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# The Crystal Structure of Trimethylcyanogermane

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Trimethylcyanogermane forms orthorhombic crystals in space group $Pmn2_1$ with $a = 7.69$, $b = 7.00$, $c = 6.70$ A, with two molecules per unit cell. The molecules have $C_{3v}$ symmetry within experimental error with Ge–C = 1.98 ± 0.04 (average for methyl carbon) and 1.98 ± 0.06 (for cyanide carbon), and C–N = 1.15 ± 0.13 A. The C–Ge–C bond angle between methyl groups is 114.8 ± 1.4° (average). The shortest intermolecular contact is between N and Ge, but the distance, 3.57 A, is that expected for a normal van der Waals interaction.

As part of a study of the intermolecular interactions between cyanide nitrogen atoms and potential Lewis acids, and, in particular, for comparison with $(CH_3)_3SnCN$, we have determined the structure of $(CH_3)_3GeCN$. The higher melting point of the cyanide (38°) compared to those of the chloride (−13°) and bromide (−25°) suggests that there might be an intermolecular interaction in the solid somewhat stronger than a van der Waals interaction. The occurrence of two peaks in the CN region of the infrared spectrum in solution[1] suggests that there is an equilibrium between the cyanide and the isocyanide, which provides a further interest in determining the structure.

## Experimental Section

**Preparation and Properties.**—Trimethylcyanogermane was prepared in three steps from germanium tetrachloride. Germanium tetrachloride was treated with methylmagnesium iodide in *n*-butyl ether to give tetramethylgermanium.[2] Tetramethylgermanium was treated with iodine in benzene to give trimethylgermanium iodide.[1] Trimethylgermanium iodide was treated with silver cyanide in benzene to give trimethylcyanogermane,[1] which was separated by distillation. A sample in a nitrogen-filled, sealed tube melted at 38–38.5°; the infrared spectrum in chloroform solution or in a halocarbon mull showed two peaks in the cyanide–isocyanide stretching region, at 2085 and 2185 $cm^{-1}$, the latter four to five times as intense as the former. This is in agreement with the reported properties.[1]

Colorless, needlelike crystals were grown by vacuum sublimation. Since the crystals decompose in air, presumably owing to hydrolysis, they were placed in capillaries for the X-ray examination. As the crystals deformed easily, great care had to be exercised in placing them in the capillaries; otherwise, the X-ray pattern showed streaky spots indicative of deformation.

**Space Group and Unit Cell.**—Oscillation and Weissenberg photographs[3] were taken with Cu Kα (λ 1.5418 A) and Mo Kα (λ 0.7107 A) radiation for rotation about the needle axis (*c* axis). The crystals were orthorhombic with $a = 7.69 \pm 0.01$, $b = 7.00 \pm 0.01$, and $c = 6.70 \pm 0.01$ A. If two molecules per unit cell were assumed, the molecular volume, 180.3 $A^3$, was the same as that of trimethylcyanostannane,[4] 180.5 $A^3$, indicating a less efficient packing in the germanium compound. The calculated density is 1.323 ± 0.003 g/cc. The only systematic extinctions were for $h0l$, $h + l$ odd, indicating $Pmn2_1$ or Pmnm to be the space group. The latter would require a structure similar to $(CH_3)_3SnCN$ with planar $(CH_3)_3Ge$ groups and disordered CN groups, while the former would allow tetrahedral molecules. The crystals gave a positive test for pyroelectricity when the spoon test described by Bunn[5] was used, so the correct space group must be $Pmn2_1$.

Three-dimensional Weissenberg film data were collected for the $hk0$–$hk5$ layers using Mo Kα radiation. The crystal was a needle with cross section 0.1 × 0.2 mm. There were 169 independent reflections of measurable intensity and 36 more reflections, too weak to observe, in the same region of reciprocal space. The latter reflections were included in the eventual refinement with an intensity equal to half the minimum observable intensity. Oscillation photographs were used to provide an initial correlation of the layers. All intensities were measured by visual comparison to a series of timed exposures of a selected reflection. The usual Lorentz and polarization corrections were made. Absorption corrections were made assuming that the crystal was a cylinder of diameter 0.14 mm ($\mu = 43.7\ cm^{-1}$).

## Determination of the Structure

The calculations described below were made on the Control Data 1604 computer of the Numerical Analysis Center of the University of Minnesota. Many of the initial calculations were done using programs prepared by the Princeton University crystallography group. The final refinement was done using programs prepared by L. W. Finger of the University of Minnesota Geology Department.

**Trial Structure.**—The germanium atoms were located from a three-dimensional Patterson map. They, alone, gave $R = 0.23$ and were used as the basis of a three-dimensional Fourier map. The *x* and *y* coordinates of the carbon and nitrogen atoms were clearly indicated, but the peaks were all elongated (but not split into two peaks) in the *z* direction since the germanium atoms alone had a center of symmetry while the light atoms did not. The *z* coordinates calculated on the assumption that the molecule was tetrahedral were consistent with the Fourier map and were used as the starting point for the refinement.

