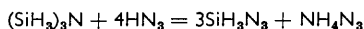


653. *The Preparation and Properties of Silyl Azide.*

By E. A. V. EBSWORTH and M. J. MAYS.

Silyl azide has been obtained by the reaction between a silylamine and hydrazoic acid, and some of its physical properties have been determined. A study of the infrared spectra of silyl azide and [$^2\text{H}_3$]silyl azide shows that the heavy-atom skeleton is non-linear, and thus probably differs in structure from the isoelectronic silyl isocyanate.

MANY silyl compounds have been prepared by passing silyl iodide vapour over the appropriate silver,¹ mercury(II),² or lead³ salt. The reactions are usually exothermic, and the desired products often decompose in the presence of the heavy-metal salts.⁴ For these reasons, yields are often low; we were unable to isolate any silyl azide from the products of small-scale reactions between silyl iodide and the azides of silver or thallium(I), even when the vapour was diluted with nitrogen (which has markedly improved yields in other cases).⁴ It has long been known, however, that the Si-N bonds in silylamines are broken by hydrogen halides, giving an ammonium salt and the appropriate silyl halide;⁵ we have used the analogous reaction between hydrazoic acid and trisilylamine to prepare silyl azide:



The reaction is carried out in ether solution, thus making it unnecessary to use pure hydrazoic acid (which is very dangerous); the reaction system can easily be cooled, and the method seems to be particularly suitable for the preparation of unstable silyl compounds.

Silyl azide, in contrast to the very thermally stable trimethylsilyl azide,⁶ decomposes slowly at room temperature, leaving a colourless solid residue and liberating monosilane. This decomposition makes it almost impossible to obtain equilibrium vapour-pressure data; however, by repeated distillation between each measurement, we have obtained values that are initially reproducible from one sample to another. They lead to a Trouton constant that is normal, and the proton resonance dilution shift is small, indicating that there is little or no association in the liquid phase. The proton chemical shift is in the range characteristic of silyl-nitrogen compounds,⁷ and the ^{29}SiH coupling constant is almost the same as in the isoelectronic silyl isocyanate.⁸

The structure of silyl azide is of particular interest in relation to the molecular geometry of related compounds. The hydrides HN_3 , HNCO , and HNCS are bent, with angles as

¹ MacDiarmid, *J. Inorg. Nuclear Chem.*, 1956, **2**, 88.

² Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.

³ Ebsworth, unpublished observations.

⁴ Ebsworth and Mays, *Spectrochim. Acta*, 1963, **19**, 1127.

⁵ Stock and Somieski, *Ber.*, 1921, **54**, 740.

⁶ Connolly and Urry, *Inorg. Chem.*, 1962, **1**, 718.

⁷ Ebsworth and Mays, *J.*, 1961, 4879.

⁸ Ebsworth and Mays, *J.*, 1962, 4844.

given in Table 1; the alkyl derivatives are also bent. On the other hand, it has been established by microwave spectroscopy¹⁵ that silyl isothiocyanate has a linear heavy-atom skeleton, and is therefore a symmetric-top molecule; in consequence, the "perpendicular" infrared bands near 2200, 950, and 720 cm^{-1} show "strong, weak,

TABLE 1.

Angles in some pseudohalogen derivatives RX.

X	R = H	R = CH ₃
-NNN	112° 39' ± 30' ⁹	120 ± 2° ¹²
-NCO	128 ± 0.5° ¹⁰	125 ± 5° ¹³
-NCS	134° 59' ± 10' ¹¹	142° ¹⁴

weak" rotational detail, with sub-branch separations of 4–7 cm^{-1} .¹⁶ The infrared spectra of silyl isocyanate⁸ and isoselenocyanate¹⁷ also show rotational detail, with roughly the same spacings, suggesting that these molecules, like the isothiocyanate, may well be symmetric tops, with linear heavy-atom skeletons; such rotational detail, however, could conceivably arise from free internal rotation of the SiH₃ group in a bent molecule, and irregular sequences of rotational sub-branches are in fact observed in the infrared spectrum of the bent methyl isothiocyanate.¹⁸ The question of the exact shapes of silyl isocyanate and isoselenocyanate must await the completion of a microwave study; at present, all we can conclude is that these molecules are unlikely to deviate much from C_{3v} symmetry. The difference in shape between silyl and methyl isothiocyanates is usually attributed to (*p*→*d*)π-bonding from nitrogen to silicon.

