twisting the aluminum atoms out of the square toward the corners of a tetrahedron.

However, extended speculation about the conformation of such puckered rings seems unwise because the assumption of tetrahedral bond angles must be a poor approximation. The very considerable polar character of Al–F bonds must tend to give larger angles for the ring. The H–F–H angle for $(HF)_n$ chain polymers in the gas phase has been reported[14] to be 140 ± 5°, and the Si–O–Si bond angle in $[(CH_3)_2SiO]_4$ puckered rings has been found[15] to be 142.5° for one crystalline form. It is likely, therefore, that the Al–F–Al bond angles on $[(C_2H_5)_2AlF]_4$ rings are 140° or larger.

We have also considered a cubic Al–F framework, analogous to the cubanes, with aluminum pentacoordinated and fluorine tricoordinated. Such unusual coordinations, as well as the highly strained 90° bond angles, make this conformation improbable.

It is indeed unfortunate that all efforts to produce crystals of $(C_2H_5)_2AlF$ so far have failed and that low volatility and pyrolysis of this compound when heated have made it impossible to obtain structural information about its vapor phase.

The molecular structure of liquid diethylfluoroalane undoubtedly differs markedly from its structure in solution. Interactions beyond association to a tetramer must be responsible for the extremely high viscosity of the liquid compound at room temperature. The rapid decrease of viscosity upon heating and the high solubility in nonpolar solvents show that such interactions are reversible and rather weak. Two explanations for this may be offered. The polar Al–F units on tetrameric rings may interact with those of neighboring rings to cause a certain random association. Or, on forming the condensed phase, the rings may open to form chains which associate to longer chains, between which considerable random polar interaction may exist. Until more complete data relating the properties of diethylfluoroalane with its structure are available the answer to the question of structure and bonding of this liquid and the extent to which Al–F bridging may occur must remain speculative.

Acknowledgments.—The authors wish to thank the Advanced Research Projects Agency and the National Science Foundation for financial support.

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(15) H. Steinfink, B. Post, and I. Fankuchen, *Acta Cryst.*, **8**, 420 (1955).

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The Crystal Structure of Trimethyltin Cyanide

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Received December 2, 1965

Trimethyltin cyanide forms orthorhombic crystals in space group Cmcm with $a = 9.96$, $b = 11.96$, $c = 6.06$ A, with four molecules per unit cell. The structure consists of planar $(CH_3)_3Sn$ groups with approximately D_{3h} symmetry and disordered cyanide groups symmetrically disposed on either side of the $(CH_3)_3Sn$ groups. The interatomic distances are Sn–C (methyl) = 2.16 ± 0.03, Sn–C (or N) = 2.49 ± 0.02, and C–N = 1.09 ± 0.03. The structure is similar to that of AgCN with infinite chains $(CH_3)_3Sn\cdots CN\cdots (CH_3)_3Sn\cdots CN$, but there appears to be considerable ionic character in the $Sn\cdots CN$ bonds.

As a first step in extending a study of the intermolecular interactions between cyanide nitrogen atoms and potential Lewis acids to compounds of group IV elements, we have determined the structure of $(CH_3)_3SnCN$. A comparison of the melting points—$(CH_3)_3SnCN$, 189°; $(CH_3)_3SnCl$, 38°; $(CH_3)_3SnBr$, 27°—suggests some special sort of interaction in the cyanide.

Experimental Section

Preparation and Properties.—Trimethyltin cyanide was prepared in three steps from tin tetrachloride. Tetramethyltin was prepared from $SnCl_4$ and CH_3MgI in *n*-butyl ether by the method of Edgell and Ward.[1] Trimethyltin iodide was prepared from $(CH_3)_4Sn$ and I_2 in benzene by the method of Seyferth.[2] Trimethyltin cyanide was prepared from $(CH_3)_3SnI$ and AgCN in benzene by the method of Seyferth and Kahlen.[3] The observed melting point, 188.5–188.9°, and cyanide stretching frequency in $CHCl_3$, 2175 cm^{-1}, agree reasonably well with the reported values[3], 184.5–184.6° and 2160 cm^{-1}. The density, measured by flotation in a CCl_4–CBr_4 mixture, was 1.754 ± 0.005 g/cc.

Although $(CH_3)_3SnCN$ is fairly insoluble in benzene and carbon tetrachloride, it is quite soluble in $CHCl_3$. Well-formed, needle-like crystals were obtained by crystallization from $CHCl_3$. By vacuum sublimation very long, thin, flexible needles were obtained. Although $(CH_3)_3SnCN$ is hydrolyzed by water, it was only slowly hydrolyzed by atmospheric moisture (in a Minnesota winter), so that crystals could be handled in air.

