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# The Crystal and Molecular Structure of an Isomer of Bis-(1,2-diethoxycarbonyl-ethyl)tin Dibromide

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Low mp isomer of bis-(1,2-diethoxycarbonyl-ethyl)tin dibromide (mp 114—115°C) crystallizes in a monoclinic form: a=11.85, b=20.24, c=9.79 Å,  $\beta=101.3^{\circ}$ ; space group,  $P2_1/a$ ; and four molecules are contained in a unit cell. Crystal structure was established by the heavy atom method. The coordination about the tin atom is nearly octahedral. Two bromine atoms attached to the tin atom are in cis-positions. Two ligands, 1,2-diethoxycarbonyl-ethyl groups, are both bound to the tin atom by carbon and oxygen, forming five-membered rings. These rings are rather puckered, and one is in d-form and another in l-form.

Present authors (S. M., S. K., and I. O.) obtained bis-(1,2-diethoxycarbonyl-ethyl)tin dibromide by the direct reaction between tin foil and diethyl bromosuccinate. From the reaction products they had two isomers isolated; their mp's being 114-115°C and 122—123°C respectively.1)

$$Sn + 2 \xrightarrow{Br-CHCOOC_2H_s} \xrightarrow{Br_2Sn} \xrightarrow{CHCOOC_2H_s} \xrightarrow{CH_2COOC_2H_s} \xrightarrow{I. \text{ mp } 114-115^{\circ}C} \xrightarrow{Isomers} \frac{I. \text{ mp } 12-123^{\circ}C}{II. \text{ mp } 122-123^{\circ}C}$$

This paper describes the three-dimensional structure analysis of the isomer crystal I.

#### Experimental

The crystals were obtained by recrystallization from ethanol as colorless needles developed along the c axis. For the determination of the lattice parameters, oscillation and Weissenberg photographs were taken around the a, b, and c axes. Debye lines of aluminum were superposed on the Weissenberg photographs for calibration.

Layers 0 through 5 around the c axis were recorded by multi-film equi-inclination Weissenberg photographs with nickel-filtered  $CuK\alpha$  radiation. 0kl and 1kl reflections were also collected mainly for the use of the inter-layer scaling.

Intensities were estimated visually by using a calibrated standard scale. Lorentz and polarization corrections were carried out, but no absorption correction was made. 2109 non-zero reflections were finally ob-

#### **Crystal Data**

Compound: Low mp isomer of Bis-(1,2-diethoxycarbonyl-ethyl)tin dibromide,

 $Br_2SnC_{16}H_{22}O_8$  $mp = 114 - 115^{\circ}C$ MW = 620.9

Unit Cell: (Cu $K\alpha$  radiation,  $\lambda = 1.5418 \text{ Å}$ ) a = 11.85 Å,Z=4

b = 20.24 Å $U=2302.5 \text{ Å}^3$  $c = 9.79 \,\text{Å},$  $D_m = 1.80 \,\mathrm{g \cdot cm^{-8}}$ 

 $D_x = 1.79 \, \text{g} \cdot \text{cm}^{-8}$  $\beta = 101.3^{\circ}$ 

Space Group:  $P2_1/a$ 

(uniquely determined from the systematic absences of reflections)

## Determination and Refinement of the Structure

Crystal structure was established by the heavy atom method. From a three-dimensional Patterson function approximate parameters of tin and two bromine atoms were obtained. Positions of all the light atoms except hydrogen were then found in the three-dimensional Fourier maps, with phases based on the heavy atoms. Successive block-diagonal least-squares refinement was carried out on a HITAC 5020E computer at the University of Tokyo. After three cycles of refinement for heavy atoms, Sn and Br's, the discrepancy factor  $R = \sum ||F_o| - |F_c||/$  $\sum |F_o|$  was reduced to 0.154. In this refinement unit weight for all the reflections was assigned. Refinement was then made for all of the nonhydrogen atoms and the following weighting scheme was applied in the least-squares refinements hereafter: 1.0 for  $|F_o| > 0.1$  and 0.1 for  $|F_o| \le 0.1$ .

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<sup>1)</sup> S. Matsuda, S. Kikkawa and I. Omae, Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.), 69, 646 (1966).

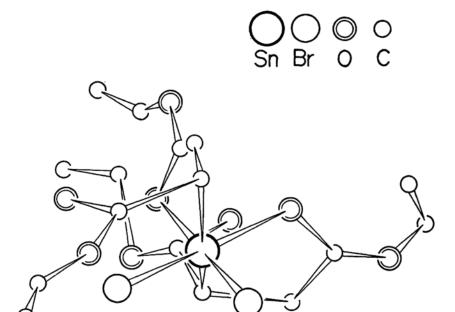


Fig. 1. Molecular structure of bis-(1,2-diethoxycarbonyl-ethyl)tin dibromide.

TABLE 1. ATOMIC POSITIONAL AND THERMAL PARAMETERS FROM THE FINAL LEAST-SQUARES REFINEMENT

Atom	x	y	z	β11	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	β13	β23
Sn	0.1671	0.1295	0.4832	42	11	55	0	29	2
Br(1)	-0.0264	0.1516	0.5434	58	20	144	1	82	-13
Br(2)	0.2862	0.1143	0.7326	79	24	96	-4	-6	6
O(1)	0.332	0.096	0.381	2.8					
O(2)	0.415	0.007	0.314	4.3					
O(3)	0.125	-0.003	0.193	5.5					
O(4)	-0.032	0.027	0.283	3.3					
C(1)	0.339	0.041	0.381	3.8					
C(2)	0.274	-0.007	0.453	4.0					
C(3)	0.147	0.021	0.430	2.4					
C(4)	0.487	0.049	0.244	4.4					
C(5)	0.415	0.065	0.101	5.4					
C(6)	0.077	0.014	0.300	4.0					
C(7)	-0.108	0.024	0.128	5.5					
<b>C</b> (8)	-0.208	0.066	0.164	5.6					
O(10)	0.100	0.153	0.237	4.9					
O(20)	0.138	0.214	0.063	5.9					
O(30)	0.077	0.304	0.391	5.3					
O(40)	0.168	0.291	0.616	3.4					
C(10)	0.158	0.196	0.191	4.8					
C(20)	0.244	0.234	0.279	4.7					
C(30)	0.235	0.229	0.437	2.5					
C(40)	0.056	0.169	-0.043	5.0					
C(50)	-0.049	0.212	-0.048	7.8					
C(60)	0.150	0.279	0.489	3.0					
C(70)	0.077	0.331	0.668	4.6					
C(80)	0.129	0.352	0.810	5.1					

The values of anisotropic thermal parameters for heavy atoms are ×104, and those for the light atoms are isotropic B in  $Å^2$ . The estimated standard deviation  $\sigma(r)$  for Sn is 0.0025 Å and for Br about 0.004 Å.

