N.M.R. Spectroscopic and *X*-Ray Crystallographic Studies on some *o*-NO_2 Substituted Aromatic Sulphur Amides

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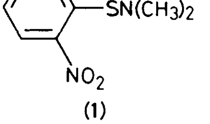
Solid state ^{13}C c.p.-m.a.s. and solution ^{13}C, ^{15}N, ^{14}N, and ^{17}O n.m.r. spectra have been measured for *N,N*-dimethyl-*o*-nitrobenzenesulphenamide, *o*-nitrobenzenesulphenamide, and *N,N*-dimethyl-*o*-nitrobenzenesulphonamide. The ^{13}C c.p.-m.a.s. n.m.r. resonance signals of the methyl carbon atoms bonded to nitrogen show a characteristic doublet pattern. In addition, like the signal of *N,N*-dimethyltoluene-*p*-sulphonamide, the *N*-methyl resonance signal of *N,N*-dimethyl-*o*-nitrobenzenesulphenamide shows extra splitting. In the solution spectra the ^{15}N nuclei of the amide group of the sulphonamides are considerably less shielded than those of the corresponding sulphenamides. The nitro-substituent of the aromatic ring has hardly any effect on the electron density of the nitrogen atom of the sulphonamide group.

The crystal structures of *N,N*-dimethyl-*o*-nitrobenzenesulphenamide (**1**) and *N,N*-dimethyl-*o*-nitrobenzenesulphonamide (**2**) have been determined by the single crystal *X*-ray diffraction technique and refined to final *R* values 0.043 and 0.049, respectively. The configurations of these sulphur(II) and sulphur(VI) amides, with respect to the geometry around the sulphur atom and the orientation of the substituents in the phenyl ring, are different. The sulphenamide adopts crystallographic σ symmetry, with all atoms except the methyl groups lying in the crystallographic mirror plane. *N,N*-Dimethyl-*o*-nitrobenzenesulphonamide has no high molecular symmetry and there is clear steric repulsion between the NO_2 group and the oxygen atoms of the SO_2N group. The nitro group is rotated 53.5(2)° relative to the plane through the phenyl group. The amide nitrogen displays a pseudo-trigonal arrangement in both compounds.

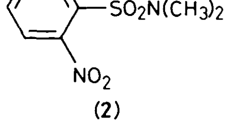
The polarity of sulphur amides, especially that of sulphonamides, is relatively high.[1–4] At the same time their complex formation ability is rather low.[5–8] A nitro substituent in the benzene ring of benzenesulphonamide increases the dipole moment still further; the value 5.14 D for benzenesulphonamides becomes 5.94 D for *o*-nitrobenzenesulphonamide.[9] In the *ortho* position, however, this increase is less than that expected from the value calculated from the partial dipole moments, indicating that there are intramolecular interactions between the *o*-nitro substituent and the sulphonamide group.[9] The two S=O bonds are the main contributors to the dipole moment of sulphonamide, as the S=O– moment has been reported to be 3.04–3.26 D.[9] The value of the dipole moment of *o*-nitrobenzenesulphenamide is also high: 5.18 D in dioxane.[9] The ^{13}C n.m.r. chemical shifts of the nitro-substituted benzenesulphonamides also deviate from the values calculated from substituent parameters.[10] This was a good reason for us to study the crystal structures of sulphur(II) and sulphur(VI) amides.[11] Furthermore, some compounds containing the S–N bond are known to be anti-radiation drugs, antioxidants, and fungicides and the sulphonamides are medically important compounds.[12] Only a few studies concerning the crystal structures of any other sulphur amides have been presented in the literature.[13–16]

In addition to the commonly used solution-state n.m.r. spectroscopy, high resolution solid-state n.m.r. spectroscopy has proved to be a useful tool in the electronic and structural characterization of many types of compounds.[17,18] Furthermore, the n.m.r. chemical shifts obtained from solid samples characterize the same conformational states of compounds as do *X*-ray diffraction studies.

In this work we continue our n.m.r. and crystallographic studies on various types of sulphur amide by presenting the synthesis, ^{13}C c.p.-m.a.s., and multinuclear solution-state n.m.r. spectral data for *o*-nitrobenzenesulphenamide, *N,N*-dimethyl-*o*-nitrobenzenesulphenamide (**1**), and *N,N*-dimethyl-*o*-nitrobenzenesulphonamide (**2**) together with the crystal and molecular structures of (**1**) and (**2**). We compare these with the earlier reported structures of *N*-methyltoluene-*p*-sulphonamide (**3**) and *N,N*-dimethyltoluene-*p*-sulphonamide (**4**).[11]



(1)



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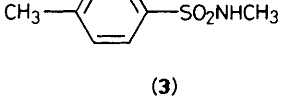

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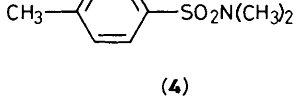

(4)

Experimental

All sulphur amides were prepared in our (P.R.) laboratory. *N,N*-Dimethyl-*o*-nitrobenzenesulphenamide (**1**) was synthesized from *o*-nitrobenzenesulphenyl chloride (Aldrich-Chemie, Steinheim, West-Germany) and *N,N*-dimethyl-o-nitrobenzene-

Table 1. Crystal data and details of data collection.

