Conformational Studies by Dynamic Nuclear Magnetic Resonance Spectroscopy. Part 21.[1] Structure, Conformation, and Stereodynamics of Sulphinylhydrazines

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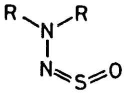
^{1}H and ^{13}C n.m.r. spectroscopy at low temperature allowed the detection of restricted rotation about the N–N bond in sulphinylhydrazines. In the case of the di-isopropyl derivative the existence of two conformers due to a ' correlated orientation ' (gear effect) was also discovered. The trend of the measured $\Delta G^\ddagger$ values and the interpretation of the chemical shifts suggested conformational assignments which were supported by an *X*-ray diffraction investigation of the solid.

In molecules containing an N–N bond joined to a double bond (*i.e.* $>$N–N=X) the N–N rotation appears to be restricted owing to the partial double bond character brought about by mesomeric structures of the type $-\overset{+}{\underset{|}{N}} = N - X^-$. Variable temperature n.m.r. spectroscopy allows the determination of the rotational barrier of this process. The corresponding free energies of activation have been reported for a number of *N*-nitrosamines (N–N=O),[2-7] triazenes (N–N=N),[8-11] and hydrazones (N–N=C).[12-14] One would expect that *N*-sulphinylhydrazines (N–N=SO) would also display restricted motion about the N–N bond and, to check this prediction, a number of these derivatives were studied in the work here reported.

RESULTS AND DISCUSSION

Compounds (1)—(4) showed, at room temperature, equivalent (homotopic) ^{1}H and ^{13}C n.m.r. signals for the corresponding parts of the two symmetrical groups



(1) R = Me
(2) R = Et
(3) R = Pr^i
(4) R = Ph

bonded to the *sp*^{3} nitrogen. This means that, as opposed to *N*-nitrosamines (R_2N–NO),[2-7] but as for triazenes (R_2NN=NPh),[8-11] N–N rotation is fast on the n.m.r. time scale at room temperature. On lowering the temperature, line broadening occurs and, eventually, a pair of signals in 1 : 1 ratio is observed for the groups *Z* (*syn*) and *E* (*anti*) to SO. Whereas in derivatives (1)—(3) the dependence of the line shape on temperature could be observed either by ^{1}H or by ^{13}C n.m.r., in the case of Ph_2N–NSO the ^{1}H spectrum is far too complex and only ^{13}C n.m.r. is suited for the interpretation of the dynamic process. In Figure 1 this spectrum is shown at +25 °C (in $CDCl_3$) and at −108 °C (in Me_2O). The four lines corresponding to C-1, C-2,-6, C-3,-5, and C-4 are all split into two at low temperature since one phenyl is *syn* (or *Z*) to SO, whereas the other is *anti* (or *E*). By studying the shape of the signals of this and of the other sulphinylhydrazines (1)—(3), it is possible to determine the rotational rate constants and to obtain, therefore, the free energies of activation ($\Delta G^\ddagger$) for N–N rotation in (1)—(4).

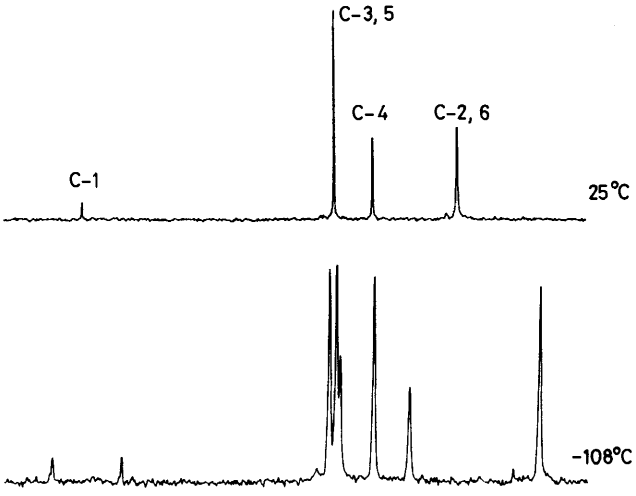


FIGURE 1 ^{13}C N.m.r. spectra (25.16 MHz) of Ph_2NNSO (4) at room (in $CDCl_3$) and lower (in Me_2O) temperatures. The signals are split in two due to slowing of the N–N rotation