Unit Cell and Space Group.—Oscillation, Weissenberg, and precession photographs 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 $a = 9.96 \pm 0.02$, $b = 11.96 \pm 0.02$, and $c = 6.06 \pm 0.01$ A. Four molecules per unit cell give a calculated density of 1.746 ± 0.005 g/cc compared to the experimental value of 1.754 ± 0.005 g/cc. Systematic extinctions $h + k$ odd in hkl and l odd in $h0l$ indicated the space group to be $Cmc2_1$, C2cm, or Cmcm. No apparatus was available to test for piezoelectricity. The spoon test described

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(1) W. F. Edgell and C. H. Ward, *J. Am. Chem. Soc.*, **76**, 1169 (1954).

(2) D. Seyferth, *J. Org. Chem.*, **22**, 1599 (1957).

(3) D. Seyferth and N. Kahlen, *ibid.*, **25**, 809 (1960).

by Bunn[4] gave a negative test for pyroelectricity so that no conclusion could be drawn with certainty.

A crystal 0.2 mm in diameter was selected for intensity measurements and was sealed in a Pyrex capillary. Multiple-film Mo Kα Weissenberg photographs were taken of the *hk*0 through *hk*5 layers, as well as 0*kl* and 1*kl* precession photographs. The relative intensities were measured by visual comparison to a series of timed exposures of a selected reflection. There were 373 independent reflections of measurable intensity and 105 reflections in the same region of reciprocal space with intensities too weak to measure. The latter were included in the least-squares calculations with values equal to half the minimum observable intensity. The usual Lorentz and polarization corrections were made. Absorption corrections were made assuming that the crystal was a cylinder of radius 0.10 mm (μ = 34.8 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 early calculations were made using programs supplied by the Princeton University crystallography group. The final refinements were made using programs prepared by L. W. Finger of the University of Minnesota Geology Department.

Trial Structure.—The tin atoms were located from a three-dimensional Patterson map. They, alone, gave $R = 0.22$ and were used as the basis for a three-dimensional Fourier map. For any remotely reasonable structure a consideration of the packing of the methyl groups ruled out C2cm as a possible space group, and, since we expected an ordered structure, we assumed the space group to be Cmc2$_1$. The tin atoms are centrically disposed in any case; hence, the Fourier map was centric, but to our surprise, the methyl carbon atoms were coplanar with the tin atom and spherical in shape. The cyanide peaks were resolved and symmetrically disposed between adjacent tin atoms in the *z* direction. This seemed to indicate that the space group was Cmcm and that the CN group was statistically disordered.

TABLE I

FINAL PARAMETERS FOR $(CH_3)_3SnCN$

		x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{23}
Sn	(4c)	0	0.2022 (1)	1/4	0.0126 (2)	0.0086 (1)	0.0114 (5)	0	0
C$_1$	(4c)	0	0.383 (3)	1/4	0.039 (7)	0.008 (2)	0.045 (11)	0	0
C$_2$	(8g)	0.185 (2)	0.110 (2)	1/4	0.014 (2)	0.017 (2)	0.061 (9)	0.006 (2)	0
CN	(8f)	0	0.197 (1)	0.660 (3)	0.013 (1)	0.013 (1)	0.045 (8)	0	0.001 (2)

[a] All β_{13} values are required to be zero. Isotropic temperature parameters from the last cycle in which that atom was isotropic are, in order: 4.3, 8.4, 7.4, 6.3. The anisotropic temperature factors are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

After some preliminary attempts to refine the structure in Cmc2$_1$ we concluded that the space group was indeed Cmcm and continued the refinement in this space group.

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 $F_o < 40$, and $w = (40/F_o)^4$ for $F_o > 40$. After the initial refinement, a comparison of the observed and calculated structure factors indicated that the correlation factors between the various layers were in error by 2 to 4%. The layers were recorrelated and refinement was continued with the tin atom anisotropic; when refinement was reached, R was 0.083 and $r = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4]^{1/2}$ was 0.149. Refinement was continued with all atoms anisotropic and R decreased to 0.080, r to 0.144. A comparison of the successive r values according to the method of Hamilton[5] indicates that the fit of the data to the model with the light atoms anisotropic is significantly better at the 99.5% confidence level.