	N,*N*-Dimethyl-*o*-nitrobenzenesulphenamide (**1**)	*N*,*N*-Dimethyl-*o*-nitrobenzenesulphonamide (**2**)
Mol. formula	$C_8H_{10}N_2O_2S$	$C_8H_{10}N_2O_4S$
Mol. weight	198.24	230.24
Crystal system	Monoclinic	Orthorhombic
a/Å	7.932 5(9)	7.999(2)
b/Å	6.880 6(6)	13.020(2)
c/Å	9.341(2)	20.176(3)
β/°	113.19(1)	90
Space group	$P2_1/m$	$Pbca$
V/Å^3	468.6(1)	2 101.3(7)
D_c/g cm^{-3}	1.42	1.46
Z	2	8
Crystal dimensions/mm	0.15 × 0.3 × 0.4	0.3 × 0.35 × 0.2
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}	2.9	3.0
Scan type	ω	ω
2θ Limits	$5° < 2\theta < 55°$	$5° < 2\theta < 50°$
Scan rate/° min^{-1}	1.0–15.0	1.5–20.0
Number of collected reflections	979	2 158
Number of observed reflections	747	791
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	102	138
R	0.043	0.049
R_w	0.047	0.035

sulphonamide (**2**) from *o*-nitrobenzenesulphonyl chloride (Fluka AG, Buchs) and dimethylamine (Fluka AG, Wasserfrei) in dry diethyl ether at −10 °C.[19,20] The amides were purified by repeated crystallization from ethanol. The melting points were 82–83 °C for *N*,*N*-dimethyl-*o*-nitrobenzenesulphenamide and 193–195 °C for *N*,*N*-dimethyl-*o*-nitrobenzenesulphonamide. For the *X*-ray crystallographic study the amides were crystallized from ligroin by slow evaporation of the solvent.

X-*Ray Crystallographic Measurements*.—Data pertaining to the crystallographic analysis of (**1**) and (**2**) are collected in Table 1. Cell parameters were determined by a least-squares method on the basis of 25 independent reflections for each compound. After collection of about 500 reflections for the sulphenamide compound, the intensities of the check reflections were decreased by about 10%. The minimum scan speed and the maximum 2θ value for the data collection were, therefore, changed from 1.0 to 2.0 ° min^{-1} and from 55 to 50 °, respectively. The intensities of the test reflections decreased by about 15% during the data collection. The data for the sulphenamide compound were corrected for decay, for Lorentz and polarization effects, and for dispersion and extinction [ε = 2.06(8)], but not for absorption (μ = 2.9 cm^{-1}). No significant variation was observed for the standard reflections of the sulphonamide compound during the data collection. The data for the sulphonamide compound were corrected for Lorentz and polarization effects and for dispersion, but not for absorption (μ = 3.0 cm^{-1}). The phase problems for both compounds were solved by direct methods.[21] After anisotropic refinements of the non-hydrogen atoms with XTAL system programs[22] a subsequent difference Fourier map revealed approximate hydrogen-atom positions for the sulphenamide compound. All atoms were refined in the final cycles. The two most prominent residual maxima near the two methyl carbons in the map for the sulphonamide were considered as hydrogens and the remaining hydrogens were placed at their calculated positions. Only the non-hydrogen atoms were refined. The functions minimized were $\Sigma w(\Delta F)^2$, where $w = 1/\sigma F_o^2$. Atomic scattering factors were those included in the programs.

N.M.R. Spectroscopic Measurements.—For liquid-state n.m.r. spectroscopic measurements the 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 noise decoupling. An external ^{7}Li lock was used to stabilize the field frequency ratio for quadrupolar nuclei. Typical spectral parameters were: operating frequency 13.46, 10.04, 7.14, and 25.05 MHz; spectral width 10, 6, 20, and 6 kHz; pulse angle 90, 30, 90, and 30° and pulse repetition 0.05, 10, 0.01, and 5 s for ^{17}O, ^{15}N, ^{14}N, and ^{13}C, respectively. The chemical shifts of the ^{17}O nucleus were measured relative to external water; those of ^{15}N and ^{14}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 n.m.r. spectrometer. The operating frequency was 50.10 MHz, spectral width 10 kHz, pulse angle 90°, and repetition time 6 s. Single contact spin-locked cross polarization was established under Hartman–Hahn conditions with contact time of 0.5 ms. The spinning frequency estimated by the position of spinning side bands was 25–30 kHz. Solid hexamethylbenzene was used as an external reference, and chemical shift values were converted to the scale of tetramethylsilane.