TABLE 2. THE OBSERVED AND CALCULATED STRUCTURE FACTORS

K FO FC K FO FC	K FO FC K FO	FC K FO FC	K FO FC	K FO FC	K PO FC K-FO FC
H,L= 0 0 10 66 61 4 218-212 11 98 -65	10 0 16 13 75 2 66 73 140 0	76 1 133-133 19 2 149-149	7 82 80 8- 0 16		5 163 160 13 0 .20 6 34 31 14 0 33
6 190 180 12 46 -41 8 258 254 13 95 57	30 0 -29 15 74 40 0 -17 16 86	80 3 138 141 93 4 44 -42	90 0 -27 100 0 -10	5 66 -61 6 59 50 7 131 137 8 66 -91	7 158-164 15 71 -85
10 35 -23 14 40 -30 12 132-129 15 41 48	0 20 -42 18* 0	81 50 0 24 6 6 130-129	11 79 -82 12• 0 -17	10 42 -20	10 0 3 1 60 45
14 68 72 16 99 63 16 28 34 17 29 -29 Hile 1 0 18 0 12		62 7 99-107 62 8 174 198	13 56 52 14 56 45 15 55 58	11 106-103 12 82 89	11 73 73 2 79 -73 12 97 96 3 71 -66
3 142-144 20 24 -34	8 97 58 20 67 90 0 26 21 37 10 38 39 H <sub>2</sub> L 8 1 130-1 0 213-403 2 44	44 9 31 -41 1 100 0 8	15 55 58 H,Le 9 1 1 38 39 2 76 -80	13. 0 29 14. 0 31 15. 0 32	12 97 96 3 71 -66 13 118 124 4 0 -18 14 0 -23 5 0 -6 15 68 -59 6 75 68
	0 213-403 2 44 1 25 15 3 35	10 134 0 35	2 76 -80	16 80 -/4	16 70 -60 7 76 63 17 58 -55 8 0 0
5 47 34 0 138 143 6 229 227 1 134 129 7 222 206 2 29 -24 8 47 44 3 97 86	1 25 15 3 35 2 36 33 4 30 3 30 36 5 56 4 215 222 6 48	17 140 0 3 54 15 39 -38	4. 0 11 5. 0 -36	18+ 6 -15 19+ 6 -17 20 56 60	18. 0 20 9 56 -49 19 70 79 10 70 -70 20. 0 6 11 71 -60
			6 68 50. 7 79 79 8 0 -13	H.L1 2	21. 0 39 12. 0 -6
11 99 -95 6 0 18 12 23 -26 7 23 -27 13 60 61 8 81 81	7 129-126 9 28 8 231-208 10 60 9- 0 -8 11 78 -	32 1 50 -35 60 2 29 26	90 0 27 100 0 -15	2 22 -21 3 197-227	23 30 -48 14 0 47 H,Lm 4 2 15 0 47 0 49 -28 16 0 -3
10 208-106 5 61-60 11 99-95 6 0 18 12 23 -26 7 23 -27 13 60 61 8 81 81 14 99 101 9 51 52 15 27 28 10 93-95 16 0 23 110 0 12	8 231-208 10 60 9 0 -8 11 78 - 10 91 77 12 0	60 2 20 26 79 3 73 -76 30 4 218 248 77 5 62 66	11 39 -39 120 0 12 130 0 -22 140 0 -15	1 41 43 2 22 -21 3 197-227 4 34 31 5 75 -78 6 42 -28	0 49 -28 160 0 -3 1 161 164 170 0 -37 2 43 -38 18 49 -49 3 73 67 H.L= -7 2
14 99 101 9 91 52 15 27 28 10 93 -55 16* 0 23 11* 0 12 17 50 -45 12 105-100	110 0 22 13 79 - 12 99 89 14 36 - 130 0 -6 15 85	42 60 8 -5 81 70 0 -3	140 0 -15 15 50 58	8 35 36	4 65 68 19 0 -28
18 06 -80 13 0 -15	14 78 -69 16 0 15 51 -39 17 0	0 8 148-152 33 9 49 -41	1 74 76	90 0 -17 10 71 57	5 102 -90
20 0 16 15 0 12 21 0 -1 16 0 23 22 26 39 17 0 -26 H,L= 2 0 18 49 -44 0 72 -73 19 0 0	16 44 -28 18 0 17 37 -34 19 104-1 18 46 39 20 0	0 8 148-152 33 9 49-41 19 10 36 42 25 110 0 9 17 12 101 106 -9 H.L6 1 -3 0 128-134 71 1 38 46 1 2 27-19	1 74 76 2 0 12 3 74 -74 4 65 -47 5 76 -76	12 46 -44 13 0 1	7 105-103 4 46 37 8 116-108 5 47 37 9 87 78 6 49 -54 10 34 -38 7 0 17 11 62 61 8+ 0 -7
A,LE 2 U 18 49 -44	190 0 20 210 0	-9 H.L = -6 1 -3 0 128-134	4 65 -47 5 76 -76 6 0 1	14 82 -79 15• 0 32	10 34 -38 7 0 17 11 62 61 8 0 -7
1 1//-100 20 25 -2/	21 0 24 23 51 22 33 -24 Hale -3	71 1 38 46 1 2. 27 -19.		160 0 48	13 _86 -79 10 .9488 .
3 84 81 1 105 111 4 84 83 2 40 -38 5 155 138 3 84 -84	20 0 26 22 0 21 0 0 24 23 51 22 33 -24 Hile -3 Hile 1 1 1 166 1 1 87 -97 2 249 2 2 112 115 3 95 - 3 90 86 4 117-1	54 3• 0 -5 250 4 70 67 78 5 66 -66	9 56 50 10 56 -10 11 39 -67	18 83 87 19 0 11 20 40 -52	15. 0 -30 12. 0 25
6 186 183 4 74 -49 7• 0 8 5 95 -52	A 07 01 E 164-1	70 7 56 47	12 39 -48	22 50 -65	170 0 33 14 83 -87
8 159-143 6 80 79	5 32 -37 6 77	63 8 56 -49 68 9 58 53 -2 10 70 78 16 11 63 -58	140 0 19 15 52 59 H,L= 10 1 00 0 12	23 46 -3 H.L. 2 2 0 98 70	19. 0 34 16. 0 29 26 74 78 17. 0 -8 H,L= -4 2 18 75 83 0 86 -96 H,L= 8 2
10 113-115 8 26 25 11 55 -47 9 54 66 12 125 123 10 68 -60	8- 0 22 9 124 1 9 89 86 10 29		0. 0 12 1 69 -65		H,L= -4 ? 18 75 83 0 86 -96 H,L= 8 2 1 207-236 0+ 0 -27
13 109 107 11* 0 -21 14 45 46 12 41 -34	10 99 81 11 62 6	60 13• 8 8 57 14 68 -68	1 69 -65 2• 0 8 3• 0 -30	2 65 -65 3 116-123 4 171-182	
15* 0 5 13 29 -38 16 90 -98 14 84 90 17 72 -78 15 41 36	13 121-119 14- 0	97 15 69 59 24 16 0 -25	3. 0 -30 4. 0 1 5 69 85 6. 0 9	5 100 91 6* 0 0 7 117 116	5 226 240   4   0   3
180 0 -20 160 0 -5	14 70 -74 15 100 1 15 52 -52 16* 0 - 16* 0 16 17 79	11 18 66 54 88 H.L. 7 1	7• 0 <b>-8</b>	8 0 15 9 136-134	6 113 99 50 0 7 7 111 117 60 0 36 80 0 -9 70 0 0 9 173-172 80 0 1
- 20 57 63 16 93 -64 21 48 62 190 0 -10	17 55 50 18 0 - 18 30 54 10 68 -	11 18 66 54 88 H.L. 7 1 12 1 64 -60 73 2 106 107	9. 5560.	10 <u>6121</u>	10 56 -47 9 41 -41
22* 0 -17 20* 0 31 23* 0 4 21* 0 -15 24* 0 -28 22 29 42	19° 0 30 H,L= 4 20 38 -45 0 45 H,L= -1 1 1 68 - 1 65 -75 2 69	1 3 61 91 53 4 67 73 66 5 59 48	0 76 91 1 103 111	12. 0 20 13 81 81	11 48 -40 10 0 -16 12 114 102 11 41 -27
