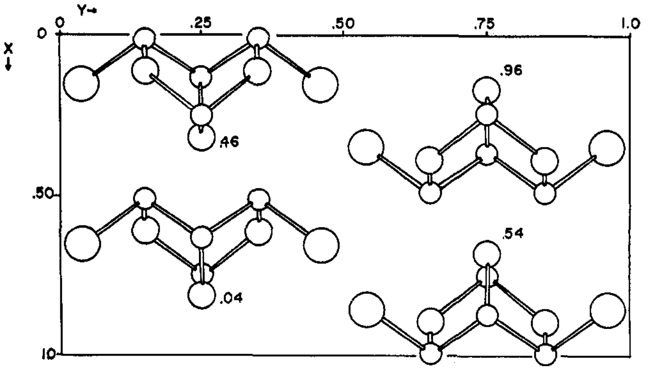

Figure 4.—The crystal packing of β-$P_4S_3I_2$ as viewed down *c*. The relative heights (*z* values) of the molecular centers are indicated.

just described, β-$P_4S_3I_2$ can be converted to α-$P_4S_3I_2$. If a benzene solution of β-$P_4S_3I_2$ is allowed to stand at room temperature for several days, crystals of the less soluble α-$P_4S_3I_2$ are slowly formed. The conversion is also carried out, with almost quantitative yields, when dry β-$P_4S_3I_2$ is held in the molten state at 122° for 10 min. The cooled product is a fused mass of α-$P_4S_3I_2$, which is soluble in warm benzene and can be obtained in a crystalline form by slow cooling of the benzene solution.

There are several means of readily differentiating between the two forms of $P_4S_3I_2$. The α form melts at 122–124° to a light orange liquid which is essentially the same color as the crystal, while the β form melts to a deep red liquid which seems to indicate some decomposition to elemental iodine. The α form usually crystallizes in a short prismatic habit, while the β form gives thin, tabular crystals frequently twinned on the large faces. Both crystals are sensitive to atmospheric moisture; the β form seems to be the most sensitive to hydrolysis. The infrared spectra (in KBr) are similar (480 (m), 460 (s), 445 (w), 410–430 (vs), 400 cm^{-1} (s)) but the β form has a broad peak at 660–700 cm^{-1} (m), a weak shoulder at 540 cm^{-1}, and an additional peak at 520 cm^{-1} (w). Initial attempts to compare the ^{31}P spectra of the two forms failed because sufficiently concentrated solutions (in CS_2, the best solvent we have found) could not be prepared.

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The Crystal Structures of Dimethyltin(IV) Bisdicyanamide and Trimethyltin(IV) Dicyanamide

BY YEH MEI CHOW

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The crystal structures of dimethyltin(IV) bisdicyanamide, $(CH_3)_2Sn[N(CN)_2]_2$, and trimethyltin(IV) dicyanamide, $(CH_3)_3Sn[N(CN)_2]$, have been determined from three-dimensional X-ray data collected by counter methods. Dimethyltin(IV) bisdicyanamide crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.178$ (3) Å, $b = 11.265$ (10) Å, $c = 6.860$ (6) Å, and $\beta = 99.56$ (5)°; $Z = 2$; $d_{obsd} = 1.94$ (3) g/cm³ and $d_{calcd} = 1.98$ g/cm³. Trimethyltin(IV) dicyanamide crystallizes in the orthorhombic space group *Pnam* with $a = 17.644$ (9) Å, $b = 6.565$ (4) Å, and $c = 7.684$ (3) Å; $Z = 4$; $d_{obsd} = 1.69$ (3) g/cm³ and $d_{calcd} = 1.71$ g/cm³. A least-squares refinement gave final conventional *R* values of 0.036 and 0.029 for dimethyltin(IV) bisdicyanamide and trimethyltin(IV) dicyanamide, respectively. Both structures are composed of planar $N(CN)_2$ groups symmetrically disposed on either side of the organotin groups. The average distances and angles of the $N(CN)_2$ groups in $(CH_3)_2Sn[N(CN)_2]_2$ and $(CH_3)_3Sn[N(CN)_2]$, respectively, are as follows: central C–N, 1.289 (10), 1.263 (15) Å, which are shorter than the normal C–N single covalent bond; cyano C–N, 1.132 (9), 1.116 (14) Å, which are no longer than the C–N triple bond; N–C–N, 172.3 (8), 173.2 (13)°; and C–N–C, 124.2 (8), 129.6 (11)°. The structure of dimethyltin(IV) bisdicyanamide consists of an infinite two-dimensional network of tin atoms and bridging dicyanamide groups with methyl groups above and below completing the octahedral coordination of the tin. The interatomic distances are Sn–CH_3 2.091 (8) Å and Sn–N 2.289 (6) Å. The network is similar to that of dimethyltin difluoride. The crystal structure of trimethyltin(IV) dicyanamide consists of infinite chains. The tin atoms are in a trigonal-bipyramidal environment with methyl groups in the equatorial plane and dicyanamide groups in the axial positions. The interatomic distances are Sn–CH_3 2.130 (11) Å and Sn–N 2.335 (9) Å. The structure is similar to that of trimethyltin cyanide.