**Refinement.**—The structure was refined by a full-matrix, least-squares fit to the function $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = {}^1/_2$ for unobserved reflections, $w = 1$ for $F_o < 20$, and $w = (20/F_o)^4$ for $F_o > 20$. After the initial refinement, a comparison of the observed and calculated structure factors indicated that the correlation factors between the various layers were

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[1] D. Seyferth and N. Kahlen, *J. Org. Chem.*, **25**, 809 (1960).

[2] B. M. Gladshtein, V. V. Rode, and L. F. Soborovskii, *J. Gen. Chem. USSR*, **29**, 2120 (1959).

[3] It was not possible to take precession photographs at room temperature since the crystals invariably sublimed in the larger X-ray beam of the precession camera.

[4] E. O. Schlemper and D. Britton, *Inorg. Chem.*, **5**, 507 (1966).

[5] C. W. Bunn, "Chemical Crystallography," 2nd ed, Oxford University Press, London, 1961, p 321.

Table I

Final Parameters for $(CH_3)_3GeCN$

| | | $x$ | $y$ | $z$ | $\beta_{11}$[a] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Ge | (2a) | 0 | 0.1912 (4) | (0.2500) | 0.0331 (7) | 0.0342 (8) | 0.0314 (10) | 0 | 0 | −0.0054 (41) |
| $C_1$ | (2a) | 0 | −0.084 (5) | 0.178 (8) | 0.042 (8) | 0.036 (7) | 0.090 (36) | 0 | 0 | 0.006 (12) |
| $C_2$ | (4b) | 0.217 (4) | 0.326 (4) | 0.184 (4) | 0.050 (7) | 0.055 (7) | 0.059 (18) | −0.015 (5) | −0.006 (6) | 0.022 (9) |
| $C_3$ | (2a) | 0 | 0.191 (6) | 0.546 (9) | 0.021 (6) | 0.044 (10) | 0.077 (25) | 0 | 0 | 0.024 (16) |
| N | (2a) | 0 | 0.180 (6) | 0.717 (19) | 0.049 (8) | 0.071 (10) | 0.028 (38) | 0 | 0 | 0.051 (20) |

[a] Isotropic temperature parameters from the last cycle in which the atom was isotropic are, in order: 6.72, 8.8, 10.8, 8.8, 11.0. The anisotropic temperature factors are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hk + 2\beta_{23}kl)]$.