Results and Discussion

Crystallographic Studies.—Crystal data for (**1**) and (**2**) are presented in Table 1 and the positional parameters in Tables 2 and 3. The numbering system of the molecules is presented in Figure 1, bond lengths and bond angles in Table 4, distances of the atoms from the aromatic ring plane in Table 5, and the torsion angle values in Table 6.*

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* *Supplementary Data:* Full lists of bond lengths and bond angles together with tables of hydrogen atom co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of the supplementary publications scheme see 'Instructions for Authors' (1989), *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

Table 2. Positional parameters for (**1**).

	x	*y*	*z*
S	0.250 6(2)	0.250 0	0.227 1(1)
O(3)	0.265 7(4)	0.250 0	0.509 1(3)
O(4)	0.489 3(4)	0.250 0	0.732 7(3)
N(1)	0.253 2(6)	0.250 0	0.050 1(4)
N(2)	0.428 9(5)	0.250 0	0.590 5(4)
C(1)	0.488 1(6)	0.250 0	0.351 0(4)
C(2)	0.555 1(5)	0.250 0	0.512 7(4)
C(3)	0.740 1(6)	0.250 0	0.604 3(4)
C(4)	0.864 9(6)	0.250 0	0.538 3(5)
C(5)	0.802 0(6)	0.250 0	0.379 8(5)
C(6)	0.621 0(6)	0.250 0	0.287 9(4)
C(7)	0.228 6(5)	0.428 3(6)	−0.033 9(3)

Table 3. Positional parameters for (**2**).

Atom	*x*	*y*	*z*
S	0.193 5(2)	0.006 7(1)	0.399 00(7)
O(1)	0.256 8(5)	−0.085 8(2)	0.427 5(2)
O(2)	0.057 8(5)	0.002 4(3)	0.353 6(2)
O(3)	0.355 0(5)	−0.133 3(2)	0.292 8(2)
O(4)	0.594 2(6)	−0.155 3(3)	0.338 3(2)
N(1)	0.139 6(5)	0.080 8(3)	0.458 1(2)
N(2)	0.479 3(5)	−0.102 4(3)	0.319 8(2)
C(1)	0.368 7(6)	0.066 2(3)	0.359 6(2)
C(2)	0.495 0(6)	0.009 8(4)	0.329 4(2)
C(3)	0.636 7(6)	0.055 8(4)	0.304 3(2)
C(4)	0.651 5(7)	0.161 2(4)	0.307 2(3)
C(5)	0.526 2(7)	0.217 0(4)	0.335 1(3)
C(6)	0.386 4(7)	0.172 2(3)	0.361 9(2)
C(7)	0.018 1(8)	0.162 1(4)	0.448 9(4)
C(8)	0.243 4(8)	0.086 4(5)	0.516 8(3)

Table 4. Selected bond lengths and bond angles for (**1**) and (**2**).

	(**1**)	(**2**)
Bond lengths/Å		
S–O(1)		1.427(4)
S–O(2)		1.422(4)
S–N(1)	1.663(4)	1.594(4)
S–C(1)	1.781(4)	1.789(5)
O(3)–N(2)	1.216(4)	1.203(6)
O(4)–N(2)	1.221(4)	1.207(6)
N(1)–C(7)	1.427(4)	1.450(7)
N(1)–C(8)		1.447(6)
N(2)–C(2)	1.450(6)	1.479(6)
C(1)–C(2)	1.390(5)	1.390(7)
C(1)–C(6)	1.396(7)	1.388(6)
C(2)–C(3)	1.377(5)	1.378(7)
Bond angles/°		
O(1)–S–O(2)		119.8(2)
O(1)–S–N(1)		107.7(2)
O(1)–S–C(1)		105.5(2)
O(2)–S–N(1)		107.4(2)
O(2)–S–C(1)		109.2(2)
N(1)–S–C(1)	102.8(2)	106.4(2)
S–N(1)–C(7)	119.6(2)	121.8(4)
S–N(1)–C(8)		119.2(4)
C(7)–N(1)–C(8)	118.5(3)[a]	116.9(5)
O(3)–N(2)–O(4)	123.0(4)	125.4(4)
O(3)–N(2)–C(2)	117.5(3)	117.3(4)
O(4)–N(2)–C(2)	119.5(3)	117.2(4)
S–C(1)–C(2)	124.1(4)	122.4(3)
S–C(1)–C(6)	120.5(3)	119.7(4)
C(2)–C(1)–C(6)	115.5(3)	117.8(5)
C(1)–C(2)–C(3)	122.2(4)	122.0(4)

[a] Denotes angle C(7)–N(1)–C(7)* with C(7)* at $x, \frac{1}{2} - y, z$.

Table 5. The distances/Å of the atoms from the best least-squares plane determined by the aromatic carbon atoms of (**2**).

S	0.134(7)	N(1)	0.918(9)
O(1)	0.971(9)	N(2)	−0.126(8)
O(2)	−1.169(9)	C(7)	0.22(1)
O(3)	−1.030(9)	C(8)	2.34(1)
O(4)	0.679(9)		

Table 6. Selected torsion angles/° for (**2**).