Introduction

In most of the known crystal structures of $(CH_3)_2SnX_2$ and $(CH_3)_3SnX$ (X = halide, pseudohalide), X is a bridging ligand.[1–7] Many dicyanamides have been prepared and their infrared spectra reported,[8–10] but no crystal structures have been reported. In isolated organotin dicyanamides the tin atom conceivably may bond either to the amide part (I) or to the cyano part (II) of the ligand. From infrared spectral evidence type II structures have been suggested for dimethyltin(IV) bisdicyanamide.[10] By comparison of the infrared spectrum of trimethyltin(IV) dicyanamide to that of

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[2] R. A. Forder and G. M. Sheldrick, *J. Organometal. Chem.*, **21**, 115 (1970).

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

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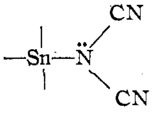

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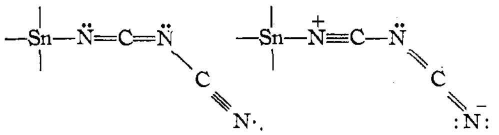

II

dimethyltin(IV) bisdicyanamide and triphenyltin(IV) dicyanamide, we would predict that tin should bond to the cyano part of the ligand in $(CH_3)_3Sn[N(CN)_2]$ also. If the tin atom were bound to the ligand through the cyano part, then there would still be other lone pairs of electrons on the dicyanamide group. The structures were determined to establish whether any further bonding occurs in the crystals and, if so, which nitrogen atoms would act as electron donors and which one of the following bridging classes it would belong to: Sn—X—Sn or Sn—X···Sn.

Preparation and Properties

Dimethyltin(IV) bisdicyanamide and trimethyltin(IV) dicyanamide were prepared by adding sodium dicyanamide solution to the aqueous solutions of dimethyltin dichloride[10] and trimethyltin chloride, respectively. Dimethyltin(IV) bisdicyanamide formed needlelike crystals. Platelike crystals of trimethyltin(IV) dicyanamide only formed after recrystallization from aqueous solution. *Anal.* Calcd for $(CH_3)_2Sn[N(CN)_2]_2$: C, 25.66; N, 30.07; H, 2.00. Found: C, 25.46; N, 29.92; H, 2.15. Calcd for $(CH_3)_3Sn[N(CN)_2]$: C, 26.13; N, 18.28; H, 3.95. Found: C, 25.96; N, 18.21; H, 3.86. Their infrared frequencies of C–N stretching vibration are compared with related compounds in Table I.

TABLE I
INFRARED FREQUENCIES (CM^{-1}) OF C–N STRETCHING VIBRATION

	ν_{sym} (C—N)	ν_{asym} (C—N)	ν_{sym} (C≡N)	ν_{asym} (C≡N)	Ref
$NaN(CN)_2$	930	1344	2179	2232	8
$(C_6H_5)_3Sn[N(CN)_2]$	939	1408	2173	2249	9
$(CH_3)_2Sn[N(CN)_2]_2$	940	1410	2210–25	2265	10
$(CH_3)_2Sn[N(CN)_2]_2$	936	1406	2190[a]	2265	*b*
$(CH_3)_3Sn[N(CN)_2]$	922	1395	2178[a]	2258	*b*

[a] Broad peak. [b] Infrared spectra were obtained with a Perkin-Elmer Model 521 using NaCl plates and Nujol, halocarbon mull.