In order to check whether the results from ^{1}H n.m.r. were in agreement with those obtained from ^{13}C spectra, *NN*-di-isopropylsulphinylhydrazine (3) was studied at both frequencies. Computer simulation[15] of the line shape of the methylic hydrogens of (3) (a pair of doublets) yielded $\Delta G^\ddagger$ 11.7 kcal mol^{-1}; measurement of the coalescence temperature[15] of the ^{13}C methyl signals yielded 11.5 kcal mol^{-1}. Because of this near coincidence we relied upon the coalescence method for other determinations: the values of free energies so obtained are reported in Table 1.

The aromatic derivative (4) has a slightly lower

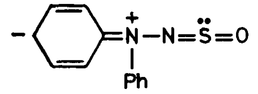
TABLE 1

Free energy of activation ($\Delta G^\ddagger$) of the N–N rotation for derivatives (1)—(4). The chemical shift differences ($\Delta\nu$ in Hz) are given at temperatures below the coalescence temperature. The ^{1}H frequency is 100 MHz, the ^{13}C frequency 25.16 MHz

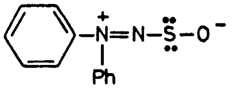
Compound	Solvent	$\Delta G^\ddagger$/ kcal mol^{-1}	Nucleus observed	Signals	$\Delta\nu$/Hz	Coalescence temp. (°C)
Me_2N–NSO (1)	$CDCl_3$	10.5 ± 0.1	^{1}H	CH_3	58	−54.5
Et_2N–NSO (2)	$CDCl_3$	11.0 ± 0.1	^{13}C	CH_2	82	−42
Pr^i_2–NSO (3)	CHF_2Cl	11.6 ± 0.1	^{13}C	CH_3	49.5	−35
		11.7 ± 0.1	^{1}H	CH_3	11.0	*a*
Ph_2N–NSO (4)	Me_2O	9.7 ± 0.15	^{13}C	C-3,-5	10.8	−83
		9.9 ± 0.1	^{13}C	C-2,-6	248.0	*b*
		9.9 ± 0.1	^{13}C	C-4	103.8	*b*

[a] Line shape analysis in the range −50 to −55°. [b] Line shape analysis in the range −78 to −83°.

barrier than the aliphatic compound (1)—(3) since conjugation between the phenyl groups and the sp^3 nitrogen reduces the ability of the latter to conjugate with the NSO group. In fact forms of type (1) compete with those of type (II) to lower the N–N double bond character

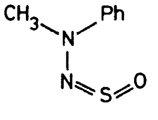


(I)

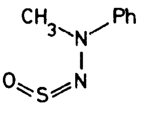


(II)

and, therefore, to reduce the energy barrier. An analogous trend has been reported for some other cases.[7,15,16] Attempts to determine the barrier for a sulphinylhydrazine in an intermediate situation (*i.e.* with both an aliphatic and an aromatic substituent) failed. *N*-Methyl-*N*-phenyl-*N'*-sulphinylhydrazine (5) always showed a single set of sharp signals even at temperatures when the other sulphinylhydrazines did split their signals. Since we observed that the rotational barrier is relatively high for sulphinylhydrazines and that at both ^{1}H and ^{13}C the chemical shift differences are quite large (Table 1), the absence of line broadening effects can only mean that the equilibrium is completely biased toward one of the two conformers (5a or b). To decide which conformation is adopted, a lanthanide induced shift (LIS)[16] experiment was carried out on (5). Addition of a certain amount of $Eu(dpm)_3$ to a $CDCl_3$ solution of (5) results in the ^{13}C methyl signal being shifted downfield much more than the C-1 signal of the phenyl ring (0.9 p.p.m. *versus* 0.3 p.p.m. in our experiment). Since Eu^{3+} is expected to co-ordinate with the SO group, the paramagmetic shift induced on the molecule will be much larger for the carbon closer to SO. This means that conformer (5b) is the preferred structure of MePhNNSO.