O(1)–S–C(1)–C(2)	34.6(4)	O(2)–S–N(1)–C(7)	−26.6(5)
O(1)–S–C(1)–C(6)	−141.6(4)	O(2)–S–N(1)–C(8)	70.2(4)
O(2)–S–C(1)–C(2)	−95.5(4)	C(1)–S–N(1)–C(7)	90.2(4)
O(2)–S–C(1)–C(6)	88.3(4)	C(1)–S–N(1)–C(8)	−72.9(4)
N(1)–S–C(1)–C(2)	148.9(4)	O(3)–N(2)–C(2)–C(1)	52.4(6)
N(1)–S–C(1)–C(6)	−27.4(4)	O(3)–N(2)–C(2)–C(3)	−124.7(4)
O(1)–S–N(1)–C(7)	−157.1(4)	O(4)–N(2)–C(2)–C(1)	−129.4(5)
O(1)–S–N(1)–C(8)	39.8(4)	O(4)–N(2)–C(2)–C(3)	53.6(6)

The most significant difference in the bond lengths is found in the S–N values, 1.662(3) Å for (**1**) and 1.593(4) Å for (**2**), which is obviously due to the oxidation state of S. It is difficult to evaluate the bond order, but the pseudo-planarity of the $(CH_3)_2NS$ moiety in both compounds suggests increased double-bond character in the S–N bond. The sum of the angles around N is 357.8(3)° for (**1**) and 357.9(4)° for (**2**).

In (**1**) the $N(CH_3)_2$ group is oriented away from the NO_2 group, reducing the steric repulsion between the groups. The molecule adopts ideal σ symmetry; all atoms except the methyl groups are in the mirror plane, and the methyl groups are situated on the opposite sides of the plane. The magnitudes of the C(2)–C(1)–S(1) and C(6)–C(1)–S(1) angles of 124.0(3) and 120.3(2)°, respectively, together with the C(1)–C(2)–N(2) and C(3)–C(2)–N(2) angles of 119.8(3) and 117.4(3)°, further characterize the decrease of steric repulsion between O(3) and S(1) (Figure 1). However, the intramolecular O(3) ••• S(1) distance [2.588(3) Å] is still *ca.* 0.7 Å shorter than the sum of the van der Waals radii. In principle a singly bonded substituent in the benzene ring is free to rotate around the joining bond, yet the NO_2 group is not rotated at all with respect to the phenyl plane. Thus, we must suppose an interaction between the S(1) and O(3) atoms, an interaction which probably helps the molecule to achieve the σ symmetry. Although the NSC_6H_4-NO_2 moiety is exactly planar, the angles around C(2) and especially around C(1) show significant deviations from the ideal bond angle of 120° typical for a sp^2 carbon atom. The other bond parameters can be assumed to be normal.

Compound (**2**) does not adopt a high molecular symmetry, owing to the steric repulsion between the *o*-substituted NO_2 group and the SO_2N group. This repulsion is reflected in several structural parameters: the N(2) and S(1) atoms are slightly shifted to opposite sides of the plane through the phenyl group [−0.126(8) and 0.134(7) Å, respectively]; the NO_2 group is rotated 53.3(2)° relative to the phenyl group; and the SO_2N group is oriented so that the O–S–C–C torsion angles (Table 6) are clearly different, with the result that there are no intramolecular $O(1)(SO_2)$–$O(3)(NO_2)$ contacts shorter than 2.894(5) Å. This is, however, slightly shorter than the van der Waals radii. Moreover, the angles around C(1) and C(2) [C(2)–C(1)–S(1) = 122.4(3), C(6)–C(1)–S(1) = 119.7(4), C(1)–C(2)–N(2) = 122.1(4), and C(3)–C(2)–N(2) = 116.8(4)°] indicate a tendency to reduce steric repulsion between neighbouring groups through bending of the corresponding bonds.

