aminotetrazole (Britts and Karle[17]), the hydrazine salt of 5-aminotetrazole (Bryden[18]), and sodium tetrazolate monohydrate (Palenik[19]).

The nature of the Zn–Tz interaction may be summarized by comparing the results of this study with the results of the determination of the crystal structure of the iodopentamethylenetetrazolium monochloride complex (PMTICl) by Baenziger and Nelson.[4]

In both complexes the following statements apply. The moiety coordinated to the tetrazole ring is essentially planar with the ring. The site of coordination to the tetrazole ring is identical (labeled N(4) in ZCTZ, N(2) in PMTICl). The coordination geometry at N(4) is essentially identical. Denoting values for the corresponding angles of PMTICl by an asterisk, the bond angles (degrees) about N(4) are as follows: N(3)–N(4)–C(5), 105 (2), 107 (2), 106* (4); N(3)–N(4)–Zn, 121 (2), 121 (2), 125* (4); C(5)–N(4)–Zn, 132 (2), 133 (2), 130* (4). These considerations suggest that the preferred mode of coordination in ZCTZ (and PMTICl) is by means of a charge-transfer σ bond to position N(4) of the tetrazole ring.

[17] K. Britts and I. L. Karle, *Acta Crystallogr.*, **22**, 308 (1967).

[18] J. H. Bryden, *ibid.*, **11**, 31 (1958).

[19] G. J. Palenik, *ibid.*, **16**, 596 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
AND THE POLYMER RESEARCH INSTITUTE OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK

Optically Active Boron. The Crystal Structure of (+)-4-Methylpyridinetrimethylaminebromohydroboron Hexafluorophosphate

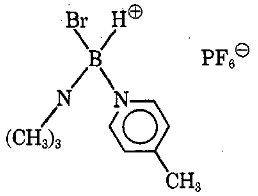
BY GIUSEPPE ALLEGRA,* ETTORE BENEDETTI, CARLO PEDONE, AND SMITH L. HOLT

Received October 30, 1969

The first crystal structure of a stable optically active compound having a boron atom as the asymmetric center has been elucidated. (+)-4-Methylpyridinetrimethylaminebromohydroboron hexafluorophosphate (I) crystallizes in the monoclinic system, space group $P2_1$, with a = 19.35 (1) Å, b = 7.870 (4) Å, c = 10.549 (5) Å, β = 90° 25′ (10′). Two crystallographically independent formula units are present in the unit cell. The structure has been solved by Patterson and Fourier methods and refined to an R factor of 0.089 for 2481 independent nonzero reflections measured with counter technique (Cu Kα); the disagreement factor increases to 0.102 if 481 reflections below the limit of detectability are included. The geometrical parameters of the two independent cations, as well as of the two independent anions, are virtually identical. An almost regular sp^3 hybridization of the boron atom results from the arrangement of the surrounding ligands. The stereochemistry of the cations is discussed on the basis of intra- and intermolecular interactions; the presence of two pairs of independent ionic species is rationalized in terms of the tendency to produce a pseudocentrosymmetric packing.

Introduction

Recently Ryschkewitsch and Garrett have reported the preparation and the resolution of the first examples of stable optically active compounds with the boron atom as the asymmetric center.[1] While the isoelectronic and isosteric analogs of this compound, having optically active carbon or nitrogen atoms, have never been resolved, the boron salts have proven to be highly stable toward racemization during the fractionation process. In view of the interest involved in the stereochemical knowledge of such compounds, we have undertaken a single-crystal X-ray investigation of one of them, namely, (+)-4-methylpyridinetrimethylaminebromohydroboron hexafluorophosphate (I). We now report the results of the detailed analysis of the crystal and molecular structure of I.



I

Experimental Section

Colorless, needlelike single crystals of I, obtained from an acetone–water mixture (mp 136–137°, $[\alpha]_D$ −60.9°), were kindly donated by Dr. Ryschkewitsch. A small crystal of approximately cylindrical shape ($r \simeq 0.05$ mm, length $\simeq$0.5 mm) was used for the X-ray investigation. From preliminary Weissenberg photographs the crystal was found to belong to monoclinic space group $P2_1$ (systematic ($0k0$) absences with k odd). A Picker four-circle automated diffractometer equipped with a PDP-8 digital computer was used for the collection of the intensity data. The unit cell dimensions were obtained from a least-squares treatment of the 2θ, χ, and φ setting angles of 12 reflections with $2\theta >$ 80°, using a program prepared by Busing and Levy.[2] The resulting parameters are $a = 19.35 \pm 0.01$ Å, $b = 7.870 \pm 0.004$ Å, $c = 10.549 \pm 0.005$ Å, β = 90° 25′ ± 10′, $d_{\text{X-ray}}$ = 1.607 (1) g/cm^3 with Z = 4, d_{exptl} = 1.58 (2) g/cm^3 (flotation), μ = 51.56 cm^{-1}, and $\lambda_{\text{Cu}K\alpha}$ 1.5418 Å.

The experimental density agreed reasonably with the calculated density assuming four molecules of I per unit cell, thus requiring the presence of two crystallographically independent formula units. A total of 2962 integrated intensities were collected using a θ–2θ scan mode (1.67°) with Ni-filtered Cu Kα radiation in the range 0–130° of 2θ. Two stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of each scan. Since μ = 51.66 cm^{-1} (λ 1.5418 Å) and

---

* To whom correspondence should be addressed at the Istituto di Chimica Industriale del Politecnico di Milano, 20133 Milan, Italy.