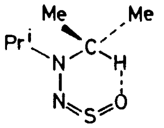
(5a)



(5b)

The trend of the energy barriers within the aliphatic series (Table 1) is quite surprising in that the values *increase* with the bulkiness of the substituent [(3) > (2) > (1)]. *N*-Sulphinylhydrazines are known to have a cisoid, planar structure in the solid state,[17] the four NNSO atoms sharing a common plane. In solution, also, in order to have non-equivalent R groups, the average dynamic CNC plane must be approximately coplanar to NNSO in the ground state, whereas the two planes are perpendicular in the rotational transition state. As a consequence, when the bulkiness of R increases from Me to Pr^i, the planar ground state is expected to be destabilized whereas the perpendicular transition state should not be much affected. The result is a net decrease of the energy difference and hence a smaller $\Delta G^\ddagger$ value. This model has been verified in a number of cases:[16,18-21] either a net *decrease* of $\Delta G^\ddagger$ was observed or, when the steric effects were small, $\Delta G^\ddagger$ was unchanged,[11,16] at least within 0.5 kcal mol^{-1}. A regular *increase* covering a range >1 kcal mol^{-1} along the sequence Me, Et, Pr^i, as in the present case, is thus unexpected.

A possible reason for such an anomalous trend would require that in Pr^i_2NNSO the methine hydrogen of the *Z*-isopropyl group lies in the same plane as NNSO, in such a way as to make an intramolecular hydrogen bond; this bond would then be relatively strong owing to the existence of a six-membered ring as in (III).



(III)

However there is no evidence that hydrogen bond can ever occur with methine hydrogens and therefore a more likely possibility is the existence of a polar interaction between a positively charged hydrogen and the negatively charged oxygen. This polarity effect would be larger in the isopropyl with respect to the ethyl or methyl derivatives since the ' acidity ' of a methine hydrogen is larger than that of methylene and methyl hydrogens. As a consequence the ground state of (3) would be more stable than that of (2) and (1), thus accounting for the trend in the barrier. A similar feature, although with a smaller, and thus less significant, interval of $\Delta G^\ddagger$ variation (0.5 kcal mol^{-1}) has been observed in the relatively similar R_2NNO derivatives.[5] In other molecules[11,16,18-20] either there was no possibility of a six-membered ring, or the substituents involved were less polar than SO, thus reducing the chance of this type of interaction. This observation could possibly explain why the reverse trend has been observed in sulphinylhydrazines. To support such a hypothesis, however, it has to be proved that the conformation of (3) is actually that proposed in (III), and for that we resorted to *X*-ray diffraction. This technique would also help us in clarifying a second dynamic process which we observed in Pr$^i_2$NNSO but not in the other sulphinylhydrazines under investigation.

At temperatures lower than required to ' freeze ' the N–N rotation (below −60 °C), selective broadening of some lines of (3) occurred for both ^{1}H and ^{13}C spectra; these lines sharpened again when the temperature was lowered even further (below −100 °C), although no additional lines were observed. The phenomenon is most evident for the ^{13}C signals of the methine carbons reported in Figure 2, but can still be observed for the signals of the methyl groups. Clearly an exchange between two conformations is taking place: one of them, however, is in such a small amount as to be undetectable.

