CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA 55455

The Crystal Structure of Dimethyltin Diisothiocyanate

BY YEH MEI CHOW

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Dimethyltin diisothiocyanate forms orthorhombic crystals in the space group Pmmn with $a = 9.82 \pm 0.02$ Å, $b = 7.87 \pm 0.01$ Å, and $c = 5.57 \pm 0.01$ Å. The structure was determined from 147 photographically collected intensities and was refined by the least-squares method to an R factor of 4.6%. The structure is polymeric and consists of infinite chains of weakly linked $Sn(CH_3)_2(NCS)_2$ molecules. The individual molecule may be considered as a strongly distorted tetrahedron with CH_3–Sn–CH_3 and N–Sn–N angles to be 145.9 ± 1.4 and 84.1 ± 1.6°, respectively. It has mm2 symmetry with the distances Sn–C(CH_3) = 2.14 ± 0.03 Å, Sn–N = 2.10 ± 0.02 Å, N–C = 1.15 ± 0.05 Å, and C–S = 1.60 ± 0.04 Å. The N–C–S angle is 179.3 ± 2.8° indicating the linearity of the NCS group. The distance between the two sulfur atoms in one molecule and the tin atom in the adjacent molecule, 3.21 ± 0.01 Å, is smaller than the sum of van der Waals radii. This suggests the presence of intermolecular donor–acceptor bonding leading to the formation of infinite chains.

Introduction

The crystal structure reported here was a part of a general investigation of intermolecular interactions of pseudohalogens and heavy atoms in the solid states. Recent review articles[1-3] have discussed intermolecular donor–acceptor bonding from the lone pairs of pseudohalogens to the unfilled orbitals of heavy atoms. The investigation of dimethyltin diisothiocyanate was motivated by the recent determination of the crystal structure of trimethyltin isothiocyanate.[4] The structure of trimethyltin isothiocyanate is polymeric, consisting of infinite zigzag chains. The discrete molecules are linked by donor–acceptor bonding between sulfur and the tin atom of the adjacent molecule, thus leading to a coordination number for tin of 5. Since in dimethyltin diisothiocyanate there are two isothiocyanate groups, the question occurs of whether the two sulfur atoms both will form intermolecular donor–acceptor bonds with tin atoms of adjacent molecules leading to a hexacoordinated tin or whether only one sulfur atom will bond to a neighboring tin atom, leading to pentacoordinated tin as in trimethyltin isothiocyanate.

Experimental Section

Dimethyltin diisothiocyanate was prepared by mixing dimethyltin dichloride and potassium thiocyanate in ethanol. Recrystallization from benzene containing a small amount of methanol gave needlelike crystals. The melting point of the crystals was 184–188°, which was lower than the reported[5] value of 194–196°. The infrared spectrum in a halocarbon mull showed two strong N–C stretching bands at 2088 and 2062 cm^{-1}, in agreement with the reported data.[6]

Space Group and Unit Cell

Oscillation, Weissenberg, and precession photographs were taken with Mo Kα radiation (λ 0.7107 Å) of a crystal mounted for rotation about the needle axis (c axis). The crystal is orthorhombic with $a = 9.82 \pm 0.02$ Å, $b = 7.87 \pm 0.01$ Å, and $c = 5.57 \pm 0.01$ Å; the errors are estimated to be 1 part in 600, characteristic accuracy with the precession camera. The molecular volume is 215 $Å^3$ and the calculated density is 2.05 g/cm^3 for two molecules per unit cell. Systematic extinctions $h + k$ odd in $hk0$ indicated $P2_1mn$ or Pmmn to be the space group. The latter would require a molecular structure similar to dimethyltin dicyanide[7] with mm2 symmetry. The spoon test for pyroelectricity described by Bunn gave negative results so that the space group could not be identified on this basis.

A crystal elongated along c with a length of 0.5 mm, and with approximate widths 0.06 mm for (010), 0.03 mm for (100) faces, was mounted in a glass capillary for intensity measurements.[8] Precession intensity data were collected for layers $0kl$ to $2kl$, $h0l$ to $h2l$, kkl to $(k + 3)kl$ using unfiltered Mo Kα radiation. All the relative intensities were estimated by visual comparison to an intensity strip. There were 147 independent reflections of observable intensity. Lorentz and polarization corrections were made. The linear absorption coefficient for the Mo Kα radiation was 33.7 cm^{-1}. The maximum effect on the intensities that the neglect of absorption causes is about 10%. No absorption correction was made.