To test further the possibility that the structure might correctly be described in Cmc2$_1$, refinement was attempted in this space group starting from parameters obtained by shifting all of the light atoms in the negative *z* direction by one standard deviation from the Cmcm positions. The refinement was made using the diagonal matrix approximation since, with the structure as close to centric as it was, the full matrix was ill behaved. After 12 cycles of refinement using fractional shifts between $^1/_4$ and $^3/_4$ the structure had refined with the methyl carbon atoms moved about 3 standard deviations along *c* from their positions in Cmcm. The CN–Sn–CH$_3$ bond angles were 93 and 94° and all the distances were normal. The refinement parameters were $R = 0.082$ and $r = 0.143$ for all atoms anisotropic. For further statistical information the light atoms were converted to the isotropic form, and refinement continued with Sn only anisotropic. The final parameters were $R = 0.083$ and $r = 0.149$. The Sn only anisotropic refinement showed no improvement at all between Cmcm and Cmc2$_1$, and the refinement with all atoms anisotropic produced only a slight improvement. Hamilton's tables[5] indicate that r should have decreased to 0.142 in the all anisotropic case to have been statistically significant at even the 50% confidence level and that it should have decreased to 0.141 or 0.140 to have been significant at the 90 or 99% confidence levels. Therefore, we reject the hypothesis that the acentric space group is to be preferred and report in Table I the final parameters for the refinement in Cmcm. The standard deviations quoted are derived from a full-matrix, least-squares treatment. In Table II the observed and calculated structure factors are compared. In Table III the anisotropic thermal parameters have been converted to ellipsoids of vibration.

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(4) C. W. Bunn, "Chemical Crystallography," 2nd ed, Oxford University Perss, London, 1961, p 321.