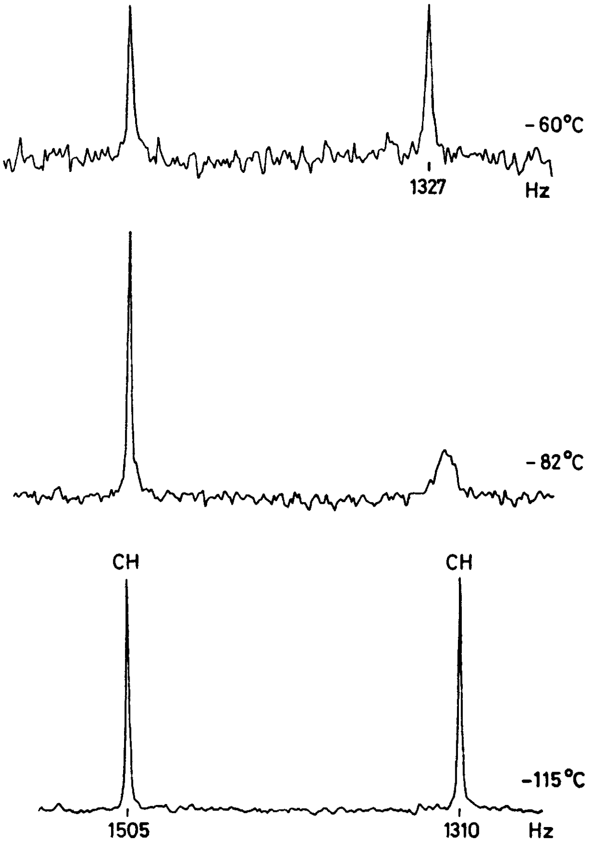


FIGURE 2 Temperature dependence of the ^{13}C signals of the methine carbons in Pr$^i_2$NNSO (3). At −60° the two signals, generated by restricted N–N rotation, have equal width since the interconversion between the two gear conformers (see text) is fast in the n.m.r. time scale. At −82° one of them is much broader than the other since the interconversion rate is slower and the internal chemical shift difference very different for the two signals. At −115° the two signals have again the same width because the interconversion rate between the gear conformers is ' locked ' in the n.m.r. time scale. The most broadened signal is also the most shifted (17 Hz at 25.16 MHz)

The very different extent of broadening occurring to the two lines of Figure 2 depends on the fact that the shift of the downfield CH of the more abundant conformer is very similar (or even equal) to that of its less abundant (and invisible) companion; line broadening is thus almost unnoticeable. On the other hand, the shift of the upfield CH is very different from that of its invisible companion, so that broadening becomes quite large. This also explains why the shift of the upfield CH varies only in the temperature range where broadening occurs (−95 to −65°) whereas it is almost temperature independent when exchange is frozen (between −100 and −130°). For, below −100° it represents the shift of a single conformer (1 310.2 Hz from Me$_4$Si) whereas at −60° it is the weighted average (1 327.3 Hz from Me$_4$Si) of a pair of conformers with different shifts and unequal populations.[22,23] The existence of these two conformers depends on the fact that the two isopropyl groups do not orient themselves independently about their CN bonds, but adopt fixed conformations with respect to one other. This phenomenon was first observed in n.m.r. in some amides [24] and investigated and interpreted later in more detail for a number of other derivatives.[25-30] It was found that two secondary carbons (and in particular two isopropyl groups) rotate, when favourable conditions occur, as a pair of cogwheels and may assume, in principle, four possible conformations, corresponding to four energy minima.[29-31] All four conformers were never simultaneously observed in the same molecule although in some cases three of them were detected.[26,30,31]

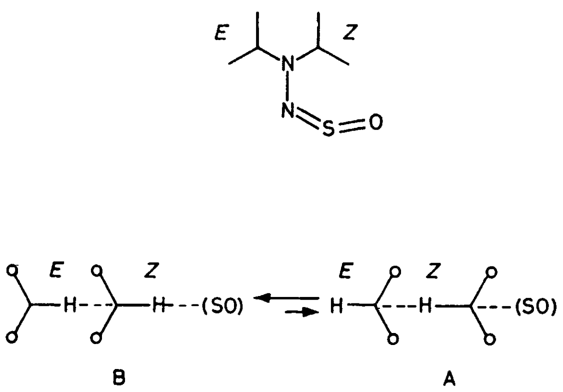


FIGURE 3 Schematic representation of the two interconverting gear conformers of Pr$^i_2$NNSO (3). The isopropyl groups are shown as projections on planes perpendicular to the respective N–Pr^i bonds. The two nitrogen atoms (underneath the sheet plane) are not reported and only the SO moiety (also underneath the sheet) is shown in parentheses. The picture and the labelling are the same as in refs. 29 and 30