Determination of the Structure

The approximate tin and sulfur positions were revealed from a three-dimensional Patterson map. A three-dimensional Fourier map obtained in the Pmmn space group with tin and sulfur determining the phases showed the positions of the light atoms with peak heights proportional to their atomic numbers. Resulting structure factor calculations, using isotropic temperature factors of 2.0, gave R $(\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.23$. Fourier maps with $P2_1mn$ as the space

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(1) D. Britton, *Perspec. Struct. Chem.*, **1**, 109 (1967).

(2) J. S. Thayer and R. West, *Advan. Organometal. Chem.*, **15**, 169 (1967).

(3) M. F. Lappert and H. Pyszora, *Advan. Inorg. Chem. Radiochem.*, **9**, 133 (1966).

(4) J. B. Hall, *Inorg. Chem.*, in press.

(5) M. Wada, M. Nishino, and R. Okawara, *J. Organometal. Chem.* (Amsterdam), **3**, 70 (1965).

(6) R. Okawara, *ibid.*, **8**, 261 (1967).

(7) J. Konnert and D. Britton, unpublished work.

(8) The crystal discolored on a few weeks standing in the air. It was felt this decomposition might be accelerated in the heat of the X-ray beam, so it was sealed in a glass capillary. It is possible that this precaution is unnecessary.

group were also calculated, but the maps confirmed that Pmmn was the space group.[9]

A full-matrix least-squares refinement was carried out with the position parameters and isotropic temperature parameters of all atoms, minimizing the function $\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$. The weighting scheme was $w = 1.0$ for $F_o < 32.6$ and $w = (32.6/F_o)^4$ for $F_o > 32.6$. After five cycles of refinement the values of r $[\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4]$ and R were 0.0403 and 0.079, respectively. A difference Fourier map showed anisotropic vibration of tin and sulfur atoms. The refinement with anisotropic thermal parameters was then continued. The successive r and R values were the following: all atoms isotropic, 0.0403 and 0.079; only Sn ansiotropic, 0.0156 and 0.047; only Sn and S anisotropic, 0.0136 and 0.046; all atoms anisotropic, 0.0129 and 0.045. A comparison of these r values according to the method of Hamilton[10] indicated the refinement should have been terminated with only tin and sulfur anisotropic. The parameters from this cycle are therefore chosen as the final set, and are given in Table I. The corresponding principal axes of the ellipsoids of vibration of tin and sulfur are given in Table II. The observed and calculated structure factors are given in Table III. The estimated standard deviations quoted from the parameters should be used with caution. The low R value may be in part fortuitous, owning to the smaller number of reflections. In addition, the neglect of the absorption corrections must surely affect the anisotropic thermal parameters significantly.

TABLE I

POSITIONAL PARAMETERS AND THERMAL PARAMETERS

Positional Parameters

	X ($10^4\sigma$)	Y ($10^4\sigma$)	Z ($10^4\sigma$)
Sn	$^1/_4$	$^1/_4$	0.0438 (5)
S	0.5325 (10)	$^1/_4$	0.3341 (14)
N	0.3930 (29)	$^1/_4$	0.7638 (45)
C(NCS)	0.4521 (32)	$^1/_4$	0.5848 (58)
C(CH_3)	$^1/_4$	0.5102 (40)	0.1567 (47)

Thermal Parameters

	β (σ)	β_{11} ($10^4\sigma$)	β_{22} ($10^4\sigma$)	β_{33} ($10^4\sigma$)	β_{13} ($10^4\sigma$)
Sn		0.0121 (5)	0.0121 (5)	0.0172 (10)	
S		0.0135 (15)	0.0236 (22)	0.0269 (36)	0.0046 (17)
N	4.88 (0.57)				
C(NCS)	4.41 (0.70)				
C(CH_3)	4.75 (0.70)				

Discussion

The crystal stucture is shown in Figure 1. The individual molecule may be considered as a distorted tetrahedron similar to that in dimethyltin dicyanide.[7] The Sn–C(CH_3) distance of 2.14 ± 0.03 is normal as compared with those in other methyl tin compounds (Table IV). The Sn–N distance, 2.10 ± 0.02 Å, is equal to the sum of the single bond covalent radii. The CH_3–Sn–CH_3 angle and the N–Sn–N angle are similar to the corresponding angles in dimethyltin dicyanide. The N–C–S angle is 179.3 ± 2.8°, indicating linearity of the NCS group. If we compare the distances N–C, C–S and the angle Sn–N–C with those in other isothiocyanates[11–13] nothing unusual is found in our $(CH_3)_2Sn(NCS)_2$ results. Bonding in organometallic isothiocyanates generally is not well understood.