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

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	OBS	CALC
0	2	0	133.3	-176.9
0	4	0	14.5	22.9
0	6	0	25.6	22.5
0	8	0	56.9	-55.1
0	10	0	60.2	58.3
0	12	0	35.0	-31.4
0	14	0*	6.3	7.5
0	16	0*	5.0	1.7
1	1	0	72.4	69.4
1	3	0	140.1	-152.2
1	5	0	154.7	149.3
1	7	0	91.5	-89.8
1	9	0	26.0	24.8
1	11	0	7.4	8.8
1	13	0	16.9	-16.1
1	15	0	13.1	13.4
1	17	0	8.6	-7.1
2	0	0	175.2	210.5
2	2	0	154.0	-165.5
2	4	0	65.3	58.0
2	6	0	29.6	30.4
2	8	0	62.9	-59.3
2	10	0	55.0	51.0
2	12	0	30.2	-28.3
2	14	0	8.4	7.8
2	16	0*	5.0	1.5
3	1	0	18.0	25.3
3	3	0	114.7	-111.8
3	5	0	138.9	141.6
3	7	0	80.3	-76.7
3	9	0	17.6	17.4
3	11	0*	3.8	6.7
3	13	0	14.2	-13.8
3	15	0	12.9	12.2
3	17	0	7.3	-6.3
4	0	0	176.5	163.8
4	2	0	127.7	-122.0
4	4	0	37.9	36.5
4	6	0	24.6	24.2
4	8	0	46.9	-45.1
4	10	0	42.3	41.7
4	12	0	26.1	-24.0
4	14	0*	4.7	6.5
4	16	0*	5.1	1.3
5	1	0	52.2	45.8
5	3	0	99.4	-93.3
5	5	0	86.6	84.7
5	7	0	58.8	-55.1
5	9	0	19.0	19.5
5	11	0*	4.2	5.5
5	13	0	12.0	-12.2
5	15	0	9.9	9.4
6	0	0	123.2	114.1
6	2	0	80.2	-76.4
6	4	0	21.8	21.0
6	6	0	10.8	11.8
6	8	0	30.3	-32.3
6	10	0	31.6	32.3
6	12	0	18.3	-17.0
6	14	0*	4.9	4.5
7	1	0	20.4	21.2
7	3	0	54.4	-53.0
7	5	0	63.7	59.9
7	7	0	41.4	-39.7
7	9	0	11.5	11.1
7	11	0*	4.5	4.5
7	13	0	6.8	-7.9
7	15	0*	5.2	6.5
8	0	0	61.3	55.3
8	2	0	52.8	-48.7
8	4	0	21.7	21.8
8	6	0	10.5	11.6
8	8	0	23.3	-23.7
8	10	0	18.7	18.6
8	12	0	12.0	-10.7
8	14	0*	5.2	3.7
9	1	0	9.0	11.3
9	3	0	31.0	-32.5
9	5	0	35.3	36.7
9	7	0	23.0	-21.3
9	9	0	8.2	6.6
9	11	0*	4.8	1.5
9	13	0*	5.2	-5.2
10	0	0	36.9	36.0
10	2	0	25.6	-26.8
10	4	0	5.8	7.8
10	6	0*	4.4	5.8
10	8	0	10.1	-11.2
10	10	0	11.4	11.5
10	12	0	8.5	-7.0
11	1	0	7.4	9.0
11	3	0	16.3	-18.3
11	5	0	16.4	16.7
11	7	0	10.7	-12.3
11	9	0*	5.0	5.1
11	11	0*	5.2	1.6
12	0	0	17.5	17.5
12	2	0	11.3	-13.0
12	4	0*	4.7	5.0
12	6	0*	4.9	2.0
12	8	0	7.1	-7.0
13	1	0*	4.9	2.8
13	3	0*	4.9	-7.8
13	5	0	7.1	9.8
13	7	0	7.2	-6.5
14	0	0*	5.1	7.3
14	2	0*	5.2	-6.5
14	4	0*	5.3	2.8
0	6	1	91.0	-89.4
0	8	1	49.2	48.8
0	10	1*	4.1	-6.3
0	12	1	12.2	-12.0
0	14	1	13.8	13.8
0	16	1	8.0	-9.6
1	5	1	3.0	-4.0
1	7	1	31.7	-29.4
1	9	1	49.5	48.7
1	11	1	40.4	-38.5
1	13	1	16.9	16.0
1	15	1*	5.5	-1.8
2	4	1	107.6	107.3
2	6	1	109.5	-97.9
2	8	1	41.2	40.2
2	10	1*	4.2	-3.3
2	12	1	7.2	-9.9
2	14	1	11.0	12.8
2	16	1	8.1	-9.3
3	3	1	80.1	78.8
3	5	1*	3.1	-8.2
3	7	1	37.6	-36.0
3	9	1	43.9	41.9
3	11	1	33.4	-31.6
3	13	1	16.1	14.7
3	15	1*	5.6	-2.0
4	2	1	52.8	-49.4
4	4	1	86.2	85.3
4	6	1	74.4	-71.5
4	8	1	33.6	33.4
4	10	1*	4.5	-5.1
4	12	1	7.4	-8.6
4	14	1	10.0	11.2
4	16	1	8.2	-7.6
5	1	1	106.7	-96.8
5	3	1	39.9	39.8
5	5	1*	3.5	-1.4
5	7	1	22.1	-19.4
5	9	1	32.2	32.4
5	11	1	27.7	-26.6
5	13	1	13.9	11.2
5	15	1*	5.8	-1.4
6	2	1	44.1	-45.2
6	4	1	55.0	54.6
6	6	1	49.2	-47.7
6	8	1	27.6	27.9