In the majority of reports two conformers out of four were present and in some cases one was in a much lower amount than the other, as observed for Pr$^i_2$NNSO. Calculations carried out [29] on the relatively similar Pr$^i_2$NCHO make us think that the pair of exchanging conformers in Pr$^i_2$NNSO should be those reported in Figure 3, since they are expected to have the lowest energy.[29]

Although we do not know the population and shift of the less intense (invisible) conformer we can still determine, under these conditions, the interconversion barrier since for very biased equilibria the maximum line width attained by the ^{13}C signal depends only on the product $c\Delta\nu$, where c represents the fraction of the lower isomer and $\Delta\nu$ the chemical shift difference between the two species. The maximum width experimentally observed for the methine signal (15 ± 1 Hz at $-83°$) could be computer simulated only with $c\Delta\nu$ of 12 ± 1 and a rate constant of 70 ± 30 s^{-1}. For values higher or lower than 12, the maximum width computed was always sharper or broader than 15 Hz, whatever the rate constant employed. As a consequence a free energy of activation of $9.3_5 \pm 0.2$ kcal mol^{-1} was obtained for the process that exchanges the more abundant into the less abundant gear conformer. An upper limit to the amount of the latter can probably be set at 5%, otherwise its signal should have been observed, at least in the proton spectrum. The lower limit is likely to be higher than 1%, otherwise $\Delta\nu$ would become larger than $12/0.01 = 1\,200$ Hz (or 47.7 p.p.m.), a difference too large for a conformational effect. One of the largest $\Delta\nu$ values observed for a conformational shift in a neutral organic molecule [32] is ' only ' 34.5 p.p.m.* This suggest $3 \pm 2\%$ as a reasonable figure for the amount of the invisible conformer.

Whereas the ^{13}C was more helpful than the ^{1}H spectrum for the determination of the energy barrier, the latter was more suited for the structural assignment of the more abundant conformer (*i.e.* whether A or B of Figure 3 represents the preferred arrangement of Pr^i_2NNSO). It is conceivable that, by analogy with similar molecules, the downfield septet of CH (δ 5.40) corresponds to the *Z*-, whereas the upfield (δ 3.50) belongs to the *E*-hydrogen.[29,30] By the same token the CH(*Z*) of conformer B is expected [29,30] to be at even lower field then CH(*Z*) of conformer A (see Figure 3). In Table 2 one can see that the shift of the weighted average of A and B (*i.e.* δ 5.49 measured at -60 °C) is at higher field than the shift of the individual abundant conformer (*i.e.* δ 5.56 measured at -100 °C). As a consequence, the intense CH(*Z*) we observed must be at lower field than the CH(*Z*) we could not detect: B is therefore the preferred conformer. It is also worth mentioning that, whereas for ^{13}C the upfield CH signal experiences the maximum broadening, for ^{1}H n.m.r. the largest broadening is observed in the downfield CH.

TABLE 2

^{13}C (25.16 MHz) and ^{1}H (100 MHz) chemical shifts of the signals of Pr^i_2NNSO (3) measured in CHF_2Cl at temperatures where N–N rotation is slow and the gear effect is operating

^{13}C	CH	CH	CH_3	CH_3
−60°	59.6	52.7_5	22.3	20.3_4
−100°	59.8	52.0_8	22.4	20.1_5
^{1}H				
−60°	5.49	3.50	1.24	1.13
−100°	5.56	3.51	1.23	1.13

The conformational assignment derived from the interpretation of the gear effect nicely agrees with the hypothesis developed to explain the reverse trend of $\Delta G^{\ddagger}$ for N–N rotation; conformation B is in fact the same as (III), at least for one of the isopropyl groups. The *X*-ray single crystal investigation has shown that conformation B is indeed the preferred arrangement of Pr^i_2NNSO in the solid. A view of the molecular structure is reported in Figure 4: bond distances and angles are reported in Table 3.