25 0 -49 H,LE 8 0	1 65 -75 2 69 2 195-192 3- 1	55 6 119-122 -6 7 79 -80	2 0 -2 3 68 66 4 68 -25	14. 0 -20 15. 0 30 16. 0 -26	10 56 -47 9 41 -41 11 48 -40 100 0 -16 12 114 107 11 41 -27 13 92 88 12 41 40 H <sub>1</sub> L <sub>0</sub> 5 2 13 0 45 -1 110 105 140 0 8 2 145 180 150 0 8
H,L+ 3 0 1 44 -46 1 27 4 2+ 0 -1	3 130 136 4 81 - 4 55 -62 5 85	71 8 36 -44 81 90 0 4	5 88-105 6• 0 -2	16. 0 -26 17 41 -54 18. 0 25	1 110 105 140 0 8 2 165 180 150 0 8 3 140-148 160 0 -26
2 137 132 3 98 -63 3 44 -34 4 65 67 4 82 -65 5 26 25	5 274 282 6 75 •	61 10 85 92 1 11 38 38 93 12 39 35	7 0 -41 8 69 54 9 68 77		4 29 -35 17 48 -56 5 61 -64 H,L= -8 2 6 136-143 0 35 -36
5 33 22 60 0 7	8 41 -41 9 118-1 90 0 12 10 64	25 130 8 16	110 0 23	20 52 29 H.L= -2 2 . 0 33 42 1 66 76 2 97-100	. 7 .116 127. 1 0 -14 6 0 21 2 0 7
7 37 -37 8 28 -29	11 96 96 12 90-1	05 160 0 -22	120 0 -25		
10 62 64 11 102-106	12. 0 -19 13 82 13. 0 30 14 38 - 14 78 74 15. 1	85 17 0 7 56 18 61 64 23 Halm -7 1	13 52 -54 H.L. 11 1 10 0 10 2 55 -62	4 49 -49 5 0 13	11 65 -59 5 0 25 12 0 -13 6 65 -58 .13 0 .20 ? 0 -11.
12 0 7 13 91 59 13 63 57 14 0 4	15. 0 -21 16 79 16. 0 -15 17. 0 -	85 1 69 -70	3. 0 14 4. 0 26 5. 0 3	6 22 -23 7 106-109 8 45 -47	14 82 -74 8 78 -64
14 0 -5 15 44 69 15 114-118 16 48 -38	17. 0 -13 18. 0	4 3. 0 29 -1 4. 0 -12 67 5. 0 8	5 0 3 6 54 61 7 0 -20	7 106-109 6 45 -37 9• 0 29 10 51 44 11 170 1/9	1 144 154 10 70 57 2 190-210 11* 0 26 3 131-131 12* 0 19 -4** 0 17 13* 0 -46. 5 143-146 14* 0 -36
16 41 -30 17 45 -57 17 51 -51 18 0 9 18 0 -11 19 39 -47	200 0 32 21 48	67 5. 0 8 49 6. 0 13 1 7 97-102	8 37 -49 H,L=-11 1	11 1/0 1/V 12 67 58 13 71 -65	3 131-131 12* 0 19 4* 0 17 13* 0 -46. 5 143-146 14* 0 -36
19 93 104 20° 0 22 20° 0 7 21 29 41	21* 0 20 H,L* -4 22 35 51 0 92 - H,L* 2 1 1 186 1 0 44 4 2 0 0	92 8. 0 23 99 9. 0 -5	10 0 -44	14* 0 -27 15 77 -80	7 85 79 H.La 9 2
22+ 0 3 1 48 -78			2 80 102 3• 0 19 4• 0 -3	16 80 -67 17 82 /3	9 73 74 20 0 4
H,L: 4 0 3 49 73	2 72 61 40 B 3 59 -48 5 229-2 4 74 66 6 35	20 12• 0 -1 29 13• 0 -6 35 14 80 83	5 68 37 6• 0 -77 7• 0 -14	19 71 53 19 71 60 20 69 64	. 10 .77 -66 .3 · 0 9. 11 95 -78 4 · 0 -15 12 75 73 5 · 0 4
0 36 -33 4 28 -13 1 109 102 5 76 81 2 23 -19 6 57 -55 3 0 -8 7 77 -89	4 74 66 6 35 - 5 46 -43 7 80 - 6 112-100 8 39 - 7- 0 -16 9 160 1	73 15 0 -23 40 16 39 -44 61 17 0 -13	8 0 36 9 36 -52 H,L= 0 2	21 67 -62	13 86 -8n 6* 0 0 H,L= 6 2 7* 0 -47
3 0 -8 7 77 -89 4 49 -48 8 41 46 5 75 -70 9 99 -59	7. 0 -16 9 160 1 8 25 12 10 0 9 66 66 11 32 10 50 35 12 0 -	7 18 63 -63	0 92 97 1 29 -30 2 126-153	22 35 -40 H.L= 3 2 1 00 -75 2 75 -77	0 200 224 8. 0 9 -1.0 -26 9. 0 -14 2 32 -37 10. 0 -30
6 38 -27 10 0 12 7 26 16 11 91 55	110 0 -19 13 88 -			3 74 62 40 0 2	30 0 0 110 0 31 4 144-169 120 0 -28
8 21 -10 12 0 -20 9 138 135 13 90 55	12 64 -56 14  0 13 102-102 15  0	24 20 0 13 4 30 0 35	4 119-129 5 43 42 6 74 79	5 126 130 6 102 104	5. 0 -8 13. 0 5 6 48 54 14. 0 19
10 46 -48 14 0 20 11 0 -3 15 94 -55 12 44 44 16 0 11	14 35 -15 16 0 15 37 12 17 56 16 54 49 H,Lm 5	28 4 72 -71 52 50 0 -27	7. 0 -23 6 61 56 9. 0 18	70 0 -13 80 0 22 9 144-149	7 35 37 15 49 -55 8 122 134 H.L= -9 2 9 37 23 1 54 -46
13 107-111 17 93 -38	17 79 89 1 0 -	35 4 67 64	10 115-121	10 79 -75 11 90 65 12 0 -31	10 54 -49 2 0 -36 11 56 -54 3 67 76
14 0 -30 18 0 -19 15 49 51 19 27 41 16 51 -45 H,L= 10 0 17 59 69 00 0 -36			11 62 48 12 66 -58 13 0 20	13 112 11/	13 70 -62 4 55 53
	0 110 110 7 111-1	24 10 0 37 18 11 69 62 91 12 60 -68 02 13 96 -93	13. 0 20 14 104 118 15. 0 -20	15 90 -85 160 0 18	14 41 52 6* 0 19 H.L= -6 2 7 69 -82 0 124 141 8 57 -52
20 48 37 3 46 72	1 123-117 6 54 -	92 140 0 -28 43 150 D -34	16. 0 13 17. 0 27	17 71 -60- 180 0 -31	10 0 -18 90 0 6 20 0 0 100 0 11
10 0 7 60 0 -12	4 25 -34 11 61	09 160 0 31 65 17 49 64 -9 H.L= -8 1	18 71 -63 19• 6 4 20• 0 -33	19 80 88 20 6 -19 21 0 29	3 133 141 11 71 66 4 121-114 12 56 62 50 0 21 H.Le 10 2
	6 71 -63 13 65 - 7 108 96 14 78	64 00 0 4 76 10 0 -17	22 35 43	220 0 13 23 29 -52	6 63 45 0 58 -49 7 86 -83 1 0 33
5 20 21 10 0 14 6 103 -95 11 0 22	8 136 131 190 0 - 9 107 -94 160 0 -	23 20 0 -5 18 30 0 -18	H,L= 1 2 1 157 194 2 65 -64	H,L= -3 2 1 102-112 20 0 -11	8 127 133 20 0 -8
7 72 62 12- 0 23 8 105 98 13 46 -49 9 75 -73 M.L. 11 0	10 90 92 17 0 11 168-182 18 38 - 12 111-109 H,Le -5	53 50 0 8	2 65 -64 3 147-171 4 45 47	2 · 0 -11 3 · 67 · 58 4 · 113 · 108	10 0 -30 40 0 37 11 84 80 5 71 -73 12 78 -74 H.Le-10 2