6	10	1*	4.7	-3.8
6	12	1*	5.2	-7.5
6	14	1	7.9	8.2
7	1	1	57.9	-55.2
7	3	1	34.8	34.2
7	5	1*	4.0	-5.9
7	7	1	15.8	-17.4
7	9	1	22.6	24.0
7	11	1	16.2	-16.7
7	13	1*	5.6	7.5
8	2	1	19.2	-18.8
8	4	1	37.9	38.1
8	6	1	35.0	-34.7
8	8	1	15.6	15.0
8	10	1*	5.1	-1.6
8	12	1*	5.5	-3.9
9	1	1	31.7	-32.5
9	3	1	21.8	22.3
9	5	1*	4.6	-1.5
9	7	1	6.9	-11.7
9	9	1	13.3	12.9
9	11	1	8.2	-10.2
10	2	1	14.7	-15.9
10	4	1	20.5	21.0
10	6	1	16.3	-16.3
10	8	1	7.4	9.5
10	10	1*	5.6	-2.4
11	1	1	19.0	-19.3
11	3	1	7.7	8.9
11	5	1*	5.2	-.9
11	7	1*	5.4	-4.3
11	9	1*	5.7	7.9
12	2	1	7.5	-7.4
12	4	1	8.3	9.8
12	6	1	7.9	-9.5
12	8	1*	5.9	5.6
13	1	1	7.9	-8.0
13	3	1	8.0	5.9
13	5	1*	5.8	-1.2
0	4	2	30.4	-25.2
0	6	2	21.9	-17.7
0	8	2	48.9	46.7
0	10	2	49.7	-50.2
0	12	2	30.5	28.0
0	14	2	7.9	-7.1
1	3	2	116.3	113.0
1	5	2	122.7	-118.5
1	7	2	75.6	75.3
1	9	2	23.4	-22.5
1	11	2	6.7	-6.9
1	13	2	14.4	14.3
1	15	2	12.4	-12.1
2	0	2	188.8	-154.3
2	2	2	133.1	123.4
2	4	2	47.8	-46.1
2	6	2	23.4	-23.0
2	8	2	49.7	49.5
2	10	2	42.0	-44.4
2	12	2	26.8	25.3
2	14	2	8.0	-7.3
3	1	2	25.5	-23.0
3	3	2	89.1	88.3
3	5	2	110.4	-112.3
3	7	2	67.3	65.0
3	9	2	15.5	-16.6
3	11	2*	4.9	-5.3
3	13	2	11.9	12.3
3	15	2	9.1	-11.0
4	0	2	142.9	-126.8
4	2	2	100.8	96.3
4	4	2	32.7	-31.3
4	6	2	18.3	-18.7
4	8	2	38.0	38.4
4	10	2	33.6	-36.5
4	12	2	19.2	21.5
4	14	2*	5.8	-6.1
5	1	2	34.6	-35.1
5	3	2	72.3	74.7
5	5	2	68.0	-71.2
5	7	2	43.3	47.8
5	9	2	15.4	-17.4
5	11	2*	5.1	-4.4
5	13	2	8.0	10.7
6	0	2	98.8	-92.0
6	2	2	66.0	63.5
6	4	2	17.6	-19.1
6	6	2	10.6	-9.7
6	8	2	23.5	27.8
6	10	2	25.2	-28.1
6	12	2	15.4	15.4
7	1	2	17.3	-17.8
7	3	2	40.7	44.6
7	5	2	45.6	-50.8
7	7	2	31.1	34.4
7	9	2	11.1	-10.3
7	11	2*	5.5	-3.6
8	0	2	47.1	-47.3
8	2	2	38.1	41.3
8	4	2	15.9	-18.6
8	6	2	6.8	-9.3
8	8	2	16.0	20.2
8	10	2	15.3	-16.6
8	12	2	8.4	9.7
9	1	2	6.6	-9.7
9	3	2	24.1	27.7
9	5	2	28.9	-31.5
9	7	2	17.3	18.9
9	9	2*	5.6	-6.2
9	11	2*	5.9	-1.3
10	0	2	26.3	-30.7
10	2	2	22.7	23.0
10	4	2*	5.2	-7.1
10	6	2*	5.4	-4.8
10	8	2	8.0	9.9
11	1	2*	5.3	-7.6
11	3	2	9.9	15.7
11	5	2	12.6	-14.7
11	7	2	8.2	10.9
12	0	2	13.2	-15.1
12	2	2	9.6	11.3
12	4	2*	5.8	-4.5
0	2	3	91.0	78.7
0	4	3	104.5	-101.7
0	6	3	94.4	83.5
0	8	3	42.0	-42.5
0	10	3*	5.9	4.6
0	12	3	15.9	11.6
0	14	3	10.3	-12.9
1	1	3	132.5	135.2
1	3	3	60.8	-64.8
1	5	3*	4.0	3.3
1	7	3	34.0	32.5
1	9	3	46.1	-45.5
1	11	3	34.3	34.3
1	13	3	11.6	-14.3
2	2	3	53.2	54.9
2	4	3	91.1	-98.8
2	6	3	82.4	85.0
2	8	3	37.2	-37.0
2	10	3*	6.0	2.9
2	12	3	10.1	10.1
2	14	3	10.4	-12.0
3	1	3	109.4	105.7
3	3	3	65.2	-67.3
3	5	3*	4.5	5.2
3	7	3	32.5	33.7
3	9	3	38.2	-39.5
3	11	3	31.3	28.8
3	13	3	10.8	-13.0
4	2	3	49.8	51.1
4	4	3	77.2	-79.3
4	6	3	64.4	65.4
4	8	3	28.9	-30.7
4	10	3*	6.2	3.8
4	12	3*	6.9	8.7
5	1	3	95.2	86.6
5	3	3	44.4	-41.8
5	5	3*	5.1	1.6
5	7	3	19.7	21.5
5	9	3	26.8	-30.8
5	11	3	21.1	23.7