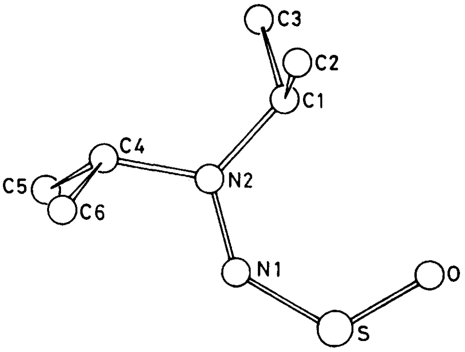


FIGURE 4 Schematic view of the *X*-ray structure of *N*-di-isopropylsulphinylhydrazine (3)

TABLE 3

Bond distances (Å) and angles with estimated standard deviations in parentheses for Pr^i_2NNSO (3). Numbering of the atoms is that of Figure 4

S–O	1.467(5)	C(1)–C(2)	1.505(8)
S–N(1)	1.565(5)	C(1)–C(3)	1.544(7)
N(1)–N(2)	1.283(5)	C(4)–C(5)	1.532(7)
N(2)–C(1)	1.463(6)	C(4)–C(6)	1.523(7)
N(2)–C(4)	1.486(6)		
O–S–N(1)	121.4(2)	N(2)–C(1)–C(2)	110.3(4)
S–N(1)–N(2)	133.1(3)	N(2)–C(1)–C(3)	109.3(4)
N(1)–N(2)–C(1)	123.5(3)	C(2)–C(1)–C(3)	112.1(4)
N(1)–N(2)–C(4)	114.2(4)	N(2)–C(4)–C(5)	110.6(4)
C(1)–N(2)–C(4)	121.9(3)	N(2)–C(4)–C(6)	111.1(4)
		C(5)–C(4)–C(6)	111.7(4)

The OSN(1)N(2)C(1)C(4) moiety (the labelling is that of Figure 4) is planar to within ± 0.05 Å and the position calculated for the methine hydrogen bonded to C(1) is very close to this plane (the deviation being only ± 0.3 Å). This hydrogen lies 2.3 Å from the oxygen atom, a distance which is even shorter than the sum of the relevant van der Waals radii. This fact supports the existence of a strong O $\cdots$ HC interaction, which leads to the widening of the OSN(1), SN(1)N(2), and N(1)N(2)C(1) bonding angles. Their values are in fact 7, 13, and 9° higher than the corresponding angles of *N*-phenylsulphinylhydrazine [17] where this intramolecular interaction does not occur.

The *X*-ray proof that B is the adopted conformation is of particular significance in that it represents the first experimental evidence that the calculations and the n.m.r. evidence used in the literature to assign these types of gear conformers are indeed correct.

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* In a work not yet published we found that in the relatively similar Pr^i_2NNO the gear effect gives a pair of conformers with a 92 : 8 ratio and a maximum $\Delta\nu$ for the methine of 7.5 p.p.m., in the ^{13}C spectrum.