Table II

Observed and Calculated Structure Factors

| H | K | L | OBS | CALC | ALPHA |
|---|---|---|---|---|---|
| 0 | 2 | 0 | 51.1 | 51.2 | -180.0 |
| 0 | 3 | 0 | 32.5 | 33.4 | -180.0 |
| 0 | 4 | 0* | 2.7 | .7 | -180.0 |
| 0 | 5 | 0 | 15.1 | 15.7 | .0 |
| 0 | 6 | 0 | 6.2 | 7.2 | -.0 |
| 0 | 7 | 0* | 3.8 | 4.0 | -180.0 |
| 1 | 1 | 0 | 61.8 | 69.1 | -270.0 |
| 1 | 2 | 0 | 32.3 | 32.6 | -270.0 |
| 1 | 3 | 0 | 23.9 | 22.8 | -90.0 |
| 1 | 4 | 0 | 29.8 | 31.1 | -90.0 |
| 1 | 5 | 0 | 5.7 | 6.7 | -90.0 |
| 1 | 6 | 0 | 10.5 | 9.0 | -270.0 |
| 1 | 7 | 0 | 5.4 | 5.6 | -270.0 |
| 2 | 0 | 0 | 60.4 | 61.4 | .0 |
| 2 | 1 | 0 | 40.5 | 34.7 | .0 |
| 2 | 2 | 0 | 29.6 | 28.8 | -180.0 |
| 2 | 3 | 0 | 37.9 | 39.4 | -180.0 |
| 2 | 4 | 0* | 2.9 | 1.5 | .0 |
| 2 | 5 | 0 | 15.7 | 15.9 | .0 |
| 2 | 6 | 0* | 3.6 | 4.5 | .0 |
| 2 | 7 | 0* | 3.9 | 3.3 | -180.0 |
| 3 | 1 | 0 | 40.3 | 37.4 | -270.0 |
| 3 | 2 | 0 | 27.7 | 27.1 | -270.0 |
| 3 | 3 | 0 | 15.3 | 15.9 | -90.0 |
| 3 | 4 | 0 | 24.8 | 23.2 | -90.0 |
| 3 | 5 | 0* | 3.4 | 3.4 | -90.0 |
| 3 | 6 | 0 | 6.0 | 6.3 | -270.0 |
| 4 | 0 | 0 | 42.2 | 41.5 | .0 |
| 4 | 1 | 0 | 13.3 | 13.4 | .0 |
| 4 | 2 | 0 | 22.1 | 21.5 | -180.0 |
| 4 | 3 | 0 | 18.8 | 17.9 | -180.0 |
| 4 | 4 | 0* | 3.2 | .8 | -.0 |
| 4 | 5 | 0 | 8.5 | 8.3 | .0 |
| 5 | 1 | 0 | 21.0 | 21.5 | -270.0 |
| 5 | 2 | 0 | 9.1 | 10.1 | -270.0 |
| 5 | 3 | 0 | 9.8 | 7.3 | -90.0 |
| 5 | 4 | 0 | 10.5 | 10.5 | -90.0 |
| 6 | 0 | 0 | 14.5 | 14.9 | .0 |
| 6 | 1 | 0 | 4.7 | 5.8 | .0 |
| 6 | 2 | 0 | 7.2 | 7.9 | -180.0 |
| 6 | 3 | 0 | 7.3 | 8.7 | -180.0 |
| 7 | 1 | 0 | 6.4 | 6.9 | -270.0 |
| 8 | 0 | 0 | 5.4 | 5.0 | .0 |
| 0 | 2 | 1 | 17.3 | 15.6 | -126.4 |
| 0 | 3 | 1 | 18.5 | 18.1 | -7.9 |
| 0 | 4 | 1 | 20.7 | 21.2 | 9.9 |
| 0 | 5 | 1 | 5.6 | 6.5 | 7.6 |
| 0 | 6 | 1 | 8.1 | 7.6 | -176.9 |
| 1 | 2 | 1 | 24.5 | 24.5 | -77.9 |
| 1 | 3 | 1 | 23.7 | 24.6 | -78.0 |
| 1 | 4 | 1* | 2.5 | .4 | 49.9 |
| 1 | 5 | 1 | 13.2 | 13.1 | -262.2 |
| 1 | 6 | 1 | 4.3 | 5.3 | -255.6 |
| 2 | 1 | 1 | 23.8 | 24.3 | -147.8 |
| 2 | 2 | 1 | 24.1 | 23.2 | -168.9 |
| 2 | 3 | 1 | 13.3 | 13.5 | .7 |
| 2 | 4 | 1 | 21.4 | 23.1 | .9 |
| 2 | 5 | 1* | 2.9 | 3.4 | 20.4 |
| 2 | 6 | 1 | 6.5 | 6.8 | -181.7 |
| 3 | 0 | 1 | 27.5 | 29.3 | -256.0 |
| 3 | 1 | 1 | 18.2 | 15.6 | -269.0 |
| 3 | 2 | 1 | 17.3 | 16.6 | -76.3 |
| 3 | 3 | 1 | 19.9 | 20.7 | -84.2 |
| 3 | 4 | 1* | 2.7 | 1.8 | 71.4 |
| 3 | 5 | 1 | 10.1 | 9.7 | -264.1 |
| 4 | 1 | 1 | 22.6 | 21.5 | -172.7 |