TABLE 2. (Continued)

K FO FC K FO FC K FO	FC -K FO FC		K FO FC		
		K FO FC		K F0 FG	K FO FC K FO FC
0 90-112 60 0-23 140 8 1 8 1-75 7 122-134 150 0 20 14 9 0 18 16 49 3 4 9 0 18 16 49 5 1 9 0 18 16 49 5 1 9 0 18 16 49 5 1 9 0 18 16 18 16 18 16 18 18 18 18 18 18 18 18 18 18 18 18 18	60 8 49 25	20 g -9 30 g -4	70 0 -9 8 89 84 90 0 -12	H.L. 1 5	2e 8 -24 8e 0 33 3 110 10 9e 0 39 4 30 33 10e 0 27 5 129 125 11 49 64 6 59 49 14 16 10 5 7 51 -35 0e 0 0 6 38 -31 1e 0 -17 9 129 123 2e 0 2 10 60 -58 3e 0 25
1 81 -75 7 122-134 150 0 20 0 14 80 0 18 16 49 3 40 -50 9 143 171 1145 -5 5 71 80 11 92 94 2 177 6 0 -13 120 0 -23 3 109	-7 9. 0 4 -52 10. 0 28	4 121 124	9. 0 -12	H.L# 1 5 1 48 -48 2 145 148 . 3 60 61 4 57 -57 5 30 -20 6 93 -95 7 70 -65 8 53 43	3 110 110 90 0 39 4 30 33 100 0 27
. 3 40 -50 9 163 171 H.Le -5	50 H.L. 10 3	5 26 -31	100 0 -12 110 0 10 110 0 22 12 79 -81	3 .6061 - 4 57 -57	169-165 11 49 -64
5 71 89 11 92 94 2 177 60 0 -13 120 0 -23 3 109	205 <b>6</b> + 0 36	7 29 -22	12 79 -81 13• 0 -19	5 30 -20	4 30 33 10 0 27 5 169-165 11 49 -64 6 50 40 M.L 10 5 7 51 -35 0 0 0 8 36 -31 1 0 0 -17
6 0 -13 12 0 -23 3 100 1 7 0 11 13 78 -76 4 0 0 8 0 -45 14 0 -20 5 89	26 2 49 3	9. 0 5	140 0 10	7 70 -65	6 36 -31 1 0 -17 9 129 123 2 0 2
8* 0 -45 14* 0 -26 5 89 9 58 -79 15* 0 -46 6 192* 10 71 16 16 49 51 7* 0 11* 0 20 H/Le -2 3 8 54	76 3 49 -41 196 4 40 -53	100 0 -24	150 0 -18 16 93 98	8 53 43	9 129 123 2 0 2 10 60 -58 3 0 -25
10 71 16 16 49 51 70 0	11 H,Le-10 3	12 81 80	17 64 62	10 59 42	12. 0 43 H.LE-10 5
70 01 13 78 -76 40 0 20 80 9 95 -79 150 10 -71 16 16 49 51 70 0 -10 110 11 16 16 49 51 70 0 110 11 16 16 170 110 11 16 16 170 110 11 16 16 170 110 11 16 170 110 110 110 110 110 110 110 110 110	33 1 49 59	1 57 -55	1 98 108	99 8 13 10 59 42 11 88 93 12 46 -56 13 0 -19 14 0 -34 15 70 -56 16 0 20 17 0 24	13 63 -82 0 49 37 H.L. 5 5 1 70 73
13 Ja 51 1 29 59 10 10 10 10 10 10 10 10 10 10 10 10 10	103 20 0 -19	2 41 -36 30 A 25	20 0 -17	12 46 -96 13• 0 -19 14• 0 -34	1 • 0 -4 2 49 -35 2 95 -89 3 70 74 3 • 0 -4 4 50 -42 4 • 0 -4 H.L= 0 6 5 44 -41 0 0 14 6 102 108 1 0 -11 7 • 0 -6 2 • 0 -2
1. 0 -4 3 40 40 12. 0	14. 40 0 -22	4 62 59	400.11	15. 70 -56 . 160 0 20 .	3. 1
2 80 90 4 45 39 13 47 30 0 -2 5 25 -18 H.Lm 6	38 5 49 -71 3 60 0 31	5 46 40 60 8 -2	5 78 -78	16. 70 -56 . 16. 0 20 17. 0 24	4- 0 -4 H.L= 0 6
4. 0 -19 4 47 45 0 121-	20 7. 0 -12	70 0 -9	7 93 94	10. 0 0	6 102 108 10 0 -11
5* 0 4 7 67 56 1* 0 6 77 -84 8 56 47 2* 0	30 9 70 74	9 87 -84	10 0 2	19 46 58 H,L= -1 5	70 0 -6 20 0 -2 80 0 4 3 25 -20
4 0 -19 6 47 45 0 121- 5 0 4 7 67 56 10 0 6 77 -84 8 56 47 20 8 10 0 22 100 0 -9 4 73 2 83-104 11 68 -44 50 88	11 H.L. 11 3	100 0 6	2. 74_62	1 40 -57	
2 83-104 11 68 -44 50 0	36 2 81 -67	12 44 49	4. 0 11	3 41 47	11. 0 14 6 38 43
40 0 11 15 76 62 70 0 50 0 -12 14 45 46 8 79	-6 40 0 17	140 0 -10	6 90 -98	4 41 -38 5 60 60	12 · 0 · A 7 · 0 · 5 13 · 50 · 58 · 8 · 53 · 43
50 0 -12 14 45 46 8 79	56 50 0 11	15 66 -75	70 0 -8	6 118 126	14 49 68 9 41 36
H.L. 12 2 16 49 68 10 96	88 H.L. 0 4	H.L3 4	9 76 67	8 61 59	1 70 -60 11 37 37
0 63 64 17 70 -78 11 0 1 0 38 H,L= 3 3 12 0	30 0 223 242 26 1 29 34	1 40 -36 2 148-174	10 90 88 11• 0 8	90 0 -27 10 143-143	2 56 49 120 0 -23 30 8 15 13 31 -33
2. 0 1 1140 187 13. 0	7 2 17 -18	3 76 77	120 0 20	11. 0 -1	4 77 -70 14 31 45
4 61 -00 3 72 -63 H.L0	34 200-220.	5 59_ 62_	14 105-108	13. 66 56	- 6 37 -34 .16 .44 .44
H,L=-12 2 4 61 -60 0 165-1	70 50 0 -6	6 102 109	150 0 4	14 97 118	10
2* 0 1 1140 187 13* 0 3* 0 22 2 49 39 14 70 4 61 -96 3 72 -63 H/L* -6 H/L* -12 2 4 61 -60 0 165* 1 0* 0 52 5 104-105 1= 0 1* 0 -16 6* 0 14 2* 0 2* 0 10 7 86 85 3* 0 3* 0 11 8* 0 30 4 155* 1 4* 0 -22 9 144 160 5 35	15 7 72 -78	8 73 -71	170 0 36	16. 0 -12	9 129 123 2 0 0 12 10 60 -55 3 0 -25 11 60 -55 4 0 0 4 12 63 -48 1 16 19 9 12 63 -48 1 16 19 9 12 63 -48 1 16 19 9 12 63 -48 1 16 19 9 13 63 -62 0 49 37 11 8 -4 2 49 -35 2 95 -69 3 70 74 3 8 4 4 1 0 0 1 16 6 102 100 1 0 0 11 7 8 -6 20 0 -2 9 9 1 4 1 4 32 -39 11 0 1 4 6 38 43 12 8 6 9 9 5 5 3 7 11 0 1 4 6 38 43 12 8 6 9 9 5 5 3 11 4 9 6 9 9 5 5 3 13 8 58 8 5 3 43 14 19 6 9 9 1 36 14 15 18 18 18 18 18 18 18 18 18 18 18 18 18