6	2	3	42.3	41.1
6	4	3	51.9	-53.6
6	6	3	41.7	45.2
6	8	3	21.5	-24.6
6	10	3*	6.7	2.9
6	12	3*	7.3	7.1
7	1	3	61.5	53.4
7	3	3	31.9	-31.9
7	5	3*	5.8	3.9
7	7	3	16.0	17.1
7	9	3	18.9	-22.3
7	11	3	15.9	15.5
8	2	3	21.4	20.8
8	4	3	33.3	-36.0
8	6	3	30.7	31.5
8	8	3	15.1	-14.2
8	10	3*	7.2	1.4
9	1	3	31.8	31.8
9	3	3	20.9	-20.4
9	5	3*	6.5	1.2
9	7	3*	6.9	11.1
9	9	3	10.3	-12.7
10	2	3	11.1	14.9
10	4	3	21.9	-20.3
10	6	3	13.3	16.1
11	1	3	20.7	18.3
11	3	3	10.1	-9.3
11	5	3*	7.3	.7
0	2	4	72.4	-81.0
0	4	4	24.6	24.2
0	6	4	14.5	12.6
0	8	4	32.9	-34.2
0	10	4	34.2	36.1
0	12	4	21.1	-21.1
1	1	4	33.9	28.7
1	3	4	71.5	-70.8
1	5	4	72.6	78.1
1	7	4	49.6	-52.5
1	9	4	17.3	17.4
1	11	4*	7.0	4.4
1	13	4*	7.8	-11.0
2	0	4	112.3	96.8
2	2	4	87.4	-77.2
2	4	4	28.1	30.1
2	6	4	14.2	14.2
2	8	4	33.4	-34.5
2	10	4	32.4	32.7
2	12	4	18.2	-19.4
3	1	4	22.3	19.7
3	3	4	60.9	-59.5
3	5	4	69.9	72.4
3	7	4	44.1	-46.0
3	9	4	12.2	14.4
3	11	4*	7.3	3.6
3	13	4*	8.0	-9.6
4	0	4	91.6	81.2
4	2	4	66.5	-63.1
4	4	4	24.4	22.9
4	6	4	11.5	11.9
4	8	4	26.6	-27.8
4	10	4	28.9	27.2
4	12	4	16.0	-16.4
5	1	4	22.3	21.5
5	3	4	48.3	-49.3
5	5	4	48.0	50.7
5	7	4	33.5	-35.0
5	9	4	9.8	13.0
5	11	4*	7.7	2.9
6	0	4	64.8	60.5
6	2	4	45.8	-44.4
6	4	4	16.4	15.4
6	6	4*	6.3	7.1
6	8	4	19.2	-20.5
6	10	4	16.5	20.8
6	12	4	11.5	-11.9
7	1	4	8.5	12.6
7	3	4	32.0	-31.8
7	5	4	35.6	36.2
7	7	4	23.9	-25.0
7	9	4*	7.5	8.4
7	11	4*	8.1	2.3
8	0	4	38.4	34.8
8	2	4	32.8	-29.3
8	4	4	9.5	12.8
8	6	4*	7.1	6.1
8	8	4	14.3	-14.5
8	10	4	11.4	12.8
9	1	4*	6.9	7.4
9	3	4	14.5	-19.9
9	5	4	20.1	22.6
9	7	4	11.9	-14.5
10	0	4	23.0	21.8
10	2	4	18.8	-16.8
10	4	4*	7.6	5.9
10	6	4*	8.0	3.3
11	1	4*	8.0	5.1
11	3	4*	8.0	-11.3
0	2	5	52.5	-52.0
0	4	5	77.1	73.1
0	6	5	63.9	-61.2
0	8	5	31.0	30.9
0	10	5*	5.4	-3.5
0	12	5	8.4	-9.0
0	14	5*	9.3	10.2
1	1	5	88.6	-90.2
1	3	5	46.2	49.0
1	5	5*	3.6	-3.2
1	7	5	25.4	-25.9
1	9	5	32.8	34.3
1	11	5	28.2	-25.5
1	13	5	8.9	11.0
2	2	5	43.3	-44.1
2	4	5	64.0	69.6
2	6	5	60.6	-59.6
2	8	5	28.0	28.1
2	10	5*	5.5	-2.8
2	12	5	8.6	-8.2
3	1	5	76.6	-76.3
3	3	5	49.0	46.1
3	5	5*	4.0	-3.5
3	7	5	25.0	-24.5
3	9	5	29.7	30.3
3	11	5	22.2	-22.1
3	13	5	9.1	9.9
4	2	5	38.4	-38.1
4	4	5	57.1	57.3
4	6	5	49.6	-48.1
4	8	5	25.9	23.5
4	10	5*	5.7	-2.9
4	12	5*	6.3	-7.0
5	1	5	70.5	-61.1
5	3	5	33.4	33.1
5	5	5*	4.7	-2.0
5	7	5	16.7	-17.7
5	9	5	21.3	23.8
5	11	5	16.3	-17.8
6	2	5	30.2	-29.5
6	4	5	40.8	40.8
6	6	5	33.8	-34.6
6	8	5	15.5	18.2
6	10	5*	6.1	-2.2
6	12	5*	6.6	-5.5
7	1	5	44.0	-40.4
7	3	5	25.8	24.0
7	5	5*	5.3	-2.4
7	7	5	8.0	-13.2
7	9	5	15.8	17.0
7	11	5	13.4	-12.1
8	2	5	19.4	-17.4
8	4	5	27.0	27.3
8	6	5	21.9	-23.5
8	8	5	11.4	11.3
8	10	5*	6.6	-1.3
9	1	5	27.2	-24.8
9	3	5	15.9	15.2
9	5	5*	6.0	-1.0
9	7	5*	6.3	-8.4
9	9	5	9.3	10.3
10	2	5	8.5	-11.2
10	4	5	15.8	15.8
10	6	5	9.1	-13.1
11	1	5	16.5	-14.1
11	3	5*	6.5	7.8