The infrared spectra of silyl azide and [²H₃]silyl azide have been studied at 250–4000 cm^{-1} under low resolution, and are described below; the frequencies assigned to vibrations of the azide group are much the same as in methyl azide,¹⁹ and we have there-

fore concluded that the silyl compound is unlikely to have the ring structure Si-N $\begin{array}{c} \diagup \text{N} \\ \diagdown \text{N} \end{array}$.

A high-resolution study of the bands associated with SiH and SiD modes, however, revealed no traces of rotational detail; this indicates that the molecules are bent, with substantial barriers to internal rotation, a conclusion that is supported by the preliminary microwave evidence already reported.²⁰ Thus, there is a difference in structure between silyl azide and the isoelectronic silyl isocyanate, which violates the widely-applicable isoelectronic principle. Linnett²¹ has rationalised this difference in terms of his "double quartet" modification to the octet rule. He writes down a number of valence-bond structures for the molecules H₃ANNN and H₃ANCO (where A is C or Si). Then, by arguing that all of those in which nitrogen is given a charge outside the range 1 to -½ can be ignored, he concludes that while four linear forms are the most important for silyl isocyanate, only three bent forms can contribute to the structure of silyl azide. Though the quantitative restriction of charge seems arbitrary, the approach is qualitatively very reasonable. At the same time, since one linear form is "allowed" for methyl isocyanate but none for methyl azide, we might expect a wider angle in the former than in the latter. Though the available structural data for the methyl compounds is not accurate enough

⁹ Amble and Dailey, *J. Chem. Phys.*, 1950, **18**, 1422.

¹⁰ Jones, Shooley, Shulman, and Yost, *J. Chem. Phys.*, 1950, **18**, 990.

¹¹ Kewley, Sastry, and Winnewisser, *J. Mol. Spectroscopy*, 1963, **10**, 418.

¹² Livingstone and Rao, *J. Phys. Chem.*, 1960, **64**, 756.

¹³ Eyster, Gillette, and Brockway, *J. Amer. Chem. Soc.*, 1940, **62**, 3236.

¹⁴ Beard and Dailey, *J. Amer. Chem. Soc.*, 1949, **71**, 929.

¹⁵ Jenkins, Kewley, and Sugden, *Trans. Faraday Soc.*, 1962, **58**, 1284.

¹⁶ Ebsworth, Mould, Taylor, Wilkinson, and Woodward, *Trans. Faraday Soc.*, 1962, **58**, 1069.

¹⁷ Ebsworth and Mays, *J.*, 1963, 3893.

¹⁸ Costoulas and Werner, *Austral. J. Chem.*, 1959, **12**, 601.

¹⁹ Mantica and Zerbi, *Gazzetta*, 1960, **90**, 53.

²⁰ Ebsworth, Jenkins, Mays, and Sugden, *Proc. Chem. Soc.*, 1963, 21.

²¹ Linnett, *Nature*, 1963, **199**, 168.

to establish this difference, the angles in the hydrides fit in with the predicted pattern. It should be noted that since non-linear forms can be written down for both silyl azide and silyl isocyanate, in which ($p \rightarrow d$) π -overlap between silicon and nitrogen is possible, a non-linear skeleton does not establish the absence of ($p \rightarrow d$) π -bonding in these compounds:



Interpretation of the chemical reactions of silyl azide is hampered by the very ready decomposition of the compound, with the formation of monosilane, even in sealed tubes. Sodium azide is formed on alkaline hydrolysis, and may be subsequently oxidised with strongly acidified cerium(IV) sulphate to give a quantitative yield of the nitrogen originally present in the compound. In the presence of boron trifluoride, decomposition to monosilane occurs even at -78° ; this decomposition has not been observed in the reactions between boron trifluoride and other silyl-nitrogen compounds.^{7,21} Silyl fluoride is also formed, however, so that there must be some reaction between silyl azide and boron trifluoride besides the catalysed decomposition. Virtually no nitrogen was evolved when silyl azide was kept with triethylphosphine at room temperature; again, the large proportion of monosilane formed makes it difficult to draw any conclusions about the course of the reaction between the two starting compounds.

