state is thus clearly negligible.

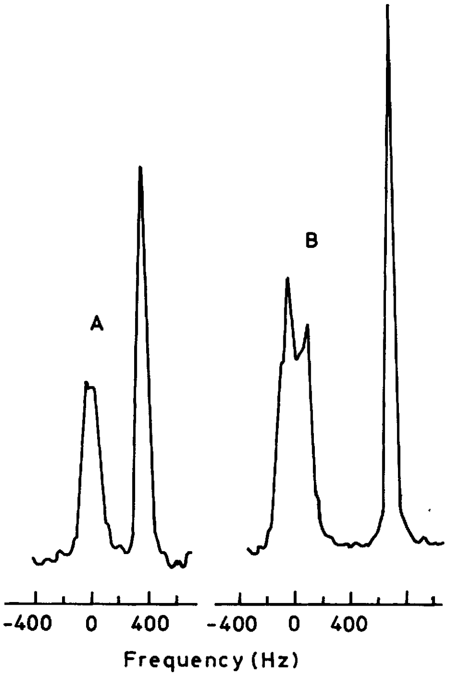


Figure 3. ^{13}C C.p.–m.a.s. n.m.r. spectra of the methyl carbons of *N*-methyltoluene-*p*-sulphonamide (A) and *NN*-dimethyltoluene-*p*-sulphonamide (B)

Figure 3 shows the ^{13}C c.p.-m.a.s. n.m.r. spectra of *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyltoluene-*p*-sulphonamide. The solid-state ^{13}C resonance lines of the carbon atoms bonded to nitrogen show a characteristic line broadening compared with those of the carbon atoms of the *para*-methyl groups of the aromatic rings. The resonances for the *N*-methyl carbon atoms exhibit asymmetric doublet patterns with the peak of the higher frequency stronger in intensity. The observed splitting is *ca.* 60 Hz for *N*-methyltoluene-*p*-sulphonamide and 150 Hz for *NN*-dimethyltoluene-*p*-sulphonamide. The signal for the *N*-methyl carbons of *NN*-dimethyl-*p*-chlorobenzenesulphonamide is broad (*ca.* 50 Hz) and the doublet pattern is poorly resolved.

The effect of the ^{14}N interaction on the resonance line splitting of the neighbouring carbon depends on the sign, magnitude, and asymmetry parameter of the ^{14}N quadrupole coupling tensor and on the orientation of the ^{14}N electric field gradient with respect to the N–C internuclear vector and the magnitude of this vector.

The splittings of the resonances of the amide methyl carbons in the studied sulphonamides are similar in magnitude to the splittings observed earlier for the carbonyl carbon in the amide group and for carbons bonded to amino groups in amino acids; and correspondingly they are much smaller than the splittings of cyano carbons at the same magnetic field strength.[1–10] The splitting of the carbonyl and cyano carbons in cyanoacetamide are 92 and 305 Hz, respectively,[7] the splitting of the carbons bonded to the amino group in alanine, serine, and glycine is 45,[7] 45,[7] and 61 Hz (^{13}C resonance frequency 37.84 MHz),[10] and the splittings of the carbons bonded to the nitro and amino groups in 2,6-dimethyl-3-nitroaniline are 56 and 102 Hz.[8] The ^{14}N quadrupole coupling constants in these amino acids[28,29] and nitro compounds[30] are small and the N–C internuclear vector is expected to lie close to the symmetry axis of the ^{14}N electric field tensor. In cyano compounds[31] the relatively large ^{14}N–^{13}C interaction is explained by the larger ^{14}N quadrupolar coupling constant and shorter N–C distance. The axial symmetry of the ^{14}N electric field gradient is a fairly good approximation in the cyano compounds. The sign of the quadrupole coupling constant is positive for the amino carbons

Table 9. Spin lattice relaxation times (T_1) of methyl carbons for some sulphonamides in 1:2 molar ratio amide–chloroform solutions and in solid state

Compound	Solvent or solid	T_1/s	
		N-CH_3	$CH_3C_6H_4$
N-Methyltoluene-*p*-sulphonamide	Chloroform	2.6	2.6
	Solid	8.3	8.5
NN-Dimethyltoluene-*p*-sulphonamide	Solid	4.5	8.6
NN-Dimethyl-*p*-chlorobenzenesulphonamide	Chloroform	3.0	
	Solid	3.8	

of the amino acids and negative for the cyano carbons and the carbons bonded to the nitro group mentioned above.

In *NN*-dimethyltoluene-*p*-sulphonamide the *N*-methyl carbons do not lie on the principal axis of the ^{14}N electric field tensor, which is assumed to be approximately in the direction of the C(1)–S–N axis; instead, the N–C vector makes an angle of 62—63° with respect to the C(1)–S–N axis. Because of the approximate axial symmetry in *NN*-dimethyltoluene-*p*-sulphonamide the asymmetry parameter of the ^{14}N electric field gradient is expected to be negligible. In *N*-methyltoluene-*p*-sulphonamide, on the other hand, a non-zero asymmetry parameter, together with the different molecular configuration and the formation of hydrogen bonds, could affect the splitting of the amide methyl carbon signal, making it smaller than the splitting in *NN*-methyltoluene-*p*-sulphonamide.

The relaxation data (Table 9) reveal a similar molecular motion in the sulphonamides in solution. The relaxation times of the aromatic carbons directly bonded to hydrogen atoms, *ca.* 0.9 and 1.2 s for *N*-methyltoluene-*p*-sulphonamide and *NN*-dimethyl-*p*-chlorobenzenesulphonamide, respectively, indicate a relatively rapid tumbling of the whole molecule in non-viscous solutions. In the solid state the molecular motion is slowed down and lengthening of the relaxation times is observed. In *N*-methyltoluene-*p*-sulphonamide the relaxation times of the different methyl carbons are similar within the limits of the experimental error. In the *NN*-dimethyl-substituted sulphonamides the relaxation times of the amide methyl carbons are much smaller (relaxation rates about two times faster) than those of the methyl carbons connected to the aromatic rings and the relaxation time of the amide methyl carbon in *N*-methyltoluene-*p*-sulphonamide. This may be because in the solid state the nearby protons have the same spin temperature and behave as an assembly.

Taken together, the present results support the view that both electronic and steric factors are influencing the n.m.r. parameters of the C, N, and O nuclei of sulphonamides, whether the spectra are run in solid or in solution state. Among other things the changes of lineshapes of ^{13}C c.p.-m.a.s. spectra open an additional perspective to study electronic distribution around nitrogen nucleus in molecules.

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