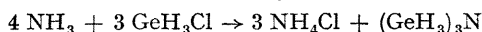


Trigermylamine

By D. W. H. RANKIN

(University Chemical Laboratory, Lensfield Road, Cambridge)

SINCE the preparation of trisilylamine,¹ a number of unsuccessful attempts have been made to prepare the analogous germyl compound.² The heavy atoms in trisilylamine are coplanar;³ this is said to indicate the existence of π -bonding between the nitrogen lone-pair electrons and the silicon d -orbitals. The possibility of similar π -bonding to germanium has increased the interest in trigermylamine, which has now been prepared (ca. 40%) by the gas-phase reaction of germyl chloride and ammonia, followed by immediate removal of the



product from the reaction vessel. If the gases are not mixed in the correct proportions, the trigermylamine produced is contaminated with one of the starting materials, but otherwise it is pure. The compound is also formed in the exchange reaction of germyl fluoride and trisilylamine, but it has not been isolated from the products.

The new compound was identified by its molecular weight, analysis (cleavage with HCl) and ¹H n.m.r. and i.r. spectroscopy: n.m.r. (100 MHz, Me₄Si, room temp.) τ 5.09s. Exchange with (SiH₃)₃¹⁵N gave $J(^{15}\text{NGeH})$ 5 Hz.

In the i.r. spectrum of solid trigermylamine at -196° (Table), the band at 639 cm.⁻¹ is rather stronger than in the spectra of other similar molecules.⁴ It is possible that the Ge₃N asymmetric stretch is coincident with one of the GeH₃ rocking modes. The presence of a band at 367 cm.⁻¹ is of great interest, since it is in the region where the Ge₃N symmetric stretching mode is expected. As this mode is

i.r.-inactive in molecules with a planar heavy-atom skeleton, it seems that trigermylamine, unlike trisilylamine, is pyramidal. However, this does not necessarily rule out the possibility of ($p \rightarrow d$) π -bonding.⁵ The absence of this band in the i.r. spectra of similar molecules has caused confusion in the past,⁶ but its presence invariably implies non-planarity.

Trigermylamine is very unstable, as evidenced by the rapid thermal decomposition of the solid (the gas phase decomposes less rapidly) to give ammonia and GeH₂ polymer with a little monogermene. It is rapidly hydrolysed by water to give digermoxane.

Infrared spectrum of solid trigermylamine

Frequency, cm. ⁻¹	Tentative assignment
2074s, sh	} Ge-H stretch
2047s	
871mw	} GeH ₃ deformation
851m	
780vs	
639ms	Ge ₃ N asymm. stretch
581lw, br	} GeH ₃ rocking
367m, v br	

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