| 4 | 2 | 1 | 12.1 | 10.5 | -153.1 |
| 4 | 3 | 1 | 9.5 | 9.0 | -5.4 |
| 4 | 4 | 1 | 10.3 | 11.5 | 8.0 |
| 5 | 1 | 3 | 4.6 | 4.1 | -86.1 |
| 5 | 2 | 3 | 7.7 | 8.1 | 84.7 |
| 5 | 3 | 3 | 7.2 | 7.4 | -263.8 |
| 6 | 1 | 3 | 7.3 | 7.4 | 1.3 |
| 6 | 2 | 3 | 6.2 | 4.6 | 3.5 |
| 7 | 0 | 3 | 6.1 | 4.9 | -91.1 |
| 7 | 1 | 3 | 4.2 | 1.8 | -99.1 |
| 0 | 2 | 4 | 16.0 | 17.2 | -189.3 |
| 0 | 3 | 4 | 18.4 | 17.9 | -171.4 |
| 0 | 4 | 4* | 2.1 | 1.0 | -81.1 |
| 0 | 5 | 4 | 9.6 | 9.8 | 3.8 |
| 0 | 6 | 4* | 2.6 | 4.0 | 11.0 |
| 1 | 2 | 4 | 15.8 | 16.5 | -264.1 |
| 1 | 3 | 4 | 8.4 | 7.8 | -106.0 |
| 1 | 4 | 4 | 14.0 | 13.7 | -93.0 |
| 1 | 5 | 4* | 2.4 | 3.1 | -68.8 |
| 1 | 6 | 4 | 5.0 | 4.5 | 82.3 |
| 2 | 0 | 4 | 20.9 | 25.3 | 1.5 |
| 2 | 1 | 4 | 8.2 | 9.1 | -10.6 |
| 2 | 2 | 4 | 16.0 | 15.8 | -178.5 |
| 2 | 3 | 4 | 15.9 | 14.8 | -184.4 |
| 2 | 4 | 4* | 2.2 | 2.2 | -49.5 |
| 2 | 5 | 4 | 7.7 | 7.4 | -3.7 |
| 2 | 6 | 4* | 2.7 | 3.6 | 25.6 |
| 3 | 1 | 4 | 18.7 | 18.0 | -268.1 |
| 3 | 2 | 4 | 11.4 | 11.8 | -270.0 |
| 3 | 3 | 4 | 5.6 | 6.1 | -106.0 |
| 3 | 4 | 4 | 10.3 | 9.5 | -92.8 |
| 3 | 5 | 4* | 2.6 | 2.5 | -55.8 |
| 3 | 6 | 4 | 5.2 | 3.0 | 84.4 |
| 4 | 0 | 4 | 15.7 | 14.6 | -6.6 |
| 4 | 1 | 4 | 4.4 | 5.2 | 2.8 |
| 4 | 2 | 4 | 9.0 | 8.8 | -185.9 |
| 4 | 3 | 4 | 9.2 | 9.1 | -173.2 |
| 4 | 4 | 4* | 2.5 | .8 | -76.3 |
| 4 | 5 | 4 | 5.2 | 5.0 | 4.6 |
| 5 | 1 | 4 | 9.2 | 9.1 | 86.6 |
| 5 | 2 | 4 | 6.4 | 6.0 | -258.6 |
| 5 | 3 | 4* | 2.5 | 2.7 | -104.1 |
| 5 | 4 | 4 | 6.5 | 5.2 | -85.4 |
| 6 | 0 | 4 | 6.9 | 6.5 | .7 |
| 6 | 1 | 4* | 2.5 | 2.3 | 1.4 |
| 6 | 2 | 4 | 5.3 | 4.0 | -178.4 |
| 0 | 2 | 5 | 10.4 | 10.7 | -157.0 |
| 0 | 3 | 5 | 4.9 | 4.5 | -24.5 |
| 0 | 4 | 5 | 10.0 | 9.1 | 8.3 |
| 0 | 5 | 5* | 2.4 | 2.2 | 39.1 |
| 1 | 2 | 5 | 10.2 | 9.7 | -91.4 |
| 1 | 3 | 5 | 9.9 | 10.0 | -77.2 |
| 1 | 4 | 5* | 2.1 | 2.2 | 20.1 |
| 1 | 5 | 5 | 6.5 | 5.6 | 87.9 |
| 2 | 1 | 5 | 13.1 | 13.4 | -170.7 |
| 2 | 2 | 5 | 7.3 | 8.0 | -169.5 |
| 2 | 3 | 5 | 4.4 | 5.0 | -21.8 |
| 2 | 4 | 5 | 7.7 | 6.5 | .1 |
| 2 | 5 | 5* | 2.4 | 2.5 | 57.9 |
| 3 | 0 | 5 | 11.0 | 11.5 | -261.3 |
| 3 | 1 | 5* | 2.6 | 3.9 | -259.7 |
| 3 | 2 | 5 | 7.6 | 7.4 | -90.5 |
| 3 | 3 | 5 | 6.1 | 6.9 | -82.2 |
| 3 | 4 | 5* | 2.4 | 2.0 | 18.4 |
| 4 | 1 | 5 | 7.5 | 7.4 | -178.1 |
| 4 | 2 | 5 | 4.5 | 5.4 | -162.2 |
| 4 | 3 | 5* | 2.4 | 2.6 | -26.5 |
| 4 | 4 | 5 | 5.3 | 4.6 | 6.7 |
| 5 | 0 | 5 | 5.1 | 5.7 | -269.5 |
| 5 | 1 | 5* | 2.4 | 2.2 | -250.4 |