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

The anisotropic temperature factors would appear to settle the question of the space group and symmetry. For the methyl carbon atoms the greatest amplitudes of vibration are in the plane of the $(CH_3)_3Sn$ group, roughly perpendicular to the Sn–C bond direction, the second greatest perpendicular to this plane, and the least roughly parallel to the bond direction. If the methyl groups should have been out of the plane, that is, if the proper space group were $Cmc2_1$, we would expect the temperature factor perpendicular to the plane of the molecule to have been abnormally large, reflecting the incorrect position. The largest amplitude for the cyanide vibration is roughly in the direction of the Sn–CN bond, but here the apparent atom is an average of two different kinds of atoms, which surely must be at slightly different positions, and the apparent amplitude of vibration reflects this.[6]

Discussion

The crystal structure is shown in Figure 1. The tin atoms are in a trigonal bipyramidal environment with three equatorial methyl groups and equally distant axial cyanide groups. Each cyanide is coordinated to two tin atoms, so that infinite chains $CN\cdots(CH_3)_2\cdots CN\cdots(CH_3)_3Sn$ are present.

The independent Sn–C distances are: C_1–Sn, 2.17 ± 0.03; C_2–Sn, 2.15 ± 0.02 A. The two independent angles are: C_1–Sn–C_2, 120.9 ± 1.5°; C_2–Sn–C_2, 118.2 ± 1.5°. These distances are between the 2.18 ± 0.01 A quoted by Sutton[7] for various tetrahedral methyltin

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(6) This same factor could contribute to the apparently short CN bond length (1.09 A) if the apparent positions are an average of carbon atoms closer to and nitrogen atoms farther from the tin atoms since the average maximum will be closer to the nitrogen position than to the carbon position. If carbon and nitrogen atoms are approximated by Gaussian curves of height 6 and 7, respectively, with widths at a half-height of 0.8 A, then a simple addition of the curves shows that the maximum is displaced from the halfway point toward the nitrogen by 0.004, 0.008, 0.014, and 0.028 A if the centers of the peaks are 0.1, 0.2, 0.3, and 0.4 A apart, respectively. The apparent shortening of the CN bond length would be twice the above values. If the amplitude of the anisotropic vibration of the CN atoms is given full credence and the difference of 0.15 A between the Sn amplitude and the CN amplitude in the bond direction is attributed to a separation of 0.3 A between the C and N positions, then a correction of 0.028 A would be made to the observed length.

(7) L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958.

TABLE III

PARAMETERS FOR THE ELLIPSOIDS OF VIBRATIONS

Root-mean-square amplitude, A	Angle (deg) from *a*	*b*	*c*
		Sn	
0.252	0	90	90
0.249	90	0	90
0.146	90	90	0
		C_1	
0.44	0	90	90
0.24	90	0	90
0.29	90	90	0
		C_2	
0.22	27	117	90
0.37	63	27	90
0.34	90	90	0
		CN	
0.26	0	90	90
0.31	90	20	70
0.29	90	110	20