EXPERIMENTAL

Preparation.—In a typical experiment, trisilylamine (5.36 mmole) was kept at room temperature (2 hr.) with a slight excess of hydrazoic acid dissolved in di-*n*-butyl ether (1.09M). The reaction products were separated from the solvent by fractional distillation and left to stand at room temperature ($\frac{1}{2}$ hr.) until reaction was complete. *N*-Ethylidisilylamine (1 mmole) was then added, and after $\frac{1}{2}$ hr., a spectroscopic examination showed that reaction of the slight excess of hydrazoic acid with *N*-ethylidisilylamine was complete. By repeated distillation at -78° and condensation at -112° , *silyl azide* (300 mg.) was obtained (Found: H, 4.1; N, 57.1%; *M*, 72.8. $\text{H}_3\text{N}_3\text{Si}$ requires H, 4.1; N, 57.5%; *M*, 73.0). The yield, based on the amount of hydrazoic acid taken, was *ca.* 25%. Silyl azide could not be separated from hydrazoic acid or from trisilylamine by trap-to-trap distillation, but when hydrazoic acid was treated with an excess of *N*-ethylidisilylamine, yields were lower than those obtained by the above method.

Physical Properties.—Silyl azide is a colourless liquid (m. p. $-81.8 \pm 0.5^\circ$). The b. p. (extrapolated over 3°) is $25.8 \pm 1^\circ$; between 0° and the b. p., the vapour pressure is related to the temperature by the expression $\log_{10} p$ (mm.) = $-1459/T + 7.745$, and is 253 mm. at 0° . Over the same range, the latent heat of vaporisation is 6680 ± 100 cal. mole⁻¹, and Trouton's constant is 22.3.

Infrared Spectra.—The infrared spectra (Table 2) of SiH_3N_3 and of SiD_3N_3 [prepared as

TABLE 2.

Infrared frequencies (in cm. ⁻¹) for silyl azide and [² H ₃]silyl azide.					
SiH_3N_3	SiD_3N_3	Assignment	SiH_3N_3	SiD_3N_3	Assignment
3440m	3460m	2170 + 1325	1325s	1324vs	$\nu_s(\text{N}_3)$
3105w		2170 + 945	(1125)w	(1088)m	Disiloxane
	2910w	2172 + 730	945vs		$\delta(\text{SiH}_3)$
2844w	2850w	2170 + 681		848m	$\delta(\text{SiH})$ of residual SiH
2620mw	2630mw	2 × 1325		730vs	$\delta(\text{SiD}_3)$
2170vs	2172vs	$\nu(\text{SiH}), \nu_s(\text{N}_3)$	690s		SiH_3 rock
	1608ms	$\nu_s(\text{SiD})$	681s	687s	$\delta(\text{N}_3)$
	1582vs	$\nu_s(\text{SiD})$	578s	568s	$\nu(\text{Si-N})$
1481m	1486m	(?) 1325 + $\delta(\text{SiN}_3)$		522m	SiD_3 rock
1410mw	1421mw				
1370mw			2 × 690		

described above, but using $(\text{SiD}_3)_3\text{N}$ instead of $(\text{SiH}_3)_3\text{N}$] were recorded by means of a Perkin-Elmer model 21 double-beam spectrometer, fitted with either a sodium chloride, a potassium bromide, or a caesium bromide prism; the samples were contained in 100-mm. cells, and were

studied in the vapour phase. The bands at 2170 and 945 cm^{-1} (SiH_3N_3) and at 1600 and 700 cm^{-1} (SiD_3N_3) were also examined under a resolution of 0.4 cm^{-1} using a Grubb-Parsons G.S.2 grating instrument.

Although the highest symmetry that the molecule can possess, if the heavy-atom skeleton is non-linear, is C_s , the most obvious mode of assignment does not require any of the observed bands to be assigned to "in-plane" and "out-of-plane" vibrations. However, both in silyl azide and in $[\text{D}_3\text{H}_3]$ silyl azide, the SiH_3 -rocking mode, which is the most likely to be split, is not only broad but is overlapped by at least one other band, so that any small splitting might well have escaped observation.

The very strong band at 2170 cm^{-1} for the SiH_3 -compound is still very strong in the spectrum of the deuterated derivative. In trimethylsilyl azide, the high-frequency stretching mode of the azide group occurs at 2180 cm^{-1} ,⁶ and the band at 2170 cm^{-1} in the spectrum of silyl azide must be due to both this mode and the (SiH_3^-) stretching vibrations. The strong band at 1325 cm^{-1} , which is not shifted appreciably on deuteration, is assigned to the low-frequency stretching mode of the azide group; the corresponding vibration of trimethylsilyl azide occurs at 1320 cm^{-1} . The band at 945 cm^{-1} in the spectrum of silyl azide represents the (SiH_3^-) deformation modes, which occur at *ca.* 950 cm^{-1} in other SiH_3N -compounds.^{4,15}