Space Groups and Unit Cells

Precession pictures indicated that $(CH_3)_2Sn[N(CN)_2]_2$ belongs to the monoclinic system and $(CH_3)_3Sn[N(CN)_2]$ belongs to the orthorhombic system. The systematic extinctions k odd in $0k0$ and l odd in $h0l$ indicate $P2_1/c$ to be the space group for the dimethyltin compound. The systematic extinctions of the trimethyltin compound $k + l$ odd in $0kl$ and h odd in $h0l$ indicate the space group to be either $Pna2_1$ or $Pnam$. The unit cell constants obtained by least-squares refinement of the θ angles of 26 and 21 reflections which had been determined accurately on the diffractometer are $a = 6.178$ (3) Å, $b = 11.265$ (10) Å, $c = 6.860$ (6) Å, and $\beta = 99.56$ (5)° for $(CH_3)_2Sn[N(CN)_2]_2$ and $a = 17.644$ (9) Å, $b = 6.565$ (4) Å, and $c = 7.684$ (3) Å for $(CH_3)_3Sn[N(CN)_2]$. The calculated densities of 1.98 g/cm^3 for two formula units of $(CH_3)_2Sn[N(CN)_2]_2$ and 1.71 g/cm^3 for four formula units of $(CH_3)_3Sn[N(CN)_2]$ per unit cell agree with their respective densities of 1.94 (3) and 1.69 (3) g/cm^3 as measured by flotation in a mixture of CH_3I and CCl_4.

Collection and Reduction of the X-Ray Data

The $(CH_3)_2Sn[N(CN)_2]_2$ crystal used in data collection was needlelike with approximate dimensions of 0.12 mm × 0.12 mm × 0.30 mm. The crystal was mounted in a glass capillary and approximately aligned along the c^* axis, which coincided with the ϕ axis of the Hilger & Watts four-circle automatic X-ray diffractometer. Zr-filtered Mo Kα radiation (λ 0.7107 Å) was used, and the takeoff angle of the X-ray tube was 3°. Data were collected by the θ–ω scan technique.[11] A symmetrical scan range of 1.0° of θ and ω was used for all reflections. The scan rate was 1°/100 sec. Stationary-crystal, stationary-counter background counts of 50 sec were taken at each end of the scan. The counter was 20 cm from the crystal and had an aperture of 6-mm diameter. Intensity data were collected for hkl and $\bar{h}kl$ of this monoclinic crystal out to a θ value 30°, and $h\bar{k}l$ and $\bar{h}\bar{k}l$ out to 32°. The intensities of two standard reflections were measured periodically every 50 reflections, and their constancy (variation <2%) provides the evidence of crystal and electronic stability. The intensity variances were estimated to be $\sigma^2(I) = T + B + (0.04(T - B))^2$, where T is the total scan count and B is the total background count.[12] Symmetry equivalent reflections were averaged. Of the 1638 independent reflections 924 had $F_o^2 > 2\sigma(F_o^2)$. These were corrected for Lorentz and polarization effects and were used in subsequent calculations. Trial calculations for one-third of the total reflections chosen to give the widest variations gave the transmission factors of 0.71–0.76; over 75% of the reflections had transmission factors within 2% of the average. Since this is comparable to the variation in the intensities of the standard reflections, no absorption corrections were made ($\mu = 27.3$ cm^{-1}).

The flat $(CH_3)_3Sn[N(CN)_2]$ crystals have identifiable faces $\{100\}$ and $\{011\}$. The crystal used in data collection was sliced normal to the $[01\bar{1}]$ axis, so that it had dimensions of 0.12 mm × 0.60 mm × 0.20 mm along the [100], [011], and $[01\bar{1}]$ axis. The procedure for intensity data collection was the same as for the dimethyltin compound. The data were collected for hkl, $h\bar{k}l$, $\bar{h}\bar{k}l$, and $\bar{h}kl$ out to a θ value of 26°. The two standard reflections decreased slowly and smoothly in intensity, the total decrease being 6% of the original intensities; this was considered to be the result of crystal instability. A linear correction was made to bring all the reflections to the same scale. The absorption and Lorentz polarization corrections were made with a locally modified version of the program DATAP2,[13] with a linear absorption coefficient of 28.4 cm^{-1}. The transmission coefficients were found to range from 0.56 to 0.73. Symmetry-equivalent reflections were averaged. Of the total of 945 independent reflections collected, 617 had $F_o^2 > 2\sigma(F_o^2)$. Only these were used in the structure determination.

Determination of Structures

Dimethyltin(IV) Bisdicyanamide.—In space group $P2_1/c$ with $Z = 2$, the tin atom can be placed at the origin. With tin determining the phases, the three-dimensional Fourier map was the equivalent of a

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(11) The θ–ω scan technique in a Hilger & Watts diffractometer is equivalent to the θ–2θ scan technique in a Picker diffractometer.

(12) G. H. Stout and L. H. Jenson, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 456.