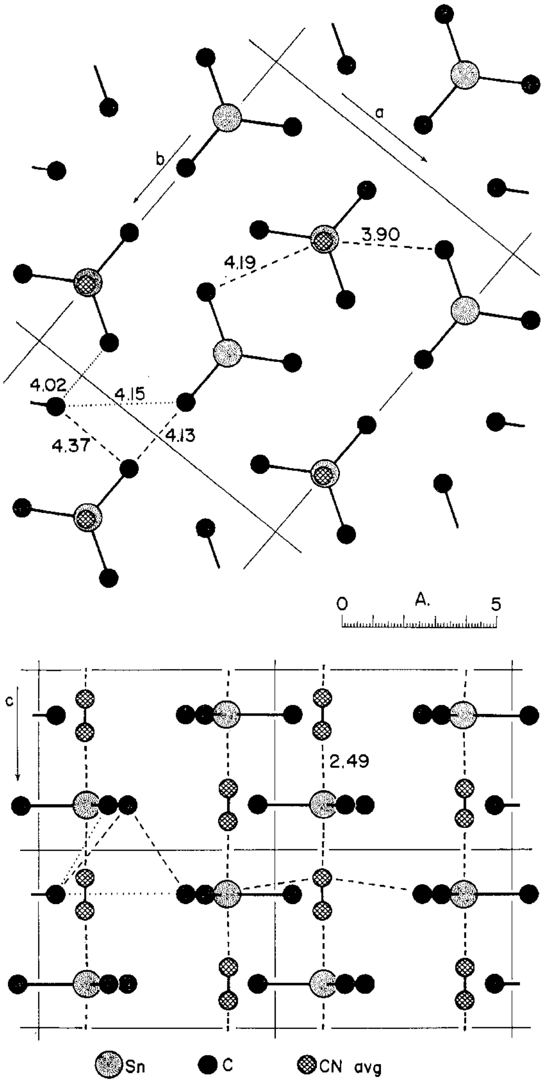

Figure 1.—The crystal structure of $(CH_3)_3SnCN$. Top view: down *c* axis. Bottom view: along [110]; this projection is taken along the diagonal to minimize the overlap between the chains Sn·CN·Sn and also to show the similarity to $(CH_3)_3GeCN$ (see next article). Interatomic distances are given in angstroms.

halides and the more accurate 2.143 A found in CH_3SnH_3. Since the geometry of the $(CH_3)_3Sn$ group is not tetrahedral, all we can say is that the distance is reasonable for a covalent bond.

The only other trigonal bipyramidal tin species whose structures have been determined are $(CH_3)_3SnCl \cdot py$,[8] the $SnCl_5^-$ ion,[9] and possibly $(CH_3)_3SnF$.[10] In $(CH_3)_3SnCl \cdot py$ projections were used to determine the geometry of the molecule, and no distances were accurately determined except Sn–Cl = 2.42 ± 0.04 A. In $SnCl_5^-$ the equatorial distances are 2.30, 2.38, and 2.40 A, and the axial distances are 2.37 and 2.39 A. In $(CH_3)_3SnF$ the Sn–C distances in the planar $(CH_3)_3Sn$ group are about 2.1 A; the fluorines are disordered and not symmetrically disposed between the tin atoms, being about 2.1 A from one tin and 2.2–2.6 A from the next. The conclusion to be drawn from these data, particularly the $SnCl_5^-$, is that covalent bond lengths are about the same in the equatorial and axial positions. This being the case, the average value of 2.49 ± 0.02 A found here for the Sn–CN bonds is clearly much longer than a normal covalent bond, and the question arises: Is this a normal ionic distance? An inspection of known ionic cyanides, particularly the low-temperature modification of KCN,[11] shows that 1.57 A is a reasonable value for the radius of the C or N atom in the direction parallel to the molecular axis. Pauling[12] gives the univalent radius of Sn^{4+} as 0.96 A, and this is a reasonable value to use here, so that we would expect $0.96 + 1.57 = 2.53$ A for the ionic distance. Considering the accuracy of the data for both the measured and the predicted distances, we conclude that this structure is best described as an arrangement of $(CH_3)_3Sn^+$ and CN^- ions with the CN ordered in direction along an axis, but disordered in orientation along this axis, with perhaps a small amount of covalent character to account for the orientation of the CN group. This Sn–CN distance cannot be accounted for in terms of a fractional covalent bond since application of Pauling's rule[13] would indicate that reduction of the bond order to 0.5 would lengthen the bond by 0.18 A, which would lead to a prediction of about 2.4 A for the bond length.

Other intermolecular distances are shown in Figure 1 and indicate that the packing is normal in other respects.

Acknowledgments.—We thank the National Aeronautical and Space Agency for a fellowship for E. O. S. and the National Science Foundation for their support of this work. We thank Professor Robert Jacobson, Mr. Byron Gorres, and Mr. L. W. Finger for providing us with copies of their computer programs and for helping us with their use. We thank Mrs. Judith Konnert for help with many of the computations.

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[12] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 514.

[13] See ref 12, p 255.