There are two bands in the spectrum of $[\text{D}_3\text{H}_3]$ silyl azide in the region near 700 cm^{-1} . One, at 730 cm^{-1} , is assigned to the (SiD_3^-) deformation modes, and the other, at 687 cm^{-1} , to the skeletal deformation mode primarily associated with deformation of the linear (N_3) group. The frequency is quite close to that (660 cm^{-1}) of one of the skeletal deformation modes of methyl azide.¹⁸ The band at about 690 cm^{-1} in the spectrum of silyl azide has a complex envelope, and must represent both the skeletal deformation mode and the rocking vibration of the (SiH_3^-) group. The band at 578 cm^{-1} , which is shifted only to 568 cm^{-1} on deuteration, is assigned to the skeletal stretching mode primarily associated with the (Si-N) bond. Satisfactory assignments can be found for all the other bands as overtones or combinations, except for those at 1481 and 1410 cm^{-1} , which seem little affected by deuteration; the tentative assignments for these lead to bending frequencies of the SiN_3 -system of *ca.* 160 and *ca.* 90 cm^{-1} , but there is no other evidence to support these suggested values.

Nuclear Magnetic Resonance Spectrum.—This was recorded with a Varian Associates V 4300B spectrometer with flux-stabiliser and sample-spinning, operating at 40 Mc./sec. The proton resonance spectrum of the compound dissolved in cyclohexane consisted of the expected single sharp peak with satellites due to $^{29}\text{SiH}_3$ molecules; measurements on 90 and 5% solutions, relative to cyclohexane as solvent and internal standard, give (by extrapolation to infinite dilution) $\tau = 5.51 \pm 0.01$ p.p.m. and $J(^{29}\text{SiH}) = 230.3 \pm 0.5$ c./sec.

Ultraviolet Spectrum.—The ultraviolet spectrum of the vapour gave one peak, with $\lambda_{\text{max.}} = 211 \text{ m}\mu$ and $\log_{10} \epsilon = 2.5$.

Stability.—Pure samples of liquid silyl azide liberated monosilane slowly at room temperature. It was thought possible that the decomposition might be caused by the presence of catalytic amounts of *N*-ethyl-disilylamine from the preparative reaction, but no monosilane was liberated when small quantities of the amine were added to a sample of disilylcarbodi-imide.

Reactions.—(a) *Hydrolysis.* The following reactions were used to analyse the compound. (i) Silyl azide (0.426 mmole) was shaken vigorously with 40% sodium hydroxide solution (15 ml.); non-condensable gas (1.263 mmole) was liberated. The molar ratio (gas evolved) : (silyl azide taken) was 2.97 : 1. (ii) Silyl azide (0.821 mmole) was similarly hydrolysed: strongly acidified cerium(IV) sulphate was added to the hydrolysate, whereupon more non-condensable gas (1.221 mmole) was evolved. The molar ratio in this case was 1.49 : 1.

(b) *With boron trifluoride.* Silyl azide (0.419 mmole) was sealed in a glass tube with boron trifluoride (1.61 mmole) and kept at -78° (18 hr.). The volatile material (1.516 mmole) was identified spectroscopically as a mixture of boron trifluoride, monosilane, and silyl fluoride; no unchanged silyl azide was recovered. The volatile material could not be separated into its components by fractional distillation, and attempts to determine its composition by quantitative analysis were unsuccessful. A ring of white solid remained in the reaction tube; this became pink on warming to room temperature, and evolved trace amounts of boron trifluoride and silyl fluoride.

(c) *With triethylphosphine.* Triethylphosphine (0.318 mmole) and silyl azide (0.321 mmole) were kept at room temperature ($\frac{1}{2}$ hr.). A trace (*ca.* 0.02 mmole) of non-condensable gas was

evolved, and monosilane [0.193 mmole (Found: *M*, 33. Calc.: *M*, 32)] was collected at -130° . At room temperature, triethylphosphine (0.156 mmole) was recovered (Found: *M*, 120; v. p. at 0° , 3.3 mm. Calc. for $C_6H_{15}P$: *M*, 118; v. p. at 0° , 3.6 mm.). No silyl azide was recovered among the products of the reaction.

(d) *With silver salts.* These reactions were carried out on a very small scale. When silyl azide was passed as vapour over a large excess of silver chloride and (in a subsequent experiment) silver thiocyanate, trace quantities of silyl chloride and silyl isothiocyanate, respectively, were identified spectroscopically among the products, though in both cases the major part of the silyl azide remained unconverted.

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UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD, CAMBRIDGE.

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