Comparison of the bond lengths and angles of compounds

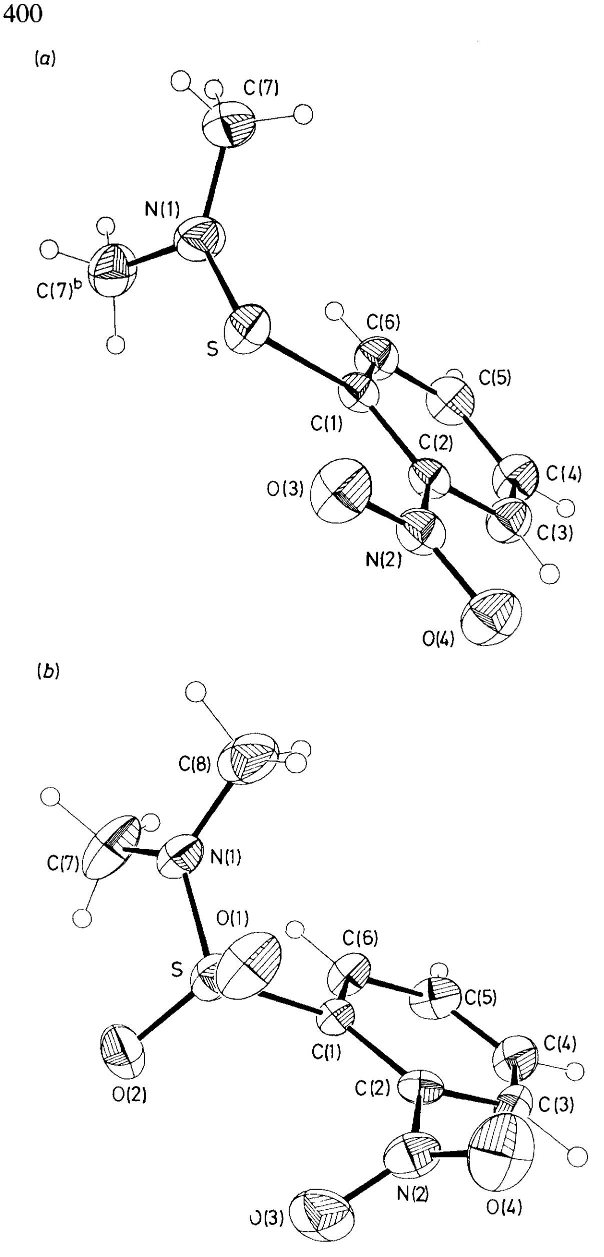

Figure 1. Molecular drawings of (*a*) *N*,*N*-dimethyl-*o*-nitrobenzenesulphenamide (**1**) and (*b*) *N*,*N*-dimethyl-*o*-nitrobenzenesulphonamide (**2**).

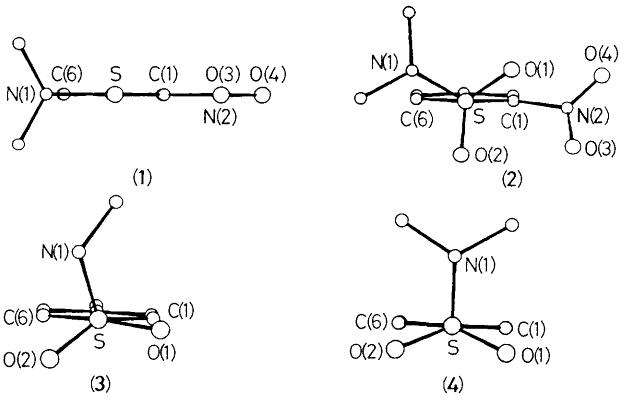

Figure 2. Compounds (**1**)–(**4**) viewed along the S(1)–C(1) bond. The N(1)–S–C(1)–C(6) torsion angle is 0° for (**1**), −27.4(5)° for (**2**), −70.1(7)° for (**3**) (molecule 1) and −88.9(2)° for (**4**).

(**1**)–(**4**) shows, as expected, that most of the bond lengths and angles are essentially similar, and the most striking difference is in the bond parameters of the sulphur atoms of the S(II) and S(VI) compounds. The C(1)–S(1)–N(1) angle of 102.8(2)° in (**1**) is 3.7–4.8° smaller than the values in the S(VI) compounds. Moreover, the S(1)–N(1) bond in (**1**) [1.662(3) Å] is 0.042–0.069 Å longer than the same bond in the S(VI) compounds.[23]

By contrast, the configuration of the four compounds is noticeably different. Comparison of the configurations of compounds (**1**)–(**4**) can be made by viewing the compounds along the S(1)–C(1) bond as presented in Figure 2 (see also Table 6). This scheme clearly demonstrates the different orientations of the atoms bonded to the sulphur atom with respect to the plane through the phenyl group.

In (**2**) the oxygen atoms bonded to the sulphur atom are situated on opposite sides of the plane through the phenyl group, whereas in *N*-methyltoluene-*p*-sulphonamide and *N*,*N*-dimethyltoluene-*p*-sulphonamide they lie on the same side of the plane. Moreover, the N(1)–S(1)–C(1)–C(6) torsion angles in (**1**)–(**4**) are very different, changing gradually from 0° in (**1**) to −88.9(2)° in (**4**). Compound (**1**) adopts σ symmetry with the N(1) atom and the phenyl group in the mirror plane, as described above; but in compound (**4**) the N(1) atom lies in a pseudo mirror plane, which bisects the molecule through the atoms S(1), N(1), C(1), and C(4). The plane is thus perpendicular to the plane passing through the phenyl group of (**4**). On the basis of these results, it seems clear that the tendency to minimize the steric repulsion and interaction between the S(II) and O atoms of the nitro group is the most significant factor determining the configuration of the compounds.