| 5 | 2 | 5 | 3.5 | 3.6 | -94.9 |
| 5 | 0 | 1 | 18.4 | 18.9 | -266.0 |
| 5 | 1 | 1 | 6.4 | 5.6 | -259.8 |
| 5 | 2 | 1 | 10.3 | 9.9 | -83.4 |
| 5 | 3 | 1 | 9.3 | 8.8 | -76.4 |
| 6 | 1 | 1 | 8.2 | 8.5 | -166.7 |
| 6 | 2 | 1 | 6.1 | 5.5 | -165.6 |
| 7 | 0 | 1 | 4.5 | 5.7 | -257.9 |
| 0 | 2 | 2 | 31.9 | 32.1 | -14.4 |
| 0 | 3 | 2 | 22.5 | 23.9 | 5.2 |
| 0 | 4 | 2* | 2.4 | 1.3 | -267.7 |
| 0 | 5 | 2 | 13.2 | 12.9 | -176.6 |
| 0 | 6 | 2 | 4.2 | 5.5 | -171.6 |
| 1 | 2 | 2 | 22.9 | 23.0 | -84.9 |
| 1 | 3 | 2 | 15.3 | 15.3 | 70.1 |
| 1 | 4 | 2 | 23.7 | 21.7 | 84.6 |
| 1 | 5 | 2 | 3.8 | 4.5 | -259.0 |
| 1 | 6 | 2 | 5.6 | 6.9 | -100.0 |
| 2 | 0 | 2 | 39.9 | 38.7 | -183.4 |
| 2 | 1 | 2 | 22.3 | 20.0 | -196.8 |
| 2 | 2 | 2 | 22.3 | 21.7 | 1.8 |
| 2 | 3 | 2 | 28.1 | 26.0 | -9.2 |
| 2 | 4 | 2* | 2.5 | 2.5 | -208.1 |
| 2 | 5 | 2 | 12.2 | 11.8 | -187.1 |
| 3 | 1 | 2 | 28.7 | 25.9 | -91.1 |
| 3 | 2 | 2 | 18.6 | 18.5 | -92.8 |
| 3 | 3 | 2 | 10.3 | 11.2 | 72.2 |
| 3 | 4 | 2 | 15.4 | 15.9 | 81.3 |
| 3 | 5 | 2* | 2.9 | 2.7 | -240.0 |
| 4 | 0 | 2 | 26.0 | 26.5 | -192.9 |
| 4 | 1 | 2 | 8.3 | 8.4 | -186.2 |
| 4 | 2 | 2 | 13.5 | 14.6 | -10.9 |
| 4 | 3 | 2 | 12.8 | 12.5 | 1.1 |
| 4 | 4 | 2* | 2.8 | 1.4 | -237.3 |
| 4 | 5 | 2 | 6.6 | 6.4 | -178.7 |
| 5 | 1 | 2 | 13.2 | 14.5 | -98.3 |
| 5 | 2 | 2 | 7.1 | 7.3 | -81.2 |
| 5 | 3 | 2 | 4.3 | 5.1 | 69.7 |
| 5 | 4 | 2 | 6.5 | 7.3 | 87.6 |
| 6 | 0 | 2 | 11.2 | 9.8 | -186.6 |
| 6 | 1 | 2* | 2.8 | 3.6 | -187.9 |
| 6 | 2 | 2 | 4.9 | 5.5 | -4.3 |
| 0 | 2 | 3 | 17.7 | 18.3 | 25.6 |
| 0 | 3 | 3 | 12.0 | 11.3 | -203.0 |
| 0 | 4 | 3 | 17.6 | 17.4 | -175.1 |
| 0 | 5 | 3* | 2.5 | 3.9 | -171.9 |
| 0 | 6 | 3 | 5.8 | 6.6 | -5.3 |
| 1 | 2 | 3 | 21.3 | 20.7 | 89.4 |
| 1 | 3 | 3 | 21.7 | 19.6 | -264.7 |
| 1 | 4 | 3* | 2.2 | 2.2 | -123.1 |
| 1 | 5 | 3 | 10.9 | 11.4 | -89.9 |
| 1 | 6 | 3* | 2.9 | 4.3 | -75.7 |
| 2 | 1 | 3 | 25.2 | 25.7 | 12.7 |
| 2 | 2 | 3 | 16.6 | 17.4 | 1.0 |
| 2 | 3 | 3 | 9.6 | 10.7 | -190.9 |
| 2 | 4 | 3 | 15.7 | 15.6 | -188.7 |
| 2 | 5 | 3* | 2.6 | 2.5 | -141.4 |
| 2 | 6 | 3 | 6.0 | 5.2 | -12.9 |
| 3 | 0 | 3 | 21.8 | 23.2 | -87.4 |
| 3 | 1 | 3 | 8.8 | 9.1 | -98.5 |
| 3 | 2 | 3 | 15.1 | 15.1 | -267.8 |
| 3 | 3 | 3 | 15.1 | 14.9 | 87.6 |
| 3 | 4 | 3* | 2.5 | 2.6 | -126.5 |
| 3 | 5 | 3 | 7.9 | 8.0 | -92.7 |
| 4 | 1 | 3 | 16.3 | 16.4 | -3.8 |
| 4 | 2 | 3 | 11.1 | 9.8 | 12.7 |
| 4 | 3 | 3 | 5.0 | 6.3 | -200.4 |
| 4 | 4 | 3 | 9.8 | 9.2 | -178.8 |
| 5 | 0 | 3 | 13.8 | 13.4 | -97.6 |

