

Preparation, Properties, and Molecular Structure of Silylsulphinylamine

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We have prepared and characterised the unstable compound silylsulphinylamine, SiH_3NSO , and report its vibrational, electronic, photoelectron, and n.m.r. spectra. Electron diffraction studies show that the skeleton is bent at nitrogen and at sulphur, has an unusually long Si-N bond, and is non-planar.

TRIMETHYLSILYLSULPHINYLAMINE, Me_3SiNSO , has been known for some while.¹ We have sought to prepare silylsulphinylamine, SiH_3NSO , in order to determine its molecular geometry and to see whether its photoelectron (p.e.) spectrum shed any light on its electronic structure.

EXPERIMENTAL

Compounds were prepared in a standard vacuum system fitted with greased taps or Sovirel Teflon valves. I.r. spectra were recorded by means of Perkin-Elmer 457 or 225 grating spectrometers; Raman spectra using a Cary 83 instrument with Ar-ion laser (488 nm) excitation; n.m.r. spectra using a Varian Associates HA100 spectrometer operating at 100 MHz for protons, whose probe had been double-tuned to accept an additional radiofrequency from a Schlumberger frequency synthesiser;² p.e. spectra by means of a Perkin-Elmer PS16 spectrometer with He^I (21.22 eV) excitation; u.v. spectra with a Unicam SP 800 visible/u.v. spectrophotometer, holding the sample in 100 mm gas cells; and mass spectra using an AEI MS902 spectrometer.

Electron-diffraction scattering patterns were recorded photographically on Agfa-Gevaert Replica 23 plates using a Balzers KD.G2 gas diffraction apparatus, and were digitised on a Joyce-Loebl microdensitometer. The sample and nozzle temperatures used were 250 and 298 K respectively. Nozzle-to-plate distances of 250, 500, and 1 000

¹ O. J. Scherer and P. Hornig, *Angew. Chem. Internat. Edn.*, 1966, **5**, 729.

² A. Charles and W. McFarlane, *Mol. Phys.*, 1968, **14**, 299.

mm were used, giving an overall range of the scattering variable, s , of 10–288 nm^{-1} . Weighting points used in setting up the off-diagonal weight matrix are given in Table 1. Data reduction and refinement calculations

TABLE 1

Weighting functions, correlation parameters, and scale factors

Camera height	Δs	s_{min}	sw_1	sw_2	s_{max}	p/h	Scale factor (k)
mm	nm^{-1}	nm^{-1}	nm^{-1}	nm^{-1}	nm^{-1}		
250	4	76	100	250	288	0.3756	0.717 ± 0.027
500	2	26	45	130	150	0.4645	0.654 ± 0.015
1 000	1	10	20	65	75	0.3825	0.706 ± 0.009

were performed using standard procedures³ on an ICL 4-75 computer, employing the scattering factors of Schäfer, Yates, and Bonham.⁴ The electron wavelength (5.660 ± 0.003 pm) was determined by direct measurement of the accelerating voltage, and from the diffraction patterns of benzene vapour.

Preparation.—(a) *From* Me_3GeNSO . Me_3GeNSO (0.30 g, 1.67 mmol) was treated with SiH_3Br (2 mmol) in an ampoule fitted with a greaseless tap (5 min). A vigorous reaction occurred, and some yellow solid material formed. The volatile products were removed, and from them *silylsulphinylamine* (1.20 mmol, 72%) was obtained by condensation at 195 K.

³ G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc. (A)*, 1971, 785; D. M. Bridges, G. C. Holywell, D. W. H. Rankin, and J. M. Freeman, *J. Organometallic Chem.*, 1971, **32**, 87.

⁴ L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, 1971, **55**, 3055.

(b) From Me_3SiNSO . Bu_3SnOMe (3.05 g, 10.0 mmol) was allowed to react with an excess of Me_3SiNSO (13.5 mmol) at room temperature (30 min). The volatile product, identified spectroscopically as Me_3SiOMe , was removed. Addition of more Me_3SiNSO to the contents of the ampoule produced no more Me_3SiOMe . All volatile materials, shown spectroscopically to be Me_3SiNSO with some $(\text{Me}_3\text{Si})_2\text{O}$, were removed from the liquid in the ampoule; the residue, involatile *in vacuo* at room temperature, was assumed to be Bu_3SnNSO and to it liquid SiH_3Br (12.0 mmol) was added, and the system kept at 195 K (30 min). The ampoule was allowed to warm to room temperature slowly, and from the volatile products silylsulphinylamine (4.0 mmol; 40% based on Bu_3SnOMe taken) was obtained by condensation at 195 K.

