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The Non-linear Skeleton and Constitution of GeH_3NCO

By JAMES E. GRIFFITHS and ALEXANDER L. BEACH
(Bell Telephone Laboratories Incorporated, Murray Hill, New Jersey, U.S.A.)

THE product of the reaction of germyl bromide with silver cyanate[1] offers an opportunity of studying in greater detail the bonding situation in a compound containing a third-row element linked to a first-row element. Infrared spectra of the product in the vapour and liquid states were examined using Beckman IR–11 and IR–12 spectrophotometers (33—4000 cm.$^{-1}$). Cell windows of KBr, CsI, and high-density polyethylene were used.

The presence of absorption bands at 2271 cm.$^{-1}$ [v.s.; ν_1 (antisym. N=C=O stretch) *cf.* CH_3NCO,[2] 2232 cm.$^{-1}$; $Ge(NCO)_4$,[3] 2304 and 2247 cm.$^{-1}$), at 1420·6 cm.$^{-1}$ [weak, ν_3 (sym. N=C=O stretch) *cf.* CH_3NCO,[2] 1412 cm.$^{-1}$; $Ge(NCO)_4$,[3] 1432 cm.$^{-1}$] and at 495 cm.$^{-1}$ (strong, ν_3 (Ge–N stretch) *cf.* $Ge(NCO)_4$,[3] 492 cm.$^{-1}$) is conclusive evidence that the isocyanate is the major chemical species formed in the reaction, but this does not preclude the presence of the normal cyanate. Indeed a weak band at 2374 cm.$^{-1}$ almost certainly arises from a few per cent of the normal cyanate (it does not shift in frequency or relative intensity upon deuteration, and cannot represent a combination involving any of the GeH_3 fundamentals). The sum-band $2271 + 115 = 2386$ cm.$^{-1}$ is a reasonable fit, if one assumes that the (observed − calculated) frequency discrepancy arises from anharmonicity, but the absence of the corresponding difference-band at 2156 cm.$^{-1}$ eliminates this possibility. The Ge–O and O–C stretching fundamentals, which are expected to be weaker are not observed with certainty. The first is probably masked by the GeH_3 deformation modes while the O–C stretch might be assigned to a weak band at 1284 cm.$^{-1}$ This seems rather high but it cannot be accounted for in another way.

Observations of the absorption band contours of two fundamentals lead us to believe that the Ge–N=C=O skeleton is not linear as is the case in SiH_3NCS.[4] If the heavy atoms are arranged in a linear configuration all of the symmetric modes would produce typical parallel-type band contours in which *P*- and *R*-branches would be prominent and the *Q*-branch is expected to be rather weak. Antisymmetric (to the threefold axis) fundamentals, however, are expected to be broad and featureless although some might be expected to show resolvable rotational structure (ζ_i is small or negative) and others may even have band contours approaching that of a parallel type fundamental (ζ_i is large and positive). As the linear structure is bent, the point group goes from C_{3v} to C_s and the degenerate fundamentals are expected to split into A' and A'' species. In addition, among the symmetric fundamentals, the dipole moment change may no longer coincide

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[3] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, 1961, **17**, 977.

[4] E. A. V. Ebsworth, R. Mould, R. Taylor, G. R. Wilkinson, and L. A. Woodward, *Trans. Faraday Soc.*, 1962, **58**, 35.

with the figure axis and consequently hybrid band contours consisting of parallel and perpendicular components may result. The relative intensity of each component will vary of course depending upon the fundamental mode in question. In particular, the mode assigned as the pseudo-symmetric N=C=O stretch has such a hybrid contour; the centres of each component are separated by about 32 cm.$^{-1}$ (the separation[5] in HNCO is about 44 cm.$^{-1}$). The possibility that the second component arises from a combination has also been considered and rejected. It does not shift on deuteration nor does it fit a combination involving the fundamentals of the isocyanate group.

The only perpendicular fundamental (under C_{3v}) which is obviously split is assigned as the GeH_3 rocking mode. The resulting bands occur at 667·5 (A') and at 656 (A'') cm.$^{-1}$ Neither of the features of the spectrum described above occur in the spectrum of the silyl isothiocyanate molecule, a fact which lends confidence to our interpretation. All of the other fundamentals in GeH_3NCO and GeD_3NCO were also located and assigned in terms of a pseudo-C_{3v} structure. The isotope product rule ratios agree satisfactorily with those calculated. The results, therefore, reaffirm previous conclusions[6] that $p\pi$–$d\pi$ bonding, if present, is significantly weaker in compounds of germanium than in those of silicon.

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