EXPERIMENTAL

Sulphinylhydrazines were obtained with a modification of the method of Michaelis.[33] Compounds (1) and (5) have been already reported [34] and the data for the other derivatives used in the present work are as follows. *NN*-Diethyl-*N′*-sulphinylhydrazine (2) had b.p. 60—62° at 11 mmHg, $\nu_{max.}$ 1 160w and 1 065vs cm^{-1}, δ_H ($CDCl_3$) 1.30 (6 H, t) and 3.70 (4 H, q), δ_C 13.0 (CH_3) and 52.3 p.p.m. (CH_2), *m*/*e* 134 (M^+). NN-*Di-isopropyl*-N′-*sulphinylhydrazine* (3) had m.p. 43—45° (Found: C, 44.2; H, 8.9; N, 17.1. $C_6H_{14}N_2OS$ requires C, 44.4; H, 8.7; N, 17.3%), $\nu_{max.}$ 1 140w and 1 065vs cm^{-1}, δ_H ($CDCl_3$) 1.28 (12 H, d) and 4.48 (2 H, sept). NN-*Diphenyl*-N′-*sulphinylhydrazine* (4) had m.p. 48—50° (Found: C, 61.8, H, 5.0; N, 11.2. $C_{12}H_{10}N_2OS$ requires C, 62.6; H, 4.4; N, 12.2%), $\nu_{max.}$ 1 160w and 1 115vs cm^{-1}, δ_C 121.6 (4 C, *ortho*), 128.9 (4 C, *meta*), 126.6 (2 C, *para*), and 143.8 p.p.m. (2 C), *m*/*e* 230 (M^+).

The preparation of di-isopropylsulphinylhydrazine (3) is typical. Into a four-necked flask equipped with condenser, mechanical stirrer, funnel, and nitrogen inlet were introduced di-isopropylhydrazine [35] (3.6 g, 0.03 mol) and triethylamine (6.06 g, 0.06 mol) in anhydrous ethyl ether (150 ml). The system was kept at $-30°$ by means of a cryostat and thionyl chloride (3.54 g, 0.03 mol), dissolved in anhydrous ethyl ether (20 ml), was added dropwise over 2 h. When addition was complete the system was left at low temperature for a further 2 h, then triethylamine hydrochloride was filtered off, and the ether removed under vacuum. The yellow solid residue was chromatographed [SiO_2; light petroleum (b.p. 40—70°)–ethyl ether (10 : 1)] and the pure product was obtained (3 g, 62%).

Spectral Determinations.—The samples for low temperature n.m.r. measurements were prepared by condensing with liquid nitrogen the gaseous solvents (Me_2O or CHF_2Cl) into a 10 mm n.m.r. tube connected to a vacuum line; the tube was sealed *in vacuo* and kept at room temperature for a while before introduction into the spectrometer. The temperatures were measured with a thermocouple inserted into a dummy tube placed into the spectrometer before or after each spectral determination. The ^{13}C spectra were obtained at 25.16 MHz (Varian XL-100) in the Fourier transform mode: the pulse angle was kept in the interval 45—60° and a few hundred transients were collected. The ^1H spectra were taken at 100 MHz in 5 mm tubes in both continuous wave and Fourier transform modes.

X-*Ray Diffraction*.—Single crystal intensity data were collected by the θ—2θ scan technique on an off-line Siemens AED diffractometer by use of Zr-filtered Mo-K_α radiation of 1 585 measured reflections, 358 were considered unobserved having $I < 2.5\,\sigma\,(I)$.

Crystal Data.—$C_6H_{14}N_2OS$, monoclinic, $M = 162.11$, $a = 12.63(2)$; $b = 7.93(1)$; $c = 9.28(1)$ Å; $\beta = 95.4(2)°$; $U = 925$ Å^3, $Z = 4$; $D_c = 1.16$ g cm^{-3}. Space group $P2_{1/n}$. Mo-K_α radiation; $\lambda = 0.7107$ Å.

The structure was solved by direct methods by use of the Multan 78 set of programs. Positional and anisotropic thermal parameters of non-hydrogen atoms were refined by full matrix least-squares. A difference Fourier map calculated with final parameters did not show any significant peak not even in the positions expected for the hydrogen atoms. The final value of the *R* factor was 0.095 for the 1 578 refined reflections. Final positional and thermal parameters and a list of structure factors are listed in Supplementary Publication No. SUP 23125 (11 pp.).*

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* For details of Supplementary Publications see Notice to Authors No. 7, in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index issue.