(c) From $(\text{SiH}_3)_3\text{N}$. $(\text{SiH}_3)_3\text{N}$ and SOCl_2 were condensed together in an ampoule fitted with a greaseless tap and allowed to warm to room temperature. The major

SiH_4 (0.15 mmol), together with traces of hydrogen, ammonia, and $(\text{SiH}_3)_3\text{N}$. There was a yellow solid residue (0.085 g). This was treated with HBr (1.0 mmol) at room temperature (2 h). Volatile products consisted of Br_2 (0.35 mmol, identified by visible/u.v. spectroscopy), with a trace of SO_2 , and residual HBr (0.1 mmol). There was a white involatile solid residue.

Vibrational Spectra.—I.r. spectra of gaseous samples showed the bands listed in Table 2; only low pressures (≤ 10 mmHg) could be used, as the decomposition was rapid at higher pressures. Even at low pressures decomposition was appreciable, so spectra were scanned rapidly. Expansion to reveal overlapping bands, to define band contours, and to resolve possible rotational fine structure was possible using a succession of fresh samples. No rotational detail was in fact resolved.

Because of rapid decomposition we were unable to record the Raman spectrum of a liquid sample, but a solid

TABLE 2
Vibrational spectra of SiH_3NSO and related molecules. Band positions/ cm^{-1}

SO_2^a I.r. (gas)	HNSO^b I.r. (gas)	CH_3NSO^c I.r. (gas)	SiH_3NSO^d		Assignment
			I.r. (gas)	Raman (solid)	
	ν_{NH} 3 345	ν_{OH} 2 900 1 458 δ_{CH} 1 367	2 195vs	2 195vs	ν_{SiH}
ν_3 1 361	1 261	1 268	1 310vs	1 290m	$\nu_{\text{as}}\text{NSO}$
ν_1 1 151	1 090	1 144	1 147s	1 130vs	$\nu_s\text{NSO}$
		ρ_{CH_3} 1 110?		995m	Impurity?
	δ_{NH} 911 ρ_{NH} 759		942vs	940s	δSiH_3
		ν_{NC} 832	710s	740m	ρSiH_3
ν_2 519	453	580	615s	605m	νSiN
		370	510m	505m	δNSO
				275w	δSiNS or τNS

s = strong, m = medium, w = weak, v = very.

^a S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, 1954, **22**, 900. ^b H. Richert, *Z. anorg. Chem.*, 1961, **309**, 171. ^c This work; cf. W. K. Glass and A. D. E. Pullin, *Trans. Faraday Soc.*, 1961, **57**, 546. ^d This work.

volatile product was silyl chloride; an involatile yellow solid was also formed. Reaction for less than 2 h gave complex mixtures of volatile compounds that included both reactants, SiH_3NSO , and SiH_3Cl ; attempts to fractionate out pure SiH_3NSO failed because it could not be separated from SOCl_2 without decomposition.

Characterisation.—Silylsulphinylamine was found to have M (vapour density) 95.2 (H_3NOSSi requires 93.2). The mass spectrum showed major peaks corresponding to the ions, $^{28}\text{Si}^{1}\text{H}_2^{14}\text{N}^{32}\text{S}^{16}\text{O}^+$ ($M - \text{H}$)⁺ (exact mass found 91.962447, calculated 91.962638), and HNSO^+ (m/e 63), and other fragments. The parent-ion peak at m/e 93 was comparatively weak even at low ionising voltages. The ^1H n.m.r. spectrum (Me_4Si solvent and standard) showed a broadened single peak (τ 5.45) with ^{29}Si satellites [$^1J(\text{SiH})$ 230 Hz; $\delta(^{29}\text{Si})$ (from heteronuclear spin decoupling) -62 p.p.m. (taking positive shift to high frequency of Me_4Si)]. The compound has a vapour pressure at 273 K of 70 ± 1 mmHg; its instability precluded a full study of the vapour pressure as a function of temperature.