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4. 0 -52 9 146 160 5 53	42 10 62 -51	11 88 93	0 80 50	190 0 -10	12 . 83 -91 H.L. 1 6
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1 32 -42 16 0 38 12 95	95 17 0 26	180 0 -7	7 82 81	20 0 -12	8 92 92 180 0 -31 9 43 -46 19 32 26 100 0 -2 20 20 -31 110 0 41 21 46 -48 12 83 -91 HrLs 1 6 13 49 47 1 22 33 HrLs 6 5 20 0 -5 0 113-100 3 38 -40 10 0 -38 4 72 68 20 0 37 5 30 -59 3 0 -43 6 40 39 4 149 142 7 72 66 6 8 8 9 6 11 6 8 8 9 6 11
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4 145 174 1 78 71 150 0	40 20 43 -44	0 98 93	1. 0 12	5 96-101	6 0 -8 9 0 11 7 0 40 10 0 17 8 86 -87 11 59 -62 9 0 -24 12 75 74 10 0 33 13 0 -9
5 24 -16 2 38 38 16 86 - 6 85 -78 30 0 -16 H.L. 7	90 21 40 -40 3 H,Lm 1 4	10 0 25 20 0 27	20 0 -10 3 50 53	6 35 -35 7* 0 -20	8 86 -87 11 59 -62 9- 0 -24 12 75 74 10- 0 33 13- 0 -9
7 145 149 4 195-112 1 89	86 1 159 174	3. 0 13	4 138 131	10 48 58 Hote -1 5 1 49 -57 3 41 -7 3 51 -7 3	10. 0 33 13. 0 -9
9-0196-07378	71 3 151-166	H.L= -4 4	6. 0 -12	10 0 17	11 71 -62 14+ 0 7. 12 70 59 15 59 66 H-L= -6 5 16 44 -50 0+ 0 20 17+ 0 24
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3 162 187 1 97-103 70 0	13 19 39 -32	150 0 -36	3 89 91	11 86 -81	7 87 -79 9 29 31
4 104-106  20 0 10 80 0 5 116 126  3 88 -91  90 0	45 H.LU -1 4 -2 10 0 -1	160 0 0 17 66 -61	4 0 29 5 64 39	12 101-106 13* 0 21 14* 0 15 15 70 76	9 0 -15 11 0 15 10 15 10 49 52 12 31 24 11 49 55 13 50 -51 14 175 -80 10 10 0 -8 12 -0 -22 16 44 35 30 0 -24 17 0 9 40 10 18 58 67 50 0 25 19 33 20
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	44 4. 0 2 .	20 0 24	0 -18 .	.Half . 3. 5	. 29_022 . 16 44 35
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11 79 81 9 41 -46 15. 0	22 7. 0 -12	5+ 0 20	3 45 59	3. 0 -11	5 0 25 19 33 20 6 0 49 20 35 -45
8 60 79 68 6 -2 128 6 1 13 6 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	92 1 8 0 2 8 1 2 1 2 2 4 2 3 3 4 1 1 2 1 2 3 4 2 3 1 1 2 1 2 3 4 2 3 3 4 2 4 1 3 3 4 2 4 1 3 3 4 2 4 1 3 3 4 2 4 1 3 3 4 2 4 1 3 4 2 4 3 3 4 2 4 1 3 4 2 4 3 4 2 4 3 3 4 2 4 1 3 4 2 4 3 4 2 4 3 4 2 4 3 4 3 4 3 4 3 4		1 45 47 20 0 4 3 45 59 40 0 20 5 44 -45 Halp-10 4	15 70 76 Half 3 5 10 0 -1 2 119 118 30 0 -11 40 0 -24 50 0 -11 - 0 .78 -70	4 0 10 18 50 67 5 0 2 5 19 33 20 6 0 49 20 35 -65 7 0 3 9 H/L 0 7 8 0 -30 1 26 -21 9 0 -30 1 2 45 34 H/L 8 5 3 46 -37 0 0 11 4 41 47
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15. 0 -33 12 76 -73 11 49 - 16. 0 -35 13 80 -73 12 50 -	93 4 78 69 - 67 5 114 112	4 84 -90	70 0 -3		0 69 73 19 41 -35
130 0 -33 12 75 -73 11 -97 - 110 0 -35 13 80 -73 12 90 - 110 0 32 H, Le 5 3 H, Le 5 10 10 10 10 10 10 10 10 10 10 10 10 10	3 6 104 104	4 84 -90 5- 0 -24 6 75 60 7- 0 -44 8- 0 43 9- 8 41	8 137-140	6 42 -49 7 0 -10 8 78 72	6 67 70 17 39 -45 7 68 65 18 0 22 8 69 73 19 41 -35 Hule 9 5 Hule 1 7 10 0 28 1 76 -75 20 0 -10 20 0 33 30 0 -10 3 97 89
19. 0 7 2 73 -63 2. 0	27 8 60 -62	7- 0 -44	10. 0 27	8 78 72	2. 0 -10 2. 0 33
	27 8 60 -62 37 9 136-147 24 10 67 -66 63 11 0 -9	80 0 43	110 0 -17 12 78 75		40 0 n 4 43 -34
21 64 -26 4 66 46 40 0 22 65 64 5 67 84 50 0 23 39 -6 6 70 56 H.L9	63 11. 0 -9	10 00 -04	13 47 42	100 0 15	50 0 -36 5 72 72
23 39 -6 6 70 56 H,L= -9 H,L= 2 3 7 83 -71 1 80	3 12 74 69 74 13 76 74	0 80 73	14. 0 -13 15. 0 10 16 50 -57	12 86 -89 13• 0 23	1 117 112 7 80 -91
A 74 45 A 47 E4 A AY	94 14 0 40 89 15 0 -9 50 16 47 -48	1 61 -62	17 40 -44	140 0 -1	3 118+108 Y 62 +61
22 65 64 5 67 84 5 0 23 39 -6 6 70 56 M <sub>1</sub> Lu -9 8 1 1 8 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	89 15 0 -9 50 16 47 -48 -6 H,L= -2 4	30 0 -18	180 0 5	16 48 65	3 118-108 9 82 -81 40 0 12 100 0 -1 5 49 -53 11 40 46
	83 0 139-169	8e 0 43 9e 8 41 10 8b -84 H,L= -6 4 0 80 73 1 81 -82 2e 8 38 3e 0 -18 4 70 -61 5e 0 58 6e 0 -6	18. 0 5 19. 0 -10 20 49 50 21 48 53	16 48 65 H.L= -4 5 0 101 -88	6. 0 -13 12 46 -40
4. 0 19 12 48 59 6 84 5 162-170 13. 0 -8 7 85	90 1 25 -34	6. 0 -6	21 48 53	1 164 1/1	7 99 93 13 45 48