N.M.R. Spectroscopic Studies.—The ^{15}N and ^{17}O n.m.r. chemical shifts of (**1**) and (**2**) together with those of some other sulphur amides are presented in Table 7, and the ^{13}C n.m.r chemical shifts both in solution and in the solid state are presented in Table 8.

The values of the ^{15}N n.m.r. chemical shifts of (**2**) (−304.0 ppm) and *N*,*N*-dimethylbenzenesulphonamide (−298.3 ppm) show the slight shielding effect of the *o*-nitro substituent of the benzene ring on the amide nitrogen nucleus.

The ^{14}N n.m.r. chemical shift for (**1**) is *ca.* −370 ppm showing the amide nitrogen to be much more shielded in the sulphenamide than in the corresponding sulphonamide. The shielding order of the amide nitrogen in *o*-nitro substituted sulphur amides follows the trend observed earlier for benzene ring unsubstituted aromatic sulphur(II) and sulphur(VI) amides,[25] *i.e.* –S–N > –SO$_2$–N. This shielding order of the nitrogen nucleus of the sulphenamide and the sulphonamide is in agreement with the S–N bond lengths: 1.662(3) Å for (**1**) and 1.594(4) Å for (**2**). These values show clearly that the double-bond character of the S–N bond is greater in the sulphonamide than in the sulphenamide and that the unshared electron pair of the nitrogen atom is more delocalized in the sulphonamide than in the sulphenamide. Thus, the electron density and thereby the shielding of the nitrogen nucleus is greater in the sulphenamide than in the sulphonamide.

A comparison of the ^{15}N n.m.r. chemical shifts of the (**2**) (−304.0 ppm) and *o*-nitrobenzenesulphonamide (−285.6 ppm) shows the nitrogen-15 nucleus to be somewhat more shielded in the *N*,*N*-dimethyl-substituted than in the *N*-unsubstituted compound. Substitution of hydrogen atoms for dimethyl groups on the sulphonamide group changes the shielding of the nitrogen nucleus in the same direction in *o*-nitro-substituted benzenesulphonamide and in benzenesulphonamide, since the n.m.r. chemical shifts of the nitrogen-15 nucleus are −298.3 ppm for *N*,*N*-dimethylbenzenesulphonamide and −288.0 ppm for benzenesulphonamide. It is noteworthy that the effect of the *o*-nitro substituent on the shielding of the nitrogen-15 nucleus is

Table 7. N.m.r. chemical shifts (ppm) of some resonance signals for benzenesulphonamides and benzenesulphenamides in acetone.

	$\delta(^{15}N)$		$\delta(^{17}O)$		$\delta(^{14}N)$	
Compound	N(S)	N(*o*-NO_2)	O(S)	O(*o*-NO_2)	N-*o*-NO_2)	Ref.
o-NO_2–$C_6H_4SO_2NH_2$	−285.6		164.4			10
o-NO_2–$C_6H_4SO_2N(CH_3)_2$	−304.0	−10.1	151.5	627.5	−5.8	
p-CH_3–$C_6H_4SO_2N(CH_3)_2$	−298.7		139.0			10
$C_6H_5SO_2NH_2$	−288.0		159.4			25
$C_6H_5SO_2N(CH_3)_2$	−298.3		139.9			
o-NO_2–$C_6H_4SNH_2$	−374.0	−13.3			−9.5	
o-NO_2–$C_6H_4SN(CH_3)_2$					−9.5	
$C_6H_5SN(CH_2CH_3)_2$	−335.1[a]					25

[a] Neat.

Table 8. ^{13}C N.m.r. chemical shifts (ppm) of some substituted benzenesulphen- and benzenesulphon-amides in acetone or in the solid state.

		Aromatic								
Compound	Solvent/solid	C1	C2	C3	C4	C5	C6	N–CH_3	C–CH_3	Ref.
o-NO_2–$C_6H_4SO_2NH_2$	Acetone	137.1	148.7	125.6	133.8	134.5	130.1			10
	Solid	138.0	149.2	129.1	135.6		130.7			
o-NO_2–$C_6H_4SO_2N(CH_3)_2$	Acetone	130.5	149.4	124.7	132.6	134.9	131.1	37.8		
	Solid	131.6	146.9	124.9	133.5	134.5	131.6	38.8		
								36.8		
								34.3		
p-CH_3–$C_6H_4SO_2NH_2$	Acetone	143.1	126.7	129.9	141.8	129.9	126.7		21.3	10
	Solid	145.5	126.5	130.3	138.3	130.3	126.5		21.1	11
p-CH_3–$C_6H_4SO_2N(CH_3)_2$	Acetone	133.4	128.4	130.2	144.0	130.2	128.4	38.0	21.3	11
	Solid[a]	133.6	129.6	130.6	145.9	131.9	129.6	39.5	20.9	
								38.1		
								36.4		
								34.9		
$C_6H_5SO_2NH_2$	Acetone	144.6	126.6	129.5	132.6	129.5	126.6			25
$C_6H_5SO_2N(CH_3)_2$	Acetone	135.1	127.5	129.0	132.7	129.0	127.5	37.7		10
	Solid	133.8	129.4		133.8		129.4	40.3		
								38.9		
o-NO_2–$C_6H_4SNH_2$	Acetone	143.6	148.9	125.4	126.7	135.4	125.8			
	Solid	142.2	145.5	124.4	126.0	136.5	126.7			
o-NO_2–$C_6H_4SN(CH_3)_2$	Acetone	142.7	145.7	125.4	126.4	134.8	125.5	47.2		
	Solid	137.7	143.0	123.0	124.6	133.0	124.6	46.7		
								44.9		
$C_6H_5SN(CH_2CH_3)_2$	Neat	141.5	124.7	128.4	125.2	128.4	124.7	52.5[b]	13.7[c]	25