Stability.—The compound is unstable as vapour or liquid; decomposition is more rapid at higher temperatures and pressures or in the liquid phase. SiH_3NSO (0.088 g, 0.95 mmol) was kept in an ampoule fitted with a greaseless tap at room temperature. Decomposition was complete within 15 min. The volatile products were identified as

sample, condensed at low temperature on a copper block, gave a Raman spectrum. The band positions are listed in Table 2, with data for CH_3NSO , HNSO , and SO_2 , and with our suggested assignments.

Electronic and Photoelectron Spectra.—The u.v. spectrum of the vapour of silylsulphinylamine to $52\,000\text{ cm}^{-1}$ showed two broad bands, at λ 35 300 (ϵ ca. $30\text{ l mol}^{-1}\text{ cm}^{-1}$) and λ 43 500 cm^{-1} (ϵ ca. $1\,000\text{ l mol}^{-1}\text{ cm}^{-1}$). The p.e. spectrum showed vertical ionisation potentials of 10.4, 10.55; 12.8, 13.2; 15.0, and 16.7 eV. The spectrum is shown in Figure 1 together with those of Me_3SiNSO and Me_3GeNSO .

Molecular Structure.—In least-squares refinements SiH_3NSO was assumed to have an SiH_3N unit with local C_{3v} symmetry. Early refinements showed that the data were fitted most closely by structures in which one Si-H bond was eclipsed with respect to the N-S bond, and this conformation was assumed in subsequent refinements. The structure was then defined by four bond lengths, one angle at each of silicon, nitrogen, and sulphur, and the Si-N-S-O dihedral angle. Of these, all except the Si-H bond length could be refined; this was set equal to that found in SiH_3NCS .⁵ The dihedral angle was not well defined, and after refinement of the other parameters a series of refinements was made with this angle fixed at

⁵ C. Glidewell, A. G. Robiette, and G. M. Sheldrick, *Chem. Phys. Letters*, 1972, **16**, 526.

values in the range 0–45°. The optimum value was found by comparison of R factors to be $30 \pm 3^\circ$.

The parameters of the best refinement, and amplitudes of vibration, are listed in Table 3, with estimated standard

TABLE 3
Molecular parameters for SiH_3NSO^a

(a) Independent distances and amplitudes (μ)			
$r_1(\text{Si-N})$	176.2(6)		6.0(7)
$r_2(\text{N-S})$	151.7(7)		4.0 (fixed)
$r_3(\text{S-O})$	144.2(5)		4.0 (fixed)
$r_4(\text{Si-H})$	148.6 (fixed)		6.5 (fixed)
(b) Dependent distances and amplitudes (μ)			
$d_5(\text{Si} \cdots \text{S})$	297.4(16)		9.9(6)
$d_6(\text{Si} \cdots \text{O})$	342.1(67)		15.5(20)
$d_7(\text{N} \cdots \text{O})$	255.3(24)		7.2(20)
$d_8(\text{N} \cdots \text{H})$	267.4(14)		10.0 (fixed)
$d_9(\text{S} \cdots \text{H})$	326.5(23)		12.0 (fixed)
$d_{10}(\text{S} \cdots \text{H})$	394.0(13)		20.0 (fixed)
$d_{11}(\text{O} \cdots \text{H})$	311.3(21)		25.0 (fixed)
$d_{12}(\text{O} \cdots \text{H})$	426.3(32)		28.0 (fixed)
$d_{13}(\text{O} \cdots \text{H})$	460.9(46)		28.0 (fixed)
$d_{14}(\text{H} \cdots \text{H})$	241.3(29)		10.0 (fixed)
(c) Angles			
$\angle_1(\text{Si-N-S})$	129.9(2)		
$\angle_2(\text{N-S-O})$	119.2(17)		
$\angle_3(\text{H-Si-N})$	110.5(21)		
$\angle_4(\text{dihedral})$	30		

^a All distances are r_i and are given in pm; angles are in degrees. Figures in parenthesis are the estimated probable errors of the last digit.