TABLE II

PARAMETERS FOR THE ELLIPSOIDS OF VIBRATION

	Root-mean square amplitude, Å ($10^3\sigma$)	Angle with a axis (σ)	Angle with b axis (σ)	Angle with c axis (σ)
Sn	0.164 (5)	90.0	90.0	0.0
	0.195 (4)	90.0	180.0	90.0
	0.244 (5)	0.0	90.0	90.0
S	0.191 (16)	113.6 (7.8)	90.0	23.7 (7.8)
	0.267 (12)	156.3 (7.8)	90.0	113.7 (7.8)
	0.272 (12)	90.0	0.0	90.0

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
H=0				0	3	495	-490	7	0	312	332	0	2	201	203	0	3	415	429	3	2	427	429
0	1	552	561	0	4	383	-384	7	1	297	300	0	3	407	399	1	1	475	-450	4	2	337	-352
0	2	290	297	0	5	320	-338	H=2				0	4	373	385	1	2	196	-167	5	0	261	-239
0	3	606	621	0	6	267	-249	0	0	421	-368	0	5	199	248	1	3	271	-247	5	1	321	-322
1	1	364	-369	1	0	948	-1018	0	1	1171	-1225	1	0	619	706	1	4	415	-428	5	2	323	-313
1	3	460	-466	1	1	761	-848	0	2	744	-720	1	1	608	634	2	0	636	-633	H=6			
1	4	663	-662	1	2	576	-586	0	4	297	-274	1	2	530	527	2	1	396	-378	0	0	495	-500
2	0	1669	-1559	1	3	323	-338	1	2	560	564	1	3	508	508	2	2	462	-453	0	1	460	-466
2	1	343	-350	1	4	275	-266	1	3	465	454	2	1	413	-420	2	3	473	-479	0	2	323	-329
2	2	373	-378	2	2	332	338	1	5	438	460	2	3	348	-349	3	1	335	355	1	2	274	243
2	3	674	-688	2	3	424	421	2	1	876	901	2	4	381	-406	3	4	353	358	1	3	290	277
3	1	366	305	2	4	388	414	2	2	747	716	3	0	600	-611	4	0	628	599	2	0	345	348
3	2	220	146	2	5	344	362	2	3	210	202	3	1	544	-534	4	1	381	371	2	1	378	370
3	3	418	391	2	6	253	245	2	6	313	304	3	2	437	-429	4	2	321	316	2	2	335	337
3	4	598	545	3	0	755	797	3	2	486	-463	3	3	437	-406	4	3	309	302	4	0	335	-351
4	0	1242	1165	3	1	699	685	3	3	410	-384	4	1	403	383	6	0	320	-332	4	1	312	-331
4	1	456	419	3	2	479	480	3	5	381	-387	4	3	274	291	H=5				H=7			
4	2	290	273	3	3	288	279	4	0	373	-328	4	4	288	285	0	2	532	-535	0	1	266	236
4	3	440	423	3	4	288	218	4	1	745	-718	5	0	405	414	0	3	242	-229	0	3	277	264
5	3	305	-278	4	2	392	-371	4	2	483	-484	5	1	321	369	0	4	207	-193	1	0	524	524
6	0	638	-593	4	3	332	-342	5	2	297	293	5	2	286	316	1	0	388	-361	1	1	301	279
6	1	256	-258	4	4	313	-289	5	3	313	277	5	3	304	302	1	1	598	-540	1	3	307	290
6	2	248	-236	5	0	490	-500	6	1	384	414	H=4				1	2	532	-524	5	0	307	302
H=1				5	1	467	-659	6	2	340	341	0	0	986	928	2	2	415	382	H=8			
0	1	203	-138	5	2	345	-359	H=3				0	1	492	513	3	0	321	333	0	0	293	301
0	2	609	-605	5	3	286	-228	0	1	745	718	0	2	452	441	3	1	451	461	0	1	288	312