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TABLE II

POSITIONAL PARAMETERS AND THERMAL PARAMETERS

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{33}
$(CH_3)_2Sn[N(CN)_2]_2$									
Sn	0	0	0	0.0122 (1)	0.0041 (1)	0.0146 (1)	0.0001 (1)	0.0011 (1)	0.0003 (2)
N(1)	0.2157 (11)	0.1657 (5)	0.0065 (9)	0.0285 (19)	0.0069 (5)	0.0230 (15)	−0.0065 (8)	0.0005 (13)	−0.0004 (8)
C(1)	0.3355 (10)	0.2432 (6)	0.0222 (9)	0.0165 (15)	0.0063 (5)	0.0131 (12)	−0.0012 (7)	0.0004 (10)	−0.0011 (6)
N	0.4575 (10)	0.3344 (6)	0.0147 (11)	0.0306 (30)	0.0100 (6)	0.0202 (15)	−0.0101 (10)	−0.0067 (11)	0.0037 (10)
C(2)	0.6063 (10)	0.3696 (6)	0.1592 (9)	0.0193 (16)	0.0051 (5)	0.0160 (13)	−0.0030 (7)	−0.0015 (11)	0.0010 (6)
N(2)	0.7392 (10)	0.4097 (6)	0.2722 (9)	0.0256 (19)	0.0084 (6)	0.0218 (15)	−0.0062 (9)	−0.0033 (14)	−0.0013 (8)
CH_3	0.8570 (13)	0.0714 (7)	0.2296 (11)	0.0267 (22)	0.0083 (7)	0.0219 (18)	0.0025 (10)	0.0082 (15)	−0.0022 (9)
$(CH_3)_3Sn[N(CN)_2]$									
Sn	0.1364 (1)	0.2084 (1)	$^1/_4$	0.0027 (1)	0.0332 (2)	0.0233 (1)	−0.0004 (1)	0	0
N(1)	0.2632 (5)	0.1056 (17)	$^1/_4$	0.0024 (3)	0.0508 (36)	0.0401 (25)	0.0012 (9)	0	0
C(1)	0.3248 (6)	0.0718 (17)	$^1/_4$	0.0040 (5)	0.0290 (33)	0.0319 (26)	−0.0019 (10)	0	0
N	0.3936 (5)	0.0063 (16)	$^1/_4$	0.0024 (3)	0.0357 (32)	0.1015 (62)	−0.0008 (9)	0	0
C(2)	0.4538 (6)	0.1032 (18)	$^1/_4$	0.0027 (4)	0.0371 (34)	0.0370 (28)	0.0009 (10)	0	0
N(2)	0.5113 (5)	0.1762 (17)	$^1/_4$	0.0030 (3)	0.0446 (37)	0.0485 (30)	−0.0004 (8)	0	0
$CH_3(1)$	0.1730 (7)	0.5174 (18)	$^1/_4$	0.0054 (5)	0.0270 (31)	0.0402 (31)	−0.0024 (11)	0	0
$CH_3(2)$	0.1186 (4)	0.0487 (13)	0.4879 (11)	0.0061 (4)	0.0444 (27)	0.0257 (17)	−0.0004 (8)	0.0024 (6)	0.0082 (18)

sharpened Patterson map. From the double set of light-atom peaks a reasonable set could be chosen for the light-atom positions. A full-matrix least-squares refinement was carried out with positional parameters and isotropic thermal parameters of all atoms minimizing the function $r = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$. The weighting scheme was $w = 1/(\sigma(F_o^2))^2$, where $\sigma(F_o^2) = K\sigma(I)/Lp$. (Lp is the Lorentz–polarization correction and a value of 1 is used for scale factor K.) The atomic scattering factors used were taken from ref 14. No effects of anomalous dispersion were included. After three cycles of isotropic refinement the values of r and R ($R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$) were 0.066 and 0.144. When the tin atoms were given anisotropic thermal parameters the r and R were reduced to 0.011 and 0.046. When all atoms were given anisotropic thermal parameters, the r and R further decreased to 0.0055 and 0.036. According to Hamilton's significance test[15] the refinement should be terminated only after refinement with all atoms anisotropic. In a final structure factor calculation the unobserved data were included. Of the 714 unobserved reflections (*i.e.*, where $F_o^2 < 2\sigma(F_o^2)$) only 47 gave $|F_o - F_c|$ values between $1.4\sigma(F_o)$ and $4\sigma(F_o)$. The final difference electron density map revealed no anomalous regions of electron density. The highest residual density was 0.95 $e^-/\text{Å}^3$ compared with 8.5 $e^-/\text{Å}^3$ for carbon atoms in the Fourier map.