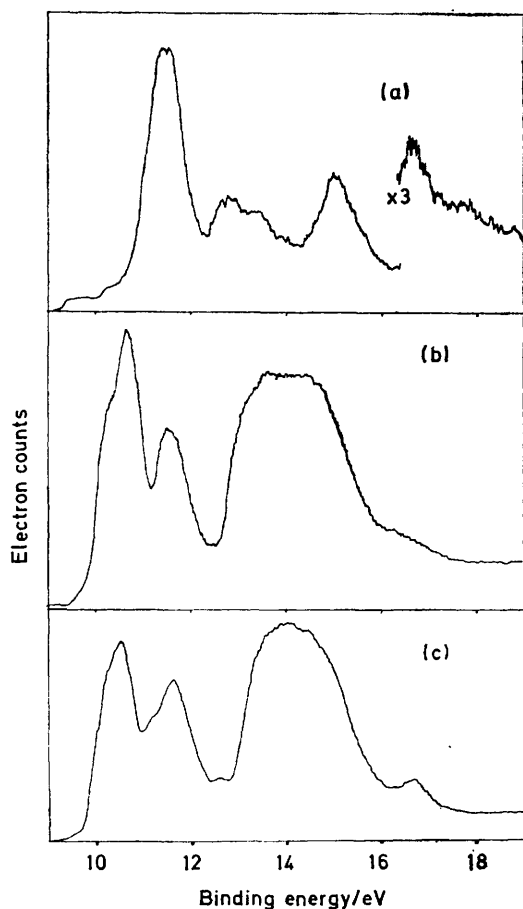


FIGURE 1 The p.e. spectra of (a) SiH_3NSO , (b) Me_3SiNSO , and (c) Me_3GeNSO

deviations derived from the least-squares analysis, increased to allow for systematic errors; the final least-squares correlation matrix is given in Table 4. The combined molecular-intensity curves (experimental, and weighted-difference) are shown in Figure 2. The final R factor (R_G) was 0.11.

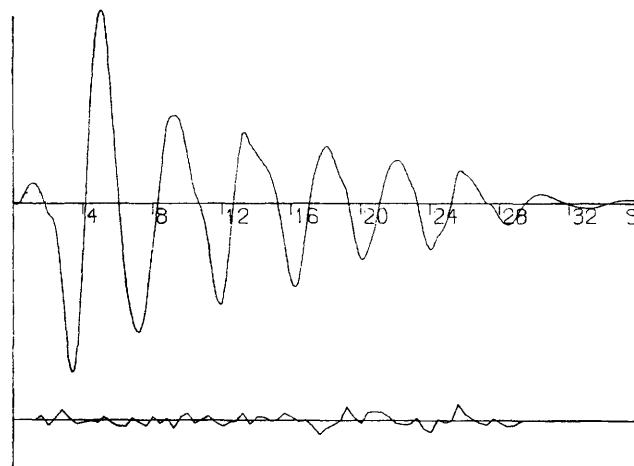


FIGURE 2 Observed and final weighted-difference molecular scattering intensities for SiH_3NSO

The correlation matrix shows that most of the parameters are reasonably well defined, though two pairs of parameters (r_2/r_3 and \angle_2/\angle_3) are strongly correlated. This arises because the five most relevant distances in the determination of these parameters ($r_2, r_3, r_4; d_7, d_8$) give rise to only two peaks in the radial distribution curve (Figure 3), one near 150 pm corresponding to the bonded distances and another near 260 pm corresponding to the non-bonded distances.