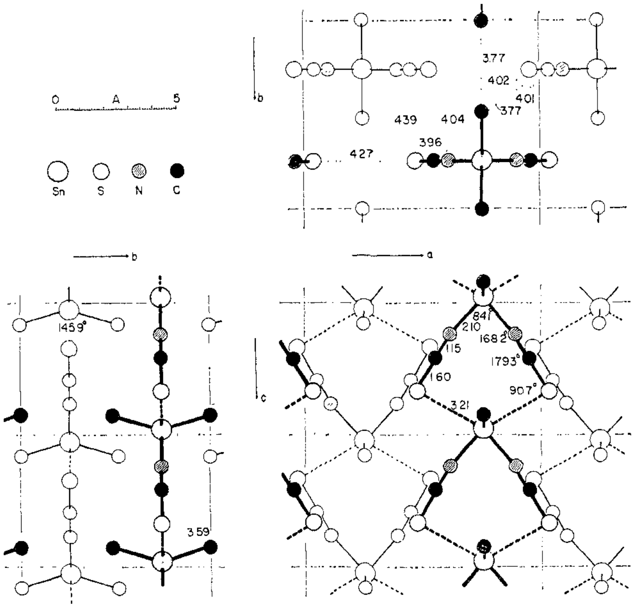

Figure 1.—The crystal structure of $(CH_3)_2Sn(NCS)_2$: top view, along c axis; bottom left view, along a axis; bottom right view, along b axis.

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[9] An all-*trans* structure (around roughly octahedral tin) in space group $P2_1mn$ fit the Patterson map as well. This structure gave a more regular octahedral environment around tin, and gave as reasonable packing as the present reported structure. However, a three-dimensional Fourier map with the phases determined by all of the atoms in the $P2_1mn$ arrangement was unambiguously inferior to that determined similarly for the Pmmn arrangement.

[10] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[11] A. Ferrari and A. Braibanti, *ibid.*, **18**, 367 (1965).

[12] A. C. Hazell, *J. Chem. Soc.*, 5745 (1963).

[13] J. R. Knox and K. Eriks, *Inorg. Chem.*, **7**, 84 (1968).