Trimethyltin(IV) Dicyanamide.—The tin atoms were located from a three-dimensional Patterson map. The remaining nonhydrogen atoms were located by Fourier syntheses. All atoms except two carbon atoms of the methyl groups appeared to have the same z coordinate. The refinement was begun with space group $Pna2_1$; after three cycles of refinement the positions of Sn and $C(CH_3)$ atoms and $N(CN)_2$ group atoms apparently remained on the plane perpendicular to the z axis. Then the refinement was switched to the space group *Pnam*, in which case the values of r and R decreased from 0.23 and 0.24 to 0.034 and 0.078, respectively, after three cycles of refinement. This indicated that the space group should be *Pnam*. Refinement with anisotropic thermal parameters was continued. The successive r and R values for tin anisotropic were 0.0125 and 0.043 and for all atoms anisotropic were 0.0067 and 0.029. On the basis of Hamilton's significance test[15] the cycle with all atoms anisotropic was chosen as the final one. An examination of $|F_c|$ for the 328 unobserved reflections revealed only 21 instances where $|F_o - F_c|$ was slightly above $1.4\sigma(F_o)$. The highest residual density of the difference Fourier map was 0.3 $e^-/\text{Å}^3$ compared with 5.2 $e^-/\text{Å}^3$ for carbon atoms in the Fourier map.

The standard deviations of observations of unit weight are 1.06 and 1.05 for $(CH_3)_2Sn[N(CN)_2]_2$ and $(CH_3)_3Sn[N(CN)_2]$, respectively, which indicate the weighting scheme used in the refinement to be valid. There was no indication of secondary extinction in either structure.[16] The final parameters are listed in Table II. In the last cycle no parameter shifted by more than 0.53σ, and the average shifts in all parameters were less than 0.13σ and 0.07σ in $(CH_3)_2Sn[N(CN)_2]_2$ and $(CH_3)_3Sn[N(CN)_2]$, respectively. The magnitudes of the principal axes of the thermal vibration ellipsoids are listed in Table III. Selected bond distances and angles are listed in Table IV.

Discussion

Both crystal structures are composed of planar $N(CN)_2$ groups symmetrically disposed on either side of the organotin groups. In trimethyltin(IV) dicyanamide the space group requires the $N(CN)_2$ group to be planar. In dimethyltin(IV) bisdicyanamide the distances of the various atoms from the weighted least-squares plane[17] are as follows: N, 0.0014 Å; C(1), −0.0017 Å; N(1), 0.0010 Å; C(2), −0.0010 Å; N(2), 0.0008 Å. Therefore the $N(CN)_2$ group should be considered planar. The central C–N distances in both structures are not merely shorter than the C–N single-bond length (1.47 Å), but their average value of 1.276 Å is about the same as the C–N double-bond length (1.287 Å).[18] The shortening, an average value

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(14) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(15) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(16) A listing of structure factor amplitudes for observed reflections will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(17) The equation or the plane in monoclinic coordinates is $-4.611X + 6.464Y + 3.144Z - 0.096 = 0$.

(18) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 228.

TABLE III
MAGNITUDES (Å) OF THE PRINCIPAL AXES OF THE THERMAL VIBRATION ELLIPSOIDS

	Axis 1	Axis 2	Axis 3
	$(CH_3)_2Sn[N(CN)_2]_2$		
Sn	0.143	0.163	0.197
N(1)	0.160	0.231	0.274
C(1)	0.158	0.189	0.207
N	0.157	0.197	0.336
C(2)	0.154	0.187	0.220
N(2)	0.156	0.237	0.278
CH_3	0.179	0.241	0.248
	$(CH_3)_3Sn[N(CN)_2]$		
Sn	0.206	0.264	0.270
N(1)	0.193	0.334	0.346
C(1)	0.229	0.274	0.309
N	0.192	0.280	0.551
C(2)	0.203	0.286	0.333
N(2)	0.216	0.312	0.381
$CH_3(1)$	0.230	0.303	0.347
$CH_3(2)$	0.240	0.314	0.337

TABLE IV
SELECTED BOND LENGTHS (Å) AND ANGLES (DEG)