[a] The refined spectrum compared with that of ref. 11. [b] $C(CH_2)$. [c] $C(CH_3)$.

negligible in *N*,*N*-dimethyl- substituted benzenesulphonamide and slight in *N*-unsubstituted benzenesulphonamide. Thus an *o*-nitro substituent has virtually no effect on the electron density of the nitrogen atom attached to the sulphur atom in the sulphonamide group.

Further, Table 7 shows that the ^{17}O n.m.r. chemical shift of (**2**) is 151.5 ppm, which is a little greater than the value of 164.4 ppm obtained earlier for *o*-nitrobenzenesulphonamide.[10] Thus, the *N*,*N*-dimethyl substituent shields the oxygen atoms of the sulphonamide group. The difference between the oxygen-17 n.m.r. chemical shift of benzenesulphonamide (159.4 ppm) and that of *N*,*N*-dimethylbenzenesulphonamide (139.9 ppm) is somewhat greater than in the *o*-nitrosubstituted analogues showing that there is some electronic and/or steric interaction between the oxygen atom of the sulphonamide group and the *o*-nitro substituent of the benzene ring. Thus, the electron-withdrawing *o*-nitro substituent deshields the oxygen-17 nucleus of benzenesulphonamide by 5.0 ppm and that of *N*,*N*-dimethylbenzenesulphonamide by 11.6 ppm. According to the crystallographic data there is a configurational difference especially in the N(1)–S–C(1)–C(6) torsion angles: −88.9(2)° for *N*,*N*-dimethyltoluene-*p*-sulphonamide and −27.6(4)° for (**2**).

The ^{17}O n.m.r. chemical shifts of the NO_2 oxygen atoms of *o*-nitrobenzenesulphenamide and (**1**) are more difficult to detect in dilute solution than those of the corresponding sulphonamides (Table 7), suggesting an interaction between the O(3) atom of the NO_2 group and the S atom of the sulphenamide group. This is in agreement with the relatively short intermolecular distance [2.589(4) Å] between the atoms. According to our earlier studies, the effect of a substituent on the benzene ring on the shielding of oxygen nuclei is usually slight in sulphonamide.[10]

The ^{13}C n.m.r. chemical shifts for solution and solid state sulphur amides are presented in Table 8. A clear shift to higher values from the 128.5 ppm of benzene is seen in the chemical shifts of the aromatic C(1) in the nitro-substituted aromatic sulphur amides, analogously to that observed earlier for the corresponding unsubstituted amides and in agreement with the electron-acceptor effect of the sulphur amide group. The substituent induced shifts for the aromatic carbons of *o*-nitro-substituted sulphur amides deviate from the values calculated from substituent parameters (Table 9). Some deviation from the calculated values is seen in the *p*-substituted compounds, too. As noted above, (**2**) and *N*,*N*-dimethyltoluene-*p*-sulphonamide differ in the orientation of the atoms bonded to the sulphur atom with respect to the benzene ring.

Table 9. The induced shifts of the phenyl ring substituents of some substituted sulphur amides (exp.), the substituent effects[24] (calc.) and the difference between the values (diff.).

Compound		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
o-NO_2-$C_6H_4SO_2NH_2$	exp.	−7.5	22.1	−3.9	1.2	5.0	3.5
	calc.	−4.8	20.0	−4.8	0.9	5.8	0.9
	diff.	−2.7	2.1	0.9	0.3	−0.8	2.6
o-NO_2-$C_6H_4SO_2(CH_3)_2$	exp.	−4.6	21.9	−4.3	−0.1	5.9	3.6
	calc.	−4.8	20.0	−4.8	0.9	5.8	0.9
	diff.	0.2	1.9	0.5	−1.0	0.1	2.7
p-CH_3-$C_6H_4SO_2NH_2$	exp.	−1.5	0.1	0.4	9.2	0.4	0.1
	calc.	−2.9	−0.1	0.7	8.9	0.7	−0.1
	diff.	1.4	0.2	−0.3	0.3	−0.3	0.2
p-CH_3-$C_6H_4SO_2(CH_3)_2$	exp.	−1.7	0.9	1.2	11.3	1.2	0.9
	calc.	−2.9	−0.1	0.7	8.9	0.7	−0.1
	diff.	1.2	0.1	0.5	2.4	0.5	1.0
o-NO_2-$C_6H_4SN(CH_3)_2$[a]	exp.	1.2	21.0	−3.0	1.2	6.4	0.8
	calc.	−4.8	20.0	−4.8	0.9	5.8	0.9
	diff.	6.0	1.0	1.8	0.3	0.6	−0.1

[a] Calculated from the chemical shifts of $C_6H_5SN(CH_2CH_3)_2$.