* Indicates unobserved reflection. Value given corresponds to one-half minimum observable intensity.

Table III

Parameters for the Ellipsoids of Vibration

| Root-mean-square amplitude, A | Angle (deg) from $a$ | $b$ | $c$ |
|---|---|---|---|
| | | Ge | |
| 0.252 | 90.0 | 58.9 | 31.1 |
| 0.304 | 90.0 | 31.1 | 121.1 |
| 0.315 | 0.0 | 90.0 | 90.0 |
| | | $C_1$ | |
| 0.30 | 90.0 | 7.0 | 97.0 |
| 0.35 | 0.0 | 90.0 | 90.0 |
| 0.45 | 90.0 | 83.0 | 7.0 |
| | | $C_2$ | |
| 0.28 | 72.6 | 42.3 | 127.1 |
| 0.36 | 38.5 | 80.1 | 53.3 |
| 0.46 | 56.9 | 130.6 | 121.8 |
| | | $C_3$ | |
| 0.25 | 0.0 | 90.0 | 90.0 |
| 0.28 | 90.0 | 29.9 | 119.9 |
| 0.45 | 90.0 | 60.1 | 29.9 |
| | | N | |
| 0.25 | 90.0 | 96.1 | 6.1 |
| 0.38 | 0.0 | 90.0 | 90.0 |
| 0.42 | 90.0 | 6.1 | 83.9 |

in error by 2 to 5%. The layers were recorrelated and refinement was continued with germanium anisotropic; when refinement was reached $R$ was 0.071 and $r = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4]^{1/2}$ was 0.127. Refinement was continued with all atoms anisotropic and $R$ decreased to 0.066, $r$ to 0.115. A comparison of the successive $r$ values according to the method of Hamilton[6] indicates that the light atoms are anisotropic at the 99.5% confidence level. Accordingly, we report the final parameters from the anisotropic refinement in Table I. The standard deviations quoted are derived from a full-matrix, least-squares treatment. The observed and calculated structure factors are given in Table II. The anisotropic temperature factors have been converted to ellipsoids of vibration in Table III.

The generally large temperature factors are a consequence of the data having been collected only 10–15° below the melting point.

A difference Fourier map using the parameters in Table I showed a number of small peaks, 0.5 e/A$^3$ and less. In general, these appeared to be due to random fluctuations in the data, but it is perhaps significant that three of the peaks appeared at positions consistent with three of the five expected independent hydrogen positions if the staggered configuration obtained around the Ge–C bonds and that no peaks appeared in the positions to be expected if the eclipsed configuration obtained. No attempt was made to refine the hydrogen positions nor to test their effect on the $R$ factors.

**The Possibility of Isocyanide.**—To test whether this might be the isocyanide rather than the cyanide, the refinement at an intermediate stage in the calculations was carried out alternatively using both assumptions. The $R$ and $r$ values were only slightly lower for the assumption that the group was cyanide, but the more telling evidence was the magnitudes of the temperature factors for the C and N atoms. The isotropic temperature factors for the atom attached to Ge and the outer atom, respectively, were 8.7 and 10.9 A$^2$ for Ge–C–N, and 11.5 and 9.1 A$^2$ for Ge–N–C. Only the former gives the reasonable result that the outer atom has the larger temperature factor, so that we conclude the compound is the cyanide. It is possible that a small fraction of the isocyanide is present in solid solution in the cyanide. We cannot decide this point from the data.

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(6) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

## Discussion

The molecular structure of trimethylcyanogermane in the solid phase is essentially the tetrahedral structure one would expect for an isolated molecule. Within experimental error the molecule has $C_{3v}$ symmetry and a linear Ge–C–N group. The bond lengths and angles are listed in Table IV, along with comparative data from other compounds.

TABLE IV
MOLECULAR DIMENSIONS FOR $(CH_3)_3GeCN$ AND RELATED COMPOUNDS

| Distance or angle | Compd | Value | Ref |
|---|---|---|---|
| Ge–$C_1(CH_3)$ | $(CH_3)_3GeCN$ | 1.99 ± 0.04 | *a* |
| Ge–$C_2(CH_3)$ | $(CH_3)_3GeCN$ | 1.97 ± 0.03 | *a* |
| Ge–$C_3$(CN) | $(CH_3)_3GeCN$ | 1.98 ± 0.06 | *a* |
| Ge–C | $(CH_3)_4Ge$ | 1.98 ± 0.03 | *b* |
| Ge–C | $CH_3GeH_3$ | 1.945 | *c* |
| C–N | $(CH_3)_3GeCN$ | 1.15 ± 0.13 | *a* |
| C–N | $CH_3CN$ | 1.157 | *b* |
| $C_1$–Ge–$C_2$ | $(CH_3)_3GeCN$ | 114.1 ± 1.5 | *a* |
| $C_2$–Ge–$C_2$ | $(CH_3)_3GeCN$ | 116.2 ± 1.2 | *a* |
| C–C–C | $(CH_3)_3CF$ | 111 ± 1.5 | *b* |
| C–C–C | $(CH_3)_3CCl$ | 109.5 ± 1.5 | *b* |
| C–C–C | $(CH_3)_3CBr$ | 108.9 ± 1.5 | *b* |
| C–C–C | $(CH_3)_3CI$ | 109.2 ± 1.5 | *b* |
| C–Si–C | $(CH_3)_3SiCl$ | 113 ± 2 | *b* |
| C–Si–C | $(CH_3)_3SiBr$ | 113.5 ± 4 | *b* |
| $C_1$–Ge–$C_3$ | $(CH_3)_3GeCN$ | 104.2 ± 1.6 | *a* |
| $C_2$–Ge–$C_3$ | $(CH_3)_3GeCN$ | 103.0 ± 1.6 | *a* |
| Ge–C–N | $(CH_3)_3GeCN$ | 175.9 ± 2.0 | *a* |