	$(CH_3)_2Sn[N(CN)_2]_2$		
Sn–N(1)	2.289 (6)	Sn–N(1)–C(1)	174.0 (6)
Sn–N(2)	2.289 (5)	Sn–N(2)–C(2)	177.1 (6)
N(1)–C(1)	1.138 (9)	N(1)–C(1)–N	171.8 (7)
N(2)–C(2)	1.125 (7)	N(2)–C(2)–N	172.8 (8)
N–C(1)	1.281 (10)	C(1)–N–C(2)	124.2 (8)
N–C(2)	1.297 (8)	N(1)–Sn–CH_3	89.4 (3)
Sn–CH_3	2.091 (8)	N(2)–Sn–CH_3	89.7 (3)
		N(1)–Sn–N(2)	90.4 (3)
	$(CH_3)_3Sn[N(CN)_2]$		
Sn–N(1)	2.338 (9)	Sn–N(1)–C(1)	174.8 (9)
Sn–N(2)	2.333 (9)	Sn–N(2)–C(2)	173.7 (10)
N(1)–C(1)	1.109 (14)	N(1)–C(1)–N	172.1 (12)
N(2)–C(2)	1.123 (13)	N(2)–C(2)–N	174.3 (13)
N–C(1)	1.288 (14)	C(1)–N–C(2)	129.6 (11)
N–C(2)	1.237 (15)	N(1)–Sn–$CH_3(1)$	89.1 (4)
Sn–$CH_3(1)$	2.129 (11)	N(1)–Sn–$CH_3(2)$	90.0 (3)
Sn–$CH_3(2)$	2.130 (8)	N(2)–Sn–$CH_3(1)$	88.7 (5)
		N(2)–Sn–$CH_3(2)$	91.2 (3)
		N(1)–Sn–N(2)	177.8 (4)
		$CH_3(1)$–Sn–$CH_3(2)$	120.9 (2)
		$CH_3(2)$–Sn–$CH_3(2)$	118.2 (4)

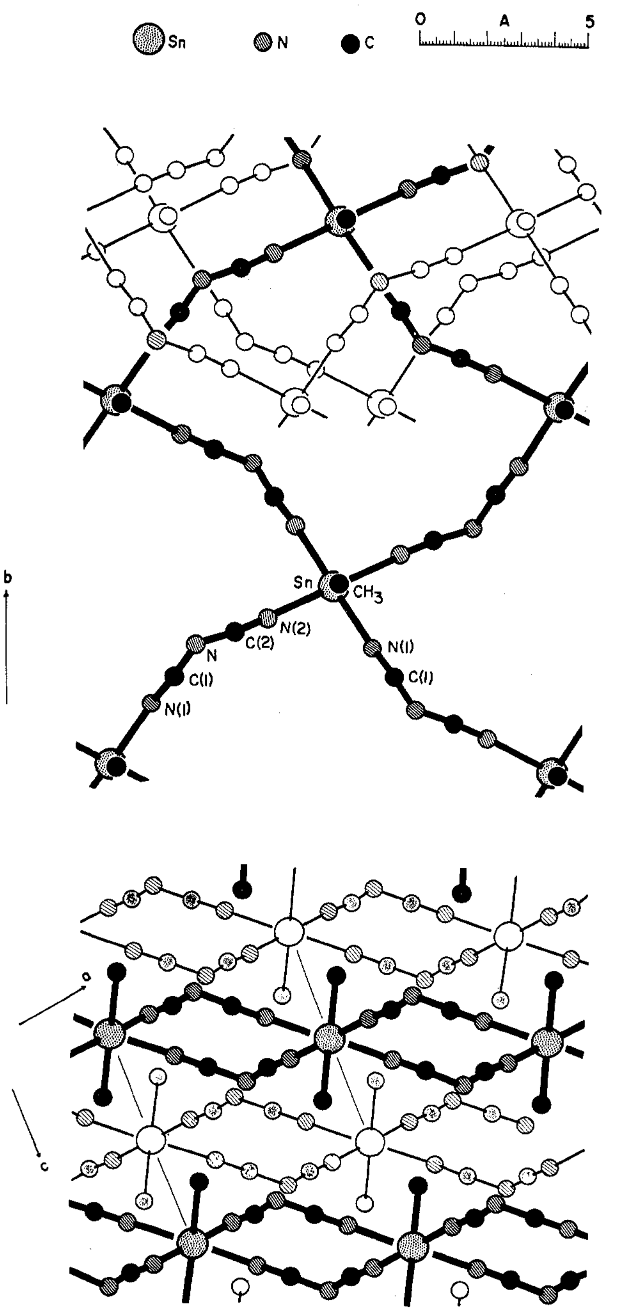
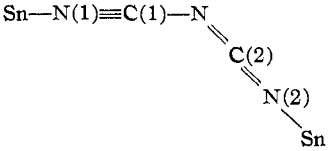
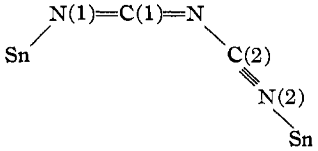


Figure 1.—Crystal structure of $(CH_3)_2Sn[N(CN)_2]_2$: top, view on ($\bar{1}$02) plane; bottom, view on (010) plane.