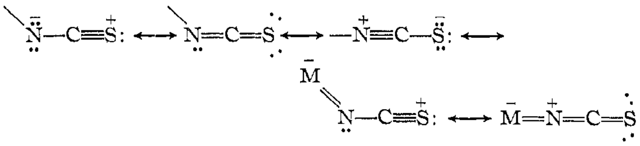
TABLE IV

INTERATOMIC DISTANCES AND ANGLES FOR $(CH_3)_2Sn(NCS)_2$ AND RELATED COMPOUNDS

Dist	Compd	Value, Å	Ref
Sn–C(CH_3)	$(CH_3)_2Sn(CN)_2$	2.11 ± 0.05	7
	$(CH_3)_3SnNCS$	2.16 ± 0.05	4
		2.12 ± 0.04	4
	$(CH_3)_2Sn(NCS)_2$	2.14 ± 0.03	This work
Sn–N	$(CH_3)_3SnNCS$	2.13 ± 0.04	4
	$(CH_3)_2Sn(NCS)_2$	2.10 ± 0.02	This work
N–C	Some other isothiocyanates and bridged thiocyanates	1.07–1.34	11–13
	$(CH_3)_3SnNCS$	1.22 ± 0.07	4
	$(CH_3)_2Sn(NCS)_2$	1.15 ± 0.05	This work
C–S	Some other isothiocyanates and bridged thiocyanates	1.55–1.80	11–13
	$(CH_3)_3SnNCS$	1.56 ± 0.05	4
	$(CH_3)_2Sn(NCS)_2$	1.60 ± 0.04	This work
Sn···S	$(CH_3)_3SnNCS$	3.17 ± 0.01	4
	$(CH_3)_2Sn(NCS)_2$	3.21 ± 0.01	This work
	Sum of van der Waals radii[a]	4.05	14
Angle	**Compd**	**Value, deg**	**Ref**
H_3C–Sn–CH_3	$(CH_3)_2Sn(CN)_2$	148.7 ± 3.5	7
	$(CH_3)_2Sn(NCS)_2$	145.9 ± 1.4	This work
NC–Sn–CN	$(CH_3)_2Sn(CN)_2$	85.3 ± 3.7	7
N–Sn–N	$(CH_3)_2Sn(NCS)_2$	84.1 ± 1.6	This work
Sn–N–C	$(CH_3)_3SnNCS$	176.3 ± 4.1	4
	$(CH_3)_2Sn(NCS)_2$	168.2 ± 2.6	This work
M–N–C	Some other isothiocyanates and bridged thiocyanates	111–180	11–13
N–C–S	$(CH_3)_3SnNCS$	177.8 ± 4.8	4
	$(CH_3)_2Sn(NCS)_2$	179.3 ± 2.8	This work
Sn–S–C	$(CH_3)_3SnNCS$	94.6 ± 1.8	4
	$(CH_3)_2Sn(NCS)_2$	90.7 ± 1.1	This work
Ag–S–C	AgSCN	103.8	*b*
	$AgSCNP(n\text{-}C_3H_7)_3$	98, 103	*c*
Cd–S–C	$Cd(etu)_2(SCN)_2$	109.1 ± 4.4	*d*
Pt–S–C	$\alpha\text{-}Pt_2(SCN)_2Cl_2(P(n\text{-}C_3H_7)_3)_2$	100.7 ± 9.7	*e*
Ni–S–C	$Ni(en)_2NCSI$	100	*f*
Cu–S–C	$Cu_2(NCS)_2(NH_3)_3$	82.6, 88.7, 96.3	*g*
I–S–S	$CHI_3 \cdot 3S_8$	104.4	*h*
	$SbI_3 \cdot 3S_8$	98.79 ± 0.17	*i*
I–S–C	$C_2I_2 \cdot C_4H_8S_2$	104 ± 2	*j*

[a] van der Waals radius of Sn was estimated. [b] I. Lindquist, *Acta Crystallogr.*, **10,** 29 (1957). [c] A. Turco, C. Panattoni, and E. Frasson, *Nature*, **187,** 772 (1960). [d] L. Cavalca, M. Nardell, and G. Fava, *Acta Crystallogr.*, **13,** 125 (1960). [e] P. G. Owston and J. M. Rowe, *ibid.*, **13,** 253 (1960). [f] A. E. Svelasvili, "Abstracts of Papers Presented Before the 7th Congress of the International Union of Crystallography," Moscow, July 1966, No. 9-61. [g] J. Garaj, *Inorg. Chem.*, **8,** 304 (1969). [h] T. Bjorvatten, *Acta Chem. Scand.*, **16,** 749 (1962). [i] T. Bjorvatten, O. Hassel, and A. Lindheim, *ibid.*, **17,** 689 (1963). [j] O. Holmestand and C. Romming, *ibid.*, **20,** 2601 (1966).

Resonance among the following valence bond structures has been discussed[2]



A comparison of our data with Pauling's values[14] (S—C = 1.81 Å, S═C = 1.61 Å, N═C = 1.29 Å, and N≡C = 1.15 Å) gives no strong suggestion of the dominant resonance form in this structure.

The 3.21 ± 0.01 Å Sn···S distance, similar to that in trimethyltin isothiocyanate, is considerably shorter than the sum of van der Waals radii and suggests the presence of intermolecular donor–acceptor bonding. These interactions lead to the formation of infinite chains along the *c* axis. With consideration of the weak donor–acceptor bonding the tin is hexacoordinated. No distance between the atoms of nearest chains is shorter than the sum of the van der Waals radii. The Sn–S–C angle is 90.7 ± 1.1°; this seems to be smaller than similar angles in some other bridged compounds and addition compounds but it is not the only case and it is also not unusual for other sulfur compounds. In $(CH_3)_3SnNCS$ and $(CH_3)_2Sn(NCS)_2$ the Sn–N–C angles are nearer to 180° than 120°. The Si–N–C angle in gaseous $(CH_3)_3SiNCS$, 154 ± 2°, shows a substantial deviation from linearity.[15] It will be interesting to know whether the Ge–N–C angles in $(CH_3)_3GeNCS$ and $(CH_3)_2Ge(NCS)_2$ are similar to those in the corresponding tin compounds or the gaseous silicon compound.

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(14) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 260, 224, 228, 274.

(15) K. Kimura, K. Katada, and S. H. Bauer, *J. Amer. Chem. Soc.*, **88,** 416 (1966).