[a] This work. [b] L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958. [c] V. W. Laurie, *J. Chem. Phys.*, **30**, 1210 (1959).

The Ge–C bond lengths are, within experimental error, equal for all the bonds and normal in length.

The C–N bond length is normal, but the uncertainty is quite large. It is possible that this crystal is a mixture of the cyanide and isocyanide. As indicated above, the crystallographic data favor the cyanide; nevertheless, the possibility of a small amount of isocyanide being randomly mixed in cannot be ruled out and is suggested by the infrared spectrum in solution. The presence of some isocyanide could contribute to the large uncertainty in the bond length.

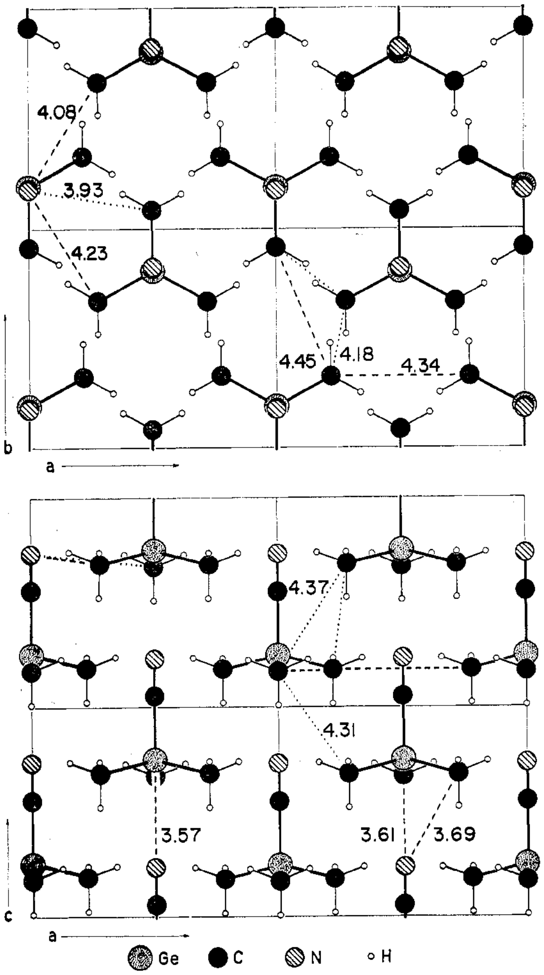

Figure 1.—The crystal structure of $(CH_3)_3GeCN$. Top view: down the *c* axis. Bottom view: along the *b* axis. Interatomic distances are in angstroms. This structure should be compared to that of $(CH_3)_3SnCN$ (see preceding article). The hydrogen positions are assumed on the basis of normal C–H distances and a staggered configuration around the Ge–C bond.

The C–Ge–C bond angles between the methyl groups are considerably larger than tetrahedral. Since the cyanide carbon is more electronegative than the methyl carbon, this increase in angle is to be expected.[7] Data for comparison with other germanium compounds are not available; the trimethylsilicon halides and the *t*-butyl halides are the most closely related compounds, of known structure, that might show a similar large angle. The increase from the tetrahedral angle in these compounds is not great in the carbon compounds although it does clearly occur in the fluoride, but it is apparent in the silicon compounds even though the uncertainty is large. Since steric effects would be more serious in the carbon compounds than in the silicon and germanium compounds, the large observed spreading in trimethylcyanogermane is probably normal. There is also the possibility that crowding from the intermolecular cyanide contributes to the spreading of these bonds. The structure of this molecule in the vapor phase would provide a most useful comparison.

The packing of the molecule in the crystal is shown in Figure 1. The molecules are aligned with the cyanide group in one molecule pointing directly toward the germanium atom in the next. The Ge–N distance is compared with similar distances in other cyanides, and with the expected van der Waals distances, in Table V.

