Gas Phase Structures of Three Germyl Pseudohalides

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Summary Germyl azide, germyl isocyanate and digermyl carbodi-imide have been found by electron diffraction to have non-linear skeletons in the gas phase.

MICROWAVE and vibrational spectroscopy have shown that silyl isocyanate has a linear heavy atom skeleton,[1,2] whereas that of silyl azide is bent.[3] Vibrational spectroscopy suggests that neither of the equivalent germyl compounds[4,5] nor digermyl carbodi-imide[6] is a symmetric top, and in the case of germyl isocyanate this is confirmed by a preliminary microwave study.[7] Examination of these three germyl compounds by electron diffraction confirms that they all have non-linear skeletons and shows that in germyl azide the angle at nitrogen is much smaller than in the other two compounds.

Samples of germyl azide and digermyl carbodi-imide were prepared by the exchange reactions of germyl fluoride with the corresponding trimethylsilyl derivatives.[8] Germyl isocyanate was prepared by the reaction of germyl bromide with silver cyanate.[9] Compounds were purified by fractional condensation *in vacuo*, and purities were checked spectroscopically. Electron diffraction data were collected photographically and processed using established procedures and programs.[10,11]

In the radial distribution curves of the compounds (Figure) the strongest peaks are those due (in $GeH_3NXY\cdots$) to the Ge–N, Ge···X, and Ge···Y atom pairs, with other important contributions from N–X, X–Y, Ge–H, and N···Y, and also, in the carbodi-imide, from Ge···Ge. In most cases these important peaks are isolated from each other, and so the heavy atom structures of the molecules are well determined. Preliminary least-squares refinements (assuming local C_{3v} symmetry of the $NGeH_3$ groups and linearity of the NXY groups) gave the parameters listed in the Table. GeNX bending frequencies are also given. At this stage R factors were 0·18 (GeH_3N_3), 0·13 (GeH_3NCO), and 0·12 ($GeH_3NCNGeH_3$).

These results reinforce the spectroscopic evidence that these molecules do not have linear skeletons, unless exceptionally large shrinkage corrections are necessary. In the difluorophosphino-pseudohalides the corrected angles are only about 4° wider than the uncorrected ones.[12] As the GeNC bending frequency in germyl isocyanate is very similar to the PNC bending frequency in difluoroisocyanatophosphine, the shrinkage corrections for the two compounds are probably about the same. The bending frequencies given in the Table suggest that shrinkages in the three germyl pseudohalides are of roughly similar magnitude.

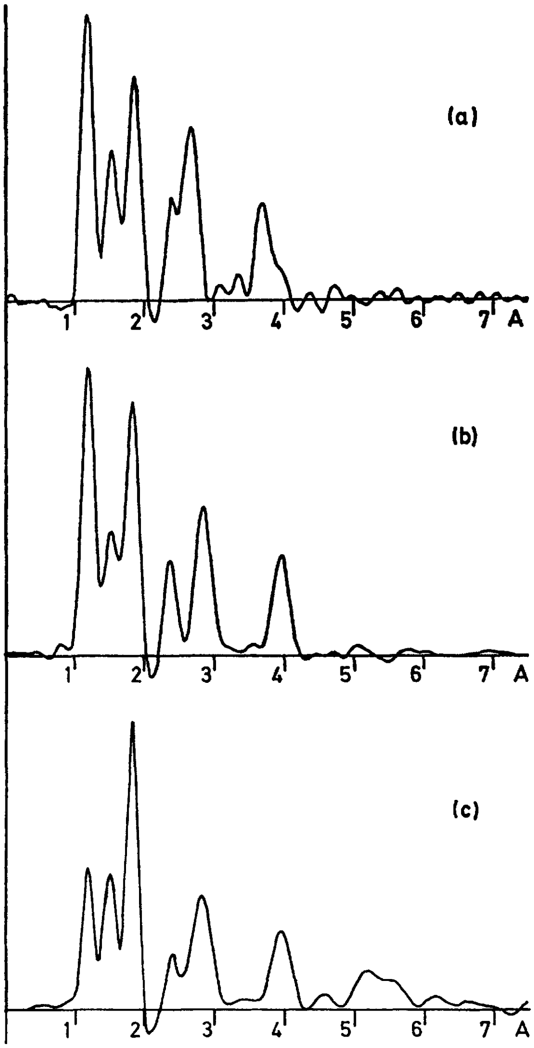


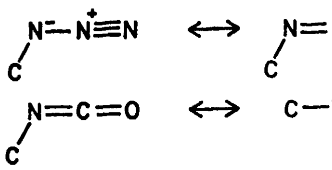
Figure. *Radial distribution curve,* P(r)/r, *for* (a) *germyl azide,* (b) *germyl isocyanate, and* (c) *digermyl carbodi-imide. Before Fourier inversion the data were multiplied by* s. $\exp(-x\,s^2)/(z_{Ge}-f_{Ge})(z_N-f_N)$, *where* x *is* (a) 0·002, (b) 0·0035, *and* (c) 0·0025. *The principal peaks, represent* N–X *and* X–Y, Ge–H, Ge–N, N · · · Y, Ge · · · X, Ge · · · Y, *and* Ge · · · Ge *atom pairs, in order of increasing inter-atomic separation.*

Table. *Molecular parameters and deformation frequencies*[a]

	GeH_3N_3	GeH_3NCO	$GeH_3NCNGeH_3$
r (GeN)	1·845(6)	1·831(4)	1·813(5)
r (NX)	1·250(9)	1·190(7)	1·184(8)
r (XY)	1·140(7)	1·182(7)	—
r (GeH)	1·533(7)	1·532(6)	1·505(9)
∠ (GeNX)	119(2)	141·3(4)	138(1)
Dihedral angle[b]	—	—	75(5)
δ (GeNX)	150[c]	115[d]	120, 170[e]

[a] Distances in Å, angles in degrees, frequencies in cm^{-1}. [b] Defined to be zero for the *cis*-configuration. [c] Ref. 5. [d] Ref 4. [e] Ref. 6.

Thus, so far as angles at nitrogen are concerned, the germyl pseudohalides resemble their silyl analogues much less closely than their methyl analogues,[13] the structures of which have been rationalised in terms of simple valence bond "resonance hybrids".[14]



However, although the bond angles in the germyl pseudohalides do not provide evidence for Ge–N π-interactions, the Ge–N bond lengths do. Estimated Ge–N bond lengths lie between 1·876 and 1·89 Å,[15] considerably greater than those reported here, even allowing for the different hybridisation of nitrogen orbitals.

Thus, the evidence for multiple bonding, involving germanium d orbitals (or GeH antibonding orbitals), is much less pronounced in these pseudohalides than in trigermylamine[15] and in the corresponding silyl compounds, which have wide valence angles at nitrogen as well as short M–N bonds.

The dihedral angle in the carbodi-imide suggests that this compound is structurally like an allene.

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