Trimethylsilyl Isocyanide

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THERE has been considerable speculation, but little experimental evidence concerning the existence of trimethylsilyl isocyanide.[1-3] The predominant species in the liquid prepared from the reaction of Me_3SiBr with AgCN (referred to as $Me_3Si[CN]$) is the cyanide,[4] but a variable-temperature study of the i.r. spectrum of the liquid has indicated that it contains a small amount (*ca.* 10% at room temperature) of the isocyanide in labile equilibrium with the cyanide.[5] The isocyanide was identified only from a weak i.r. band near 2100 cm.$^{-1}$, which was assigned to the NC stretch. It has been suggested that this band may be a combination tone in the cyanide,[2] or even a "hot band" associated with the CN stretch in the cyanide.[3] We find, however, that this band comes from a second species in equilibrium with the cyanide, and which is almost certainly the isocyanide (Me_3SiNC). This is believed to be the first definitive evidence for a simple inorganic isocyanide.

Pure $Me_3Si[CN]$ was introduced into a Perkin-Elmer variable path-length 10 m. gas cell, fitted into a Perkin-Elmer 225 spectrophotometer, after the cell had been thoroughly evacuated and dried. A series of spectra were recorded at room temperature in the range 1850—2250 cm.$^{-1}$, with gradually increasing and then decreasing sample pressure (see Figure). At low pressure (spectrum A) only the weak 1906, 1966, 2030, and 2128 cm.$^{-1}$ bands (which are combination tones in Me_3SiCN) and the strong 2198 cm.$^{-1}$ band (the CN stretch in Me_3SiCN) were observed. When the pressure was increased a band at 2095 cm.$^{-1}$ was observed to increase markedly in intensity relative to the combination tones (spectra B and C). On reducing the pressure the relative intensities of the 2095 cm.$^{-1}$ band and the combination tones remained approximately the same; in the final spectrum D it is seen that the intensity of the 2095 cm.$^{-1}$ band relative to that at 2198 cm.$^{-1}$ has increased significantly when compared with the initial spectrum A. This nonreversible change of relative intensities (which shows that the 2095 cm.$^{-1}$ band is not pressure-induced) was reproduced several times using different samples in different spectrophotometers. It shows that the 2095 cm.$^{-1}$ band cannot be a combination tone or a "hot band", but it must come from a second species in $Me_3Si[CN]$ which appears to be preferentially adsorbed on the interior optics or walls of the gas cell. The variable-temperature study of $Me_3Si[CN]$ has shown that this second form is in labile equilibrium with the cyanide.[5]

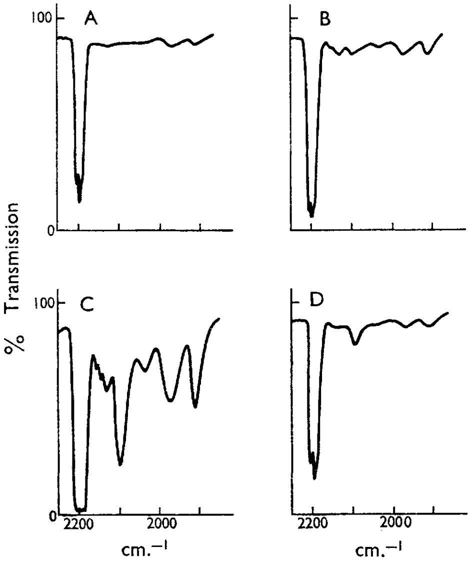

FIGURE. *The i.r. spectrum of* $Me_3Si[CN]$ *vapour. Path length,* 1·25 *m.; spectral slit width,* 1·3 *cm.*$^{-1}$*; successive vapour pressures*: A 2, B 4, C 12, *and* D 2 *torr*

We have recorded the i.r. spectra of $Me_3Si[CN]$ vapour prepared from both ^{13}C- and ^{15}N-enriched AgCN in order to confirm that the 2095 cm.$^{-1}$ band is not a combination tone, and to determine its origin. Our results are summarized in the Table. The large shift of the 2095 cm.$^{-1}$ band on ^{13}C- and on ^{15}N-isotopic substitution shows that it must be a CN stretch of an isocyanide group. The possibility that the 2095 cm.$^{-1}$ band comes from HCN is eliminated by the absence of an i.r. band near 3312 cm.$^{-1}$. A simple calculation of the ^{13}C and ^{15}N isotopic shifts of the [CN] stretch in Me_3SiCN, assuming a triatomic SiCN model with a harmonic valence force field and no interaction force constants, gives very satisfactory agreement with the observed shifts in the Table. A similar calculation for a SiNC model gives isotopic shifts that agree very well with those observed for the 2095 cm.$^{-1}$ band in the Table, thus providing strong evidence that the 2095 cm.$^{-1}$ band is the NC stretch in Me_3SiNC.

TABLE

			^{13}C shift (cm.$^{-1}$)		^{15}N shift (cm.$^{-1}$)	
Molecule	Fundamental	cm.$^{-1}$	calc.	obs.	calc.	obs.
Me_3SiCN (vapour)	CN stretch	2198	-51	-51	-30	-31
Me_3SiNC (vapour)	NC stretch	2095	-40	-43	-36	-35

The temperature dependence of the absorbance maxima of the 2190 and 2095 cm.$^{-1}$ bands in liquid $Me_3Si[CN]$ has been re-examined. If it is assumed that they obey the Beer-Lambert law, and that $\Delta G^\circ = - RT \ln Kp$, then a plot of $1/T$ against $\ln(A_{2190}/A_{2100})$ gives $\Delta H^\circ = 4{\cdot}1 \pm 0{\cdot}2$ kcal./mole for the reaction $Me_3SiCN \rightleftharpoons Me_3SiNC$. Using an estimate of $\Delta S^\circ = 0{\cdot}7$ e.u. for this reaction, we find that $Me_3Si[CN]$ at 25° contains only 0·2% (mole/mole) of Me_3SiNC.

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[1] C. Eaborn, "Organosilicon Compounds", Butterworths, London, 1960.
[2] E. A. V. Ebsworth, "Volatile Silicon Compounds", Pergamon, London, 1963.
[3] D. F. Shriver, *Structure and Bonding*, 1966, **1**, 32.
[4] H. R. Linton and E. R. Nixon, *J. Chem. Phys.*, 1958, **28**, 990.
[5] T. A. Bither, W. H. Knoth, R. V. Lindsey, and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1958, **80**, 4141.