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140 0 4 15 53 -59	14 75 76 15• 0 10	12 56 -68 13 -42 -47	140 0 9 15 38 46	0 66 -67 10 0 -14	6 32 -34 10 7• 0 -33 11	1 38 -26 H,	L= 1 10 11 20 27
16 0 32 17 47 -46 18 0 -10	160 0 -34 170 0 6	140 0 -12 15 48 -46 16 31 36	16° 0 2 17 32 33 H,L= -1 8	4 46 49	90 0 -7 13	3. 1 6 . 3	10 0 15 H.L. 0 11 10 0 8 00 0 13 10 0 -13 1 41 -35
19 23 34 H,L= -1 7 1 64 70	19- 0-10 20 34 44 H,L= 0 8	17 29 30 H.L= 1 8 1 67 60	1 91 -80 2 82 83 3 62 62	5 0 25 6 0 26 7 0 24	12. 0 6	7 5	6 0 7 2 0 3 6 0 -16 3 41 -39 6 0 -7 4 0 -6
2. 0 -27 3. 0 -26	0 53 57 1 93 44	2 71 -74 3 59 -58	4* 0 11 5 44 38 6 100-110	8 45 -42 90 0 -30 100 0 -25	15 .53 -41	300. 14	0 27 5 39 36 1 21 -17 6 0 -5
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12. 0 13 13. 0 -12	10° 0 6 11 49 55	12 0 4 13 36 -39	H,L. 0 9	50 0 24			0 0 17