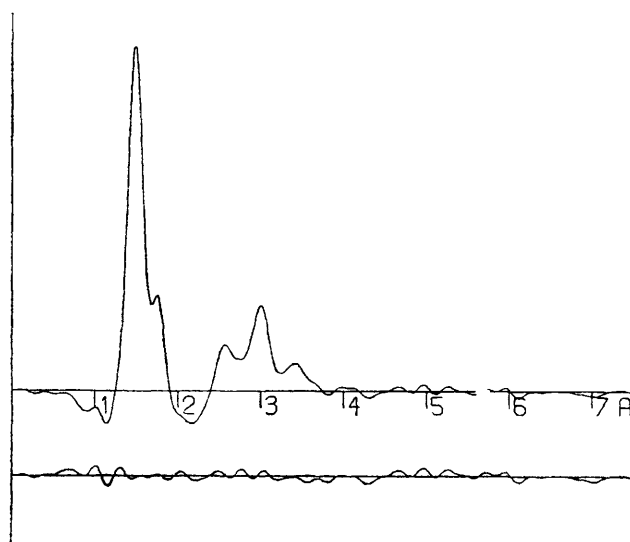


FIGURE 3 Radial distribution curve, $P(r)/r$, for SiH_3NSO . Before Fourier inversion the data were multiplied by $s \exp[-0.0015s^2(z_{\text{Si}} - f_{\text{Si}})(z_{\text{S}} - f_{\text{S}})]$

DISCUSSION

The molecular-structure parameters set out in Table 3 may be compared with those found for the related

TABLE 4
Least-squares correlation matrix for SiH₃NSO multiplied by 100

r_1	r_2	r_3	\angle_1	\angle_2	\angle_3	u_1	u_5	u_6	u_7	k_1	k_2	k_3
100	20	-3	3	14	-14	-8	4	-12	8	-4	21	41
	100	-73	8	14	-16	-19	34	-8	19	75	41	25
		100	-1	-5	6	9	-30	2	-12	-71	-37	-19
			100	21	-33	-6	-3	-30	35	5	5	12
				100	-98	-7	-3	-60	68	7	8	10
					100	9	2	60	-70	-9	-8	-13
						100	-4	8	-4	-5	-16	-2
							100	2	-2	41	24	7
								100	-42	-1	-7	-7
									100	18	11	15
										100	36	14
											100	17
												100

molecules CH₃NSO⁶ and SiH₃NCO.⁵ The structures of methyl- and silyl-sulphinylamines are similar, the only significant differences in the molecular parameters (apart from bond lengths involving C and Si) being a slightly wider bond angle at nitrogen in the silicon compound and the apparent non-planarity of its skeleton. The dihedral angle is not well-defined in either structure, and the apparent difference may well be due to shrinkage effects (vibrational averaging).

The differences in structure between SiH₃NSO and SiH₃NCO are more striking. Apart from the fact that the NSO group is, as expected, bent at S the skeleton is also sharply bent at N in the sulphinylamine. In this respect the structure is more similar to that of silyl azide⁷ than to that of the isocyanate. The other major difference is the significantly greater Si-N bond length (176 pm) in the sulphinylamine, apparently the largest molecular Si-N bond length known. The value for the isocyanate is 170 pm, and that for trisilylamine is 173.4 pm;⁸ the sum of the covalent radii has been estimated as 186 pm.

The increased Si-N bond length and the low bond angle at N may be related, as the resulting Si...S non-bonded distance (300 pm) is close to the estimated sum of the 'hard sphere radii' for these atoms. One could say that either the low bond angle requires that the Si-N bond be long to prevent too close an approach of the Si and S atoms, or that the longer Si-N bond allows bending of the skeleton at N such that the Si...S distance is no longer than 300 pm.

The p.e. spectrum of SiH₃NSO (Figure 1) is extremely similar to that of SiH₃NCO.⁹ Apart from the structural differences discussed above, the major electronic difference between the valence shells of these molecules is that the sulphinylamine has an extra pair of electrons, which may be thought of as forming a 'sulphur lone-pair.' It is of course this extra pair of electrons that is responsible for the non-linearity of the skeleton at S. The absence of any distinct band in the p.e. spectrum related to the extra pair of electrons leads us to suppose that they give rise to a band coincident with one of the other bands, probably that at 11.5 eV. This band we may assign to the sulphur lone-pair and both com-

* Figure 4 shows diagrammatically the correlations between energy levels involved in our discussion; OCS represents a limiting linear system, SO₂ a simple non-linear case. It is of course impossible to label the levels of SiH₃NSO in the absence of molecular symmetry.

ponents of the '2 π ' level that give rise to the single band at 11.1 eV in the spectrum of SiH₃NCO.