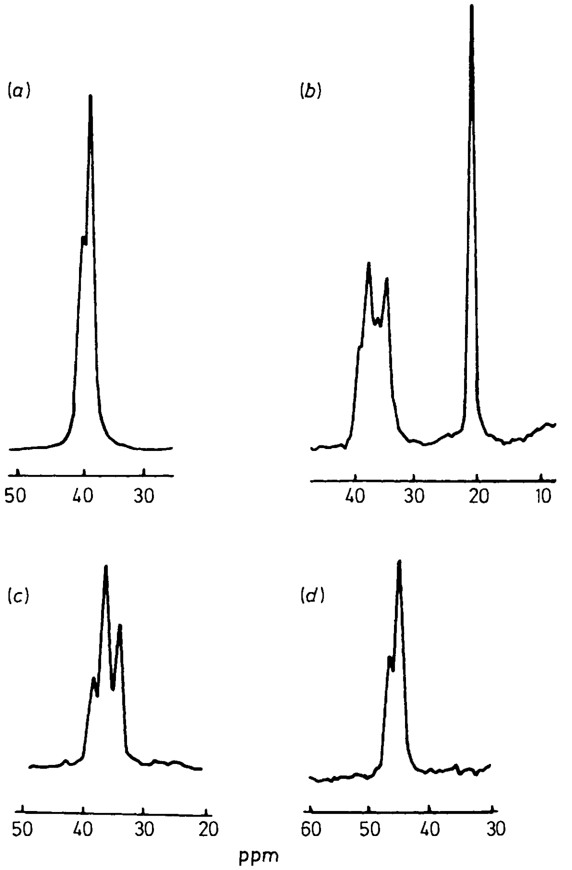

Figure 3. Methyl carbon signals (δ/ppm) in the ^{13}C c.p.-m.a.s. n.m.r. spectra of some sulphur amides. (*a*) *N,N*-Dimethylbenzenesulphonamide; (*b*) *N,N*-dimethyltoluene-*p*-sulphonamide; (*c*) *N,N*-dimethyl-*o*-nitrobenzenesulphonamide (**2**), and (*d*) *N,N*-dimethyl-*o*-nitrobenzenesulphenamide (**1**).

The shieldings of the amide methyl carbons which are observed to be dependent of the oxidation state of sulphur, barely change with *o*-nitro substitution on the benzene ring.

The ^{13}C c.p.-m.a.s. n.m.r. spectra (Figure 3) show the characteristic splitting in the *N*-methyl carbon signals due to the interaction of the quadrupolar ^{14}N nucleus attached to the methyl carbons. The width of the splitting is very similar in the aromatic sulphur amides: 70 Hz in *N,N*-dimethylbenzenesulphonamide, 80 Hz in *N,N*-dimethyltoluene-*p*-sulphonamide, 100 Hz in (**2**) and 90 Hz in (**1**).

In addition, the solid state spectra of *N,N*-dimethyltoluene-*p*-sulphonamide and (**2**) show extra splitting of the *N*-methyl resonance signals (Figure 3). The relatively short S–N bond [1.594(4) Å in (**2**) and 1.614(2) Å in *N,N*-dimethyltoluene-*p*-sulphonamide],[2] may be due to steric hindrance of the rotation of the methyl group around the C–N bond in the sulphonamide group. Moreover, there are two short intramolecular distances between a CH_3 hydrogen and SO_2 oxygen atoms: O(2) ··· H(73), 2.34 Å; O(1) ··· H(81), 2.46 Å. These values suggest at least some interaction between the methyl groups and the oxygen atoms of the SO_2 group. On the other hand, the configuration of the substituted sulphonamides (Figures 1 and 2) may give rise to a difference in the two methyl groups of the sulphonamide group, manifested by an extra splitting in the ^{13}C c.p.-m.a.s. spectra of (**2**) (Figure 3), and probably in *N,N*-dimethyltoluene-*p*-sulphonamide, too. The splitting is slightly greater in the former compound.

A comparison of the solid state and solution ^{13}C chemical shifts shows some differences between the solid state and solution spectra (Table 8) indicating the possibility of some slight differences in the solid and solution state conformations. Taken together, the results show that the multinuclear n.m.r. spectra together with ^{13}C c.p.-m.a.s. spectra show changes in the electronic distribution and molecular interaction when interpreted together with the *X*-ray crystallographic data.

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