R=0.116 was obtained after 2 cycles. Anisotropic temperature factors were introduced at this stage, and three cycles of refinement gave the R=0.098.

Atomic and thermal parameters are listed in Table 1. In Table 2 listed are the observed and calculated structure factors.

### Description of the Structure and Discussion

The molecular structure of the complex is shown in Fig. 1. The bond lengths and angles in the environment of tin atom are listed in Table 3. As seen in Fig. 1 and also in Table 3, the tin atom is coordinated by two bromine atoms in cis-positions as assumed before, 1) and also by two oxygen and two carbon atoms from 1,2-diethoxycarbonyl-ethyl groups. The coordination about the tin atom is a six-coordinated, distorted octahedron, and this may probably be the first structure of the six-coordinated organotin compounds analysed by means of X-ray diffraction.

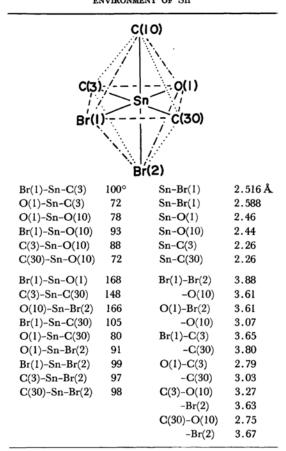
Sn-Br distances are 2.52 and 2.59 Å respectively, and these values are close to the sum of the covalent radii of tin and bromine atoms, 2.54 Å. The deviations may be due to distortion of the configuration from the regular octahedron (Table 3) and also to different contacts between bromine atoms and other atoms in the adjacent molecules.

Two equal Sn-C distances, 2.26 Å, seem to be slightly longer than the sum of the covalent radii, 2.17 Å, and also longer than that in SnH<sub>3</sub>CH<sub>3</sub>,<sup>2)</sup> 2.15 Å, in which the tin atom takes an usual tetrahedral configuration.

As regards the Sn-O bonds, the distances 2.44 and 2.46 Å are much longer than the sum of covalent radii, 2.06 Å. These Sn-O distances may be the longest values hitherto reported, and this suggests that the Sn-O are weak coordination bonds.