as large as 0.20 Å, cannot be ascribed solely to the effect of the hybridization of the carbon and nitrogen atoms.[19] If the effects of resonance forms III and IV are accounted for, then the central C–N distances should have values which correspond to partially single-bond



III



IV

and partially double-bond character, and the cyano C–N distances should have values which correspond to partially double-bond and partially triple-bond character. However, in addition to the shorter central C–N distances the cyano C–N distances reported here are no longer than the usual C–N triple-bond length of 1.158 Å.[20] It is still by no means clear what other factors are important in causing these shorter C–N distances. This phenomenon occurs in many other compounds, for example, N_2O, HN_3, cyanates, isothiocyanates,[6] $S(CN)_2$,[21,22] H_2NCN,[23] $Se(SeCN)_2$,[24] $Se(SCN)_2$,[25] and $CH_2(SCN)_2$.[26] In nitrous oxide the N–N distance is almost as short as the triple bond in N_2; at the same time the N–O distance is almost as short as a nitrogen–oxygen double bond. Although the effect of intramolecular donor–acceptor interactions to some extent offers an explanation for the bond

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TABLE V
COMPARISON OF AVERAGE BOND DISTANCES IN DICYANAMIDES WITH THOSE IN RELATED COMPOUNDS

Compd	Confign[a] around tin	Value, Å	Ref
	Sn–N		
$(CH_3)_3Sn[N(CN)_2]$	$\sim D_{3h}$	2.335 (9)	*b*
$(CH_3)_3SnNCS$	$\sim D_{3h}$	2.15 (6)	*c*
$(CH_3)_3SnCN$	$\sim D_{3h}$	2.49 (2)	*d*
$(CH_3)_3SnC(CN)_3 \cdot H_2O$	$\sim D_{3h}$	2.36 (3)	*e*
$[((CH_3)_2SnNCS)_2O]_2$	v dist D_{3h}	2.39 (8)	*f*
	v dist O_h	2.06 (4)	
$(CH_3)_2Sn[N(CN)_2]_2$	$\sim O_h$	2.289 (6)	*b*
$(CH_3)_2Sn(NCS)_2$	v dist O_h	2.10 (2)	*g*
$(CH_3)_2Sn(CN)_2$	v dist O_h	2.27 (7)	*h*
$(CH_3)_2Sn(C_9H_6NO)_2$	v dist O_h	2.35 (4)	*i*
	$Sn–CH_3$		
$(CH_3)_ySnX_{4-y}$ (X = Cl, Br, I; y = 1–3)	$\sim T_d$	2.18 (3)	*j*
$(CH_3)_3Sn[N(CN)_2]$	$\sim D_{3h}$	2.130 (11)	*b*
$(CH_3)_3SnNCS$	$\sim D_{3h}$	2.13 (3)	*c*
$(CH_3)_3SnCN$	$\sim D_{3h}$	2.16 (3)	*d*
$(CH_3)_3SnC(CN)_3 \cdot H_2O$	$\sim D_{3h}$	2.21 (7)	*e*
$(CH_3)_3SnNCO \cdot (CH_3)_3SnOH$	$\sim D_{3h}$	2.16 (8)	*k*
$[(CH_3)_2SnNCS)_2O]_2$	v dist D_{3h}	2.15 (3)	*f*
	v dist O_h	2.07 (3)	
$(CH_3)_2Sn[N(CN)_2]_2$	$\sim O_h$	2.091 (8)	*b*
$(CH_3)_2Sn(NCS)_2$	v dist O_h	2.14 (3)	*g*
$(CH_3)_2Sn(CN)_2$	v dist O_h	2.11 (5)	*h*
$(CH_3)_2SnCl_2$	v dist O_h	2.21 (8)	*l*
$(CH_3)_2SnF_2$	O_h	2.08 (2)	*m*
	C–N		
$(CH_3)_3Sn[N(CN)_2]$	$\sim D_{3h}$	1.116 (14) 1.263 (15)	*b*
$(CH_3)_2Sn[N(CN)_2]_2$	$\sim O_h$	1.132 (9) 1.289 (10)	*b*
$(CH_3)_3SnNCS$	$\sim D_{3h}$	1.15 (7)	*l*
$(CH_3)_2Sn(NCS)_2$	v dist O_h	1.15 (5)	*g*
$(CH_3)_3SnC(CN)_3 \cdot H_2O$	$\sim D_{3h}$	1.15 (5)	*e*
$(CH_3)_3SnNCO \cdot (CH_3)_3SnOH$	$\sim D_{3h}$	1.03 (9)	*k*