As can be seen, there is no shortening of the distances of the sort found with arsenic, selenium, and bromine. Nevertheless, the packing suggests that there might be an incipient interaction here. In $SiF_4$, a relatively polar molecule, a similar sort of packing occurs, with the fluorine atoms in one molecule pointing directly toward the silicon atoms in the surrounding molecules, but in $SiI_4$, $GeI_4$, and $SnI_4$ the iodide atoms do not

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(7) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

Table V

Intermolecular Distances in Cyanide Compounds

| Distance | Compd | Value, A | van der Waals distance,[a] A | Ref |
|---|---|---|---|---|
| Ge–N | $(CH_3)_3GeCN$ | 3.57 | 3.5 | *b* |
| As–N | $As(CN)_3$ | 2.74 | 3.5 | *c, d* |
| As–N | $CH_3As(CN)_2$ | 2.94 | 3.5 | *d* |
| As–N | $(CH_3)_2AsCN$ | 3.18 | 3.5 | *e* |
| Se–N | $Se(CN)_2$ | 2.6 | 3.5 | *f* |
| Br–N | BrCN | 2.9 | 3.45 | *g* |

[a] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260. [b] This work. [c] K. Emerson and D. Britton, *Acta Cryst.*, **16**, 113 (1963). [d] E. O. Schlemper and D. Britton, *ibid.*, in press. [e] N. Camerman and J. Trotter, *Can. J. Chem.*, **41**, 460 (1963). [f] A. C. Hazell, *Acta Cryst.*, **16**, 843 (1963). The value given in this table is based on C–N = 1.16 rather than the 1.42 reported; Hazell gives Se–N = 2.35. [g] S. Geller and A. L. Schawlow, *J. Chem. Phys.*, **23**, 779 (1955).

point toward the next central atom.[8] In the latter compounds the packing is determined by the approximate cubic close packing of the iodide atoms. In the trimethylcyanogermane structure, the packing can be regarded as approximate hexagonal close packing of the methyl and cyano groups, and this alone may be the significance of the molecular arrangement.

In summary, the packing and the distances in crystalline $(CH_3)_3GeCN$ do not rule out the possibility of an interaction between the adjacent nitrogen and germanium atoms, but they also do not demonstrate one. It is only a pleasant speculation to imagine that the arrangement in the crystal is the first step toward the more striking arrangement of planar $(CH_3)_3Sn$ groups and equally shared CN groups found in $(CH_3)_3SnCN$.[4]

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[8] R. W. G. Wyckoff, "Crystal Structures," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 5.

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# Structure of $K_2BaCo(NO_2)_6$

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The structure of $K_2BaCo(NO_2)_6$ has been determined from three-dimensional data. The substance crystallizes as cubic crystals of space group Fm3 with $a$ = 10.66 A. The cobalt occupies a site of $S_6$ symmetry; the nitrite ion is not significantly distorted from its structure in sodium nitrite.

## Introduction

As part of a study of low-spin $d^7$ complexes, we became interested in the structure of the complex $Co(NO_2)_6{}^{4-}$. Although low-spin octahedral complexes of $d^7$ ions are expected to be distorted by a Jahn–Teller effect, various compounds of the formula $M_2M'Co(NO_2)_6$ (where M represents a univalent and M′ a divalent cation) are cubic,[2] according to powder patterns. It is also of interest that corresponding copper(II) compounds show identical powder patterns,[2] and single-crystal X-ray studies have been carried out on $K_2PbCu(NO_2)_6$,[3,4] using two-dimensional data. There is some disagreement, however, as to the space group, and the results of the two studies are somewhat different; the differences are limited to the oxygen positions since the other atoms occupy the same special positions in either of the two space groups, Fm3 or F23.

Because of the disagreement over space group and because both studies show the nitrite ion considerably distorted from its structure in sodium nitrite,[5] we have collected three-dimensional X-ray diffraction data for a crystal of $K_2BaCo(NO_2)_6$ and have redetermined the structure.

## Collection and Reduction of the X-Ray Data

Previous studies employed $K_2PbCu(NO_2)_6$ because it readily forms large crystals, while most other copper and cobalt compounds of the same type give only microcrystalline products which are unsuitable for single crystal studies. By employing slow mixing and using acetate as anion for both the cobalt and barium ions, it was possible to grow crystals of $K_2BaCo(NO_2)_6$ *ca.* 0.1 mm at their widest point; the crystals were octahedral in shape.

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[1] U. S. Steel Fellow, Georgia Institute of Technology, 1965.

[2] A. Ferrari, L. Cavalca, and M. Nardelli, *Gazz. Chim. Ital.*, **81**, 982 (1951); A. Ferrari and C. Cola, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [6] **14**, 435 (1931); [6] **11**, 755 (1930).

[3] M. van Driel and H. J. Verwell, *Z. Krist.*, **95**, 308 (1936).

[4] L. Cavalca, M. Nardelli, and D. Grazioli, *Gazz. Chim. Ital.*, **86**, 1041 (1956).

[5] M. I. Kay and R. C. Fraser, *Acta Cryst.*, **14**, 56 (1961).