Two ligands, 1,2-diethoxycarbonyl-ethyl groups, are bound to the tin atom by carbon and oxygen atoms, forming rather puckered five-membered rings. Each pair of corresponding atoms in two rings deviate from the least-squares planes in a similar

TABLE 3. BOND LENGTHS AND ANGLES IN THE ENVIRONMENT OF Sn



The standard deviations of bonds in Sn-Br are 0.006 Å, in Sn-C 0.05 Å, in Sn-O 0.03 Å, Br-C 0.05 Å, Br-O 0.03 Å and C-O 0.05 Å. Those for the angles are of the order of 3°.

way (Fig. 2). C(3) and C(30) show the largest deviations from the planes, 0.35 and 0.31 Å respectively. The three planes Br(1)-O(10)-O(1)-Br(2), Br(1)-C(3)-O(10)-C(30), and C(3)-Br(2)-C(30)-O(10), all centered with tin, make dihedral angles,

<sup>2)</sup> D. R. Lide, J. Chem. Phys., 19, 1605 (1951).

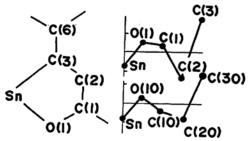


Fig. 2. Deviations of atoms from the least-squares planes in Sn-O(1)-C(1)-C(2)-C(3) and Sn-O(10)-C(10)-C(20)-C(30) rings.

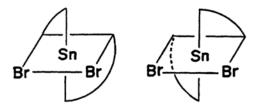


Fig. 3. Two optically active antipodes.

85°, 88°, and 91° each other. Some atoms in these planes show deviations more than 0.2 Å. The coordination configuration is the distorted octahedron as mensioned before. The bond lengths and angles in the ligands are shown in Table 4. The estimated standard deviations for these values are too big to discuss the dimensions of ligand groups in detail.

TABLE 4. THE AVERAGE BOND LENGTHS AND ANGLES IN TWO LIGAND GROUPS OF MOLECULE

0(3	S) 0(4 C(6)	C(7) C(3)	
Sń	C(3) C(1)	2) (1) C(4) (5) C(5)	
Sn-O(1)	2.45 Å	O(1)-Sn-C(3)	72°
Sn-C(3)	2.26	Sn-O(1)-C(1)	112
C(1)-O(1)	1.18	O(1)-C(1)-O(2)	123
C(1)-O(2)	1.34	O(1)-C(1)-C(2)	125
C(1)-C(2)	1.46	O(2)-C(1)-C(2)	113
C(4)-O(2)	1.52	C(1)-O(2)-C(4)	116
C(4)-C(5)	1.52	O(2)-C(4)-C(5)	103
C(3)-C(2)	1.57	C(1)-C(2)-C(3)	109
C(3)-C(6)	1.48	Sn-C(3)-C(2)	108
C(6)-O(3)	1.29	Sn-C(3)-C(6)	107
C(6)-O(4)	1.27	C(2)-C(3)-C(6)	117
C(7)-O(4)	1.56	C(3)-C(6)-O(3)	116
C(7)-C(8)	1.51	C(3)-C(6)-O(4)	118
		O(3)-C(6)-O(4)	126
		C(6)-O(4)-C(7)	117
		O(4)-C(7)-C(8)	100

The standard deviations for the bonds between light atoms are estimated to be 0.04-0.06 Å, and for angles about 4°.

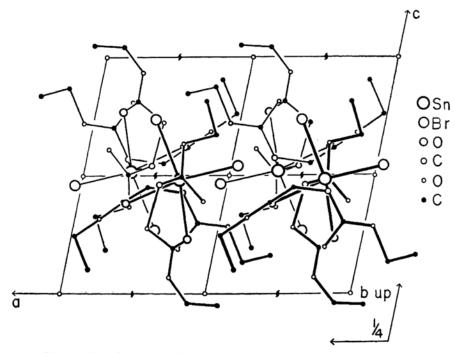


Fig. 4. Crystal structure of bis-(1,2-diethoxycarbonyl-ethyl)tin dibromide.

Both ligands in a molecule contain an asymmetric carbon atom, C(3) and C(30) respectively, of which one is in d-form and another in l-form, and the optical activity due to the asymmetric carbon atom does not exist. However, the whole molecule is still asymmetric and the molecule must possess the optical activity due to such molecular asymmetry. Since there are glide planes in the unit cell of this crystal

Table 5. Some close intermolecular atomic contacts in the crystal (those less than 4.0 Å are listed)

Br(2)-C(701)	3.79 Å	O(3)-C(7ii)	3.15 Å
$O(1)-C(70^1)$	3.91	$C(4)-C(8^{111})$	3.86
$C(4)-O(30^{1})$	3.38	Br(1)-C(40iv)	3.99
C(30)-Br(1 <sup>i</sup> )	3.71	$Br(2)-C(5^{iv})$	3.77
$O(1)-O(30^{1})$	3.52	$Br(2)-C(40^{iv})$	3.99
$C(20)-O(30^{1})$	3.95	$C(80)-C(50^{iv})$	3.94
		$C(80)-O(20^{iv})$	3.72

#### Code for superscript

- i 1/2+x, 1/2-y, z
- ii -x, -y, -z
- iii 1+x, y, z
- iv x, y, 1+z

(space group:  $P2_1/a$ ) and since a unit cell contains four molecules, there are equal numbers of molecules of two optically active antipodes (Fig. 3) in the crystal. Therefore, the crystal, as a whole, exhibits no optical activity.

The crystal structure is shown in Fig. 4. There are not so many close intermolecular atomic distances. The shortest intermolecular contacts are O(3)-C(7ii), 3.15 Å, and C(4)-O(30i), 3.38 Å, and other contacts less than 4.0 Å are all listed in Table 5.

The three-dimensional structure analysis of another isomer crystal, II (mp 122—123°C), is now being carried out.

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<sup>3)</sup> Tosio Sakurai Ed., UNICS, Japan Crystallographic Association (1967).