In SiH₃NSO some splitting of the π levels might have been expected, as the skeleton is bent at N as well as at S. If such a splitting exists it is small, no more than about 0.3 eV, and obscured by the overlapping sulphur lone-pair band.

The other bands in the spectrum of the sulphinylamine correlate very simply with those found for the isocyanate; the broad band near 13 eV is due to the SiH bonding orbitals derived from Si 3*p*, the band at 15.0 eV is due to the '1 π ' levels (no splitting can be detected), and the weaker band at 16.7 eV is due to the mainly SiH bonding orbital derived from Si 3s.

The photoelectron spectra of Me₃SiNSO and Me₃GeNSO are more complex than that of SiH₃NSO, because the C₃M bonding level near 11.5 eV interacts with the NSO levels in the same region.⁹ In particular a shoulder appears on the low-energy side of the first band. We assign this shoulder to one component of the '2 π ' level perturbed by mixing with the C₃M bonding level. The main band is then due to the other component of '2 π ' and the sulphur lone-pair. The C₃M bonding levels occur at 11.6 eV in each case, and the remainder of the spectra are dominated by strong bands arising from CH bonding levels.

The first u.v. band of SiH₃NSO (284 nm) probably correlates with the 340–260 nm band of SO₂, due to the $a_1 \rightarrow b_1^*$ excitation¹⁰ of an electron from the sulphur lone-pair orbital to the b_1 component of the '3 π ' level. The second, stronger, band of SiH₃NSO (230 nm) may well correlate with the next stronger band of SO₂ between 240 and 180 nm.¹⁰ The origin of this band is not certain, and it seems likely that several transitions are involved, but obvious possibilities include excitation from the a_1 sulphur lone-pair to the anti-bonding a_1^* orbital or from the a_2 component of '2 π ' to the b_1 component of '3 π .' We prefer the former assignment for SiH₃NSO, where the a_1 sulphur lone-pair and '2 π ' levels seem to coincide in energy.*

⁶ B. Beagley, S. J. Chantrell, R. G. Kirby, and D. G. Schmidling, unpublished work.

⁷ E. A. V. Ebsworth and M. J. Mays, *J. Chem. Soc.*, 1964, 3450.

⁸ B. Beagley and A. R. Conrad, *Trans. Faraday Soc.*, 1970, **66**, 2740.

⁹ S. Cradock, E. A. V. Ebsworth, and J. D. Murdoch, *J.C.S. Faraday II*, 1972, 86.

¹⁰ A. D. Walsh, *J. Chem. Soc.*, 1953, 2266.

It then becomes possible to define the positions of the a_1^* and b_1^* levels for SO_2 and the corresponding

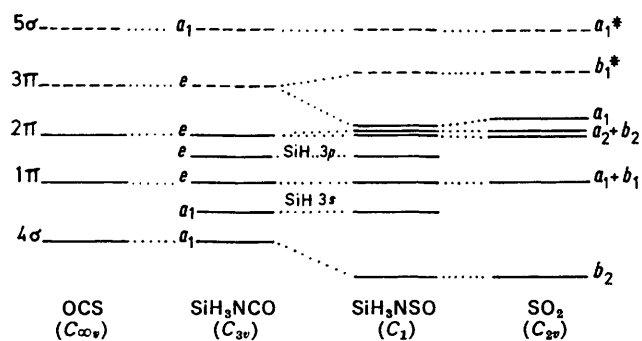


FIGURE 4 Correlation of energy levels

levels for SiH_3NSO . The a_1^* level does not change significantly in energy (SO_2 6.2 eV, SiH_3NSO 6.1 eV binding energy) but the b_1^* level is significantly less

tightly bound in SiH_3NSO (SO_2 8.3 eV, SiH_3NSO 7.1 eV binding energy). This may be due to interaction with the SiH antibonding levels or with Si 3d orbitals.

The mechanism of the decomposition reaction is uncertain, but it is clear that it is essentially a polymerisation, though elimination of silane occurs to a small extent. Internal oxidation-reduction reactions are probably involved. The formation of bromine by reaction of the yellow polymer with HBr is remarkable, as it implies that the polymer retains some oxidising capacity. Further investigation of the natures of the yellow and white solids is clearly needed.

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