[a] Key: ~, slightly distorted; v dist, very distorted. [b] This work. [c] Reference 2. [d] Reference 3. [e] Y. M. Chow, Ph.D. Thesis, University of Minnesota, 1970. [f] Y. M. Chow, *Inorg. Chem.*, **10**, 673 (1971) [g] Reference 6. [h] Reference 7. [i] E. O. Schlemper, *Inorg. Chem.*, **6**, 2012 (1967). [j] L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958. [k] J. B. Hall, Ph.D. Thesis, University of Minnesota, 1969. [l] Reference 5. [m] Reference 4.

shortening in N_2O and its isoelectronic molecules,[27] it is still far from perfect.

The N–C(1)–N(1) and N–C(2)–N(2) angles clearly indicate the nonlinear bonding at the cyanide carbon atom, which also has been found in $As(CN)_3$,[28] $P(CN)_3$,[29] $(CH_3)As(CN)_2$,[30] and $S(CN)_2$. Steric repulsion has been used to explain this kind of bending.[31]

The crystal structure of dimethyltin(IV) bisdicyanamide is shown in Figure 1. It is similar to that of dimethyltin difluoride, consisting of an infinite two-dimensional network of tin atoms and bridging $N(CN)_2$ groups with the methyl groups above and below the $Sn(N(1),N(2))_2$ plane completing the slightly distorted octahedral arrangement of the tin. There is no significant difference between the Sn–N(1) and Sn–N(2) distances, which are longer than the calculated single-bond covalent distance. The van der Waals radius of nitrogen is about 0.15 Å larger than that of fluoride. The difference between the Sn–N bond distance in dimethyltin(IV) bisdicyanamide and the Sn–F bond distance in dimethyltin difluoride is 0.17 Å. It seems reasonable to consider the Sn–N bond in $(CH_3)_2Sn[N(CN)_2]_2$ to be as ionic as the Sn–F bond in $(CH_3)_2SnF_2$. The $(CH_3)_2Sn$ group for slightly distorted octahedral hexacoordinated tin is linear. The $Sn–CH_3$ distance is 2.091 (8) Å, as short as that in dimethyltin difluoride, and significantly shorter than that in tetrahedrally coordinated tin and trigonal-bipyramidally coordinated tin (Table V). It is possible that in the octahedral structures the two bonds in the linear dimethyltin group may be constructed essentially with sp hybridization of the tin atom and that this causes the shortening of $Sn–CH_3$ bond.

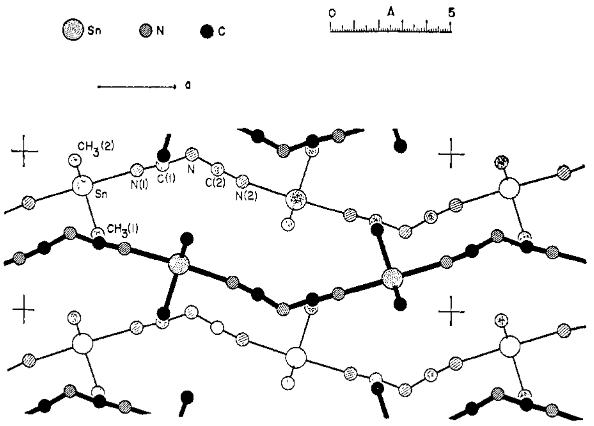

Figure 2.—Crystal structure of $(CH_3)_3Sn[N(CN)_2]$; view on (001) plane.

The crystal structure of trimethyltin(IV) dicyanamide is shown in Figure 2. It is similar to trimethyltin cyanide, consisting of infinite chains. The tin atoms are in a trigonal-bipyramidal environment with three equatorial methyl groups and equidistant axial dicyanamide groups. The average Sn–N distance is 2.335 (9) Å, which is longer than that in dimethyltin(IV) bisdicyanamide and similar to that in trimethyltin tricyanomethanide hydrate.[32] Probably the Sn–N bond is more ionic in trimethyltin compounds than in dimethyltin compounds. The trimethyltin group is planar with approximate D_{3h} symmetry and the $Sn–CH_3$ distance of 2.130 (11) Å is not as short as that in dimethyltin(IV) bisdicyanamide. No distance between the atoms of the nearest chains is shorter than the sum of the van der Waals radii. From the crystal structures of the dicyanamides reported here, one probably would expect chain and layer structures consisting of bridging planar $C(CN)_3$ groups in dimethyltin(IV) bistricyanomethanide and trimethyltin(IV) tricyanomethanide.

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