[1] G. E. Ryschkewitsch and J. M. Garrett, *J. Amer. Chem. Soc.*, **90**, 7234 (1968).

[2] Z. W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).

TABLE I: FINAL ATOMIC PARAMETERS[a]

A. Final Positional Parameters

	1. Molecule a			2. Molecule b		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Br(1)	0.3937 (1)	0.0134 (4)	0.6857 (1)	0.0329 (1)	0.0000	−0.1441 (2)
P(1)	0.1769 (2)	0.2520 (6)	0.4518 (2)	0.3334 (2)	−0.3883 (5)	0.0547 (3)
F(1)	0.1145 (5)	0.2815 (19)	0.3610 (11)	0.4008 (5)	−0.4290 (19)	0.1364 (9)
F(2)	0.2046 (9)	0.1153 (26)	0.3581 (11)	0.3085 (6)	−0.2571 (17)	0.1597 (9)
F(3)	0.2149 (8)	0.3872 (25)	0.3715 (14)	0.2963 (7)	−0.5349 (17)	0.1273 (11)
F(4)	0.2429 (5)	0.2252 (16)	0.5414 (11)	0.2664 (5)	−0.3580 (21)	−0.0269 (9)
F(5)	0.1347 (7)	0.1217 (25)	0.5315 (11)	0.3712 (7)	−0.2462 (18)	−0.0184 (12)
F(6)	0.1528 (9)	0.3904 (25)	0.5416 (15)	0.3566 (6)	−0.5240 (16)	−0.0514 (18)
N(1)	0.4218 (5)	−0.0795 (15)	0.4201 (9)	0.0980 (5)	−0.0860 (15)	0.0978 (9)
N(2)	0.3476 (5)	−0.2995 (16)	0.5458 (9)	0.1662 (6)	0.1269 (16)	−0.0370 (10)
C(1)	0.4698 (7)	−0.1370 (19)	0.3406 (13)	0.1324 (6)	−0.2153 (19)	0.1554 (13)
C(2)	0.4793 (7)	−0.0693 (22)	0.2257 (12)	0.1175 (7)	−0.2667 (19)	0.2751 (13)
C(3)	0.4413 (7)	0.0701 (17)	0.1794 (11)	0.0669 (6)	−0.1922 (19)	0.3408 (11)
C(4)	0.3900 (22)	0.1234 (22)	0.2638 (12)	0.0273 (7)	−0.0615 (22)	0.2848 (14)
C(5)	0.3820 (6)	0.0553 (17)	0.3827 (11)	0.0442 (6)	−0.0171 (20)	0.1623 (12)
C(6)	0.4502 (10)	0.1396 (26)	0.0492 (15)	0.0479 (11)	−0.2439 (33)	0.4762 (17)
C(7)	0.3635 (9)	−0.4306 (23)	0.4485 (17)	0.2324 (8)	0.0945 (24)	0.0369 (17)
C(8)	0.2789 (8)	−0.2187 (28)	0.5092 (19)	0.1351 (11)	0.2840 (23)	0.0203 (18)
C(9)	0.3391 (11)	−0.3799 (30)	0.6743 (15)	0.1915 (10)	0.1658 (33)	−0.1728 (15)
B(1)	0.4098 (9)	−0.1686 (32)	0.5526 (14)	0.1209 (8)	−0.0409 (22)	−0.0401 (14)

B. Final Thermal Parameters $T = \exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$

1. Molecule a

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	10.9 (1)	9.5 (1)	4.5 (1)	−4.1 (1)	0.1 (1)	−1.3 (1)
P(1)	5.0 (1)	5.5 (2)	4.0 (1)	−0.2 (1)	0.1 (1)	0.0 (1)
F(1)	6.6 (5)	9.9 (7)	8.9 (6)	−0.1 (5)	−2.8 (4)	0.3 (6)
F(2)	17.4 (12)	14.2 (12)	5.9 (5)	5.6 (11)	−0.6 (6)	−2.2 (7)
F(3)	11.9 (9)	14.0 (12)	10.9 (8)	−4.0 (9)	−2.3 (7)	6.2 (9)
F(4)	5.7 (4)	8.7 (7)	8.9 (6)	−0.6 (5)	−1.8 (4)	0.3 (6)
F(5)	11.7 (8)	15.3 (13)	7.9 (6)	−6.1 (9)	−1.2 (6)	3.6 (8)
F(6)	15.4 (11)	13.0 (11)	11.5 (9)	7.0 (10)	−4.7 (8)	−5.4 (9)
N(1)	4.7 (4)	4.6 (5)	4.1 (4)	−0.6 (4)	−0.4 (3)	0.7 (4)
N(2)	4.0 (5)	6.1 (5)	3.3 (4)	−1.5 (4)	−0.7 (4)	1.0 (4)
C(1)	5.2 (6)	4.5 (6)	5.2 (6)	0.7 (5)	0.6 (4)	−1.2 (5)
C(2)	5.2 (6)	6.4 (8)	4.0 (5)	−0.2 (6)	0.2 (4)	−0.1 (6)
C(3)	5.5 (6)	4.5 (6)	3.7 (5)	−1.1 (5)	0.0 (4)	0.1 (4)
C(4)	4.9 (5)	6.2 (7)	4.0 (5)	−1.3 (6)	0.8 (4)	1.1 (5)
C(5)	4.6 (5)	4.8 (6)	4.0 (5)	−0.5 (5)	1.0 (4)	−0.6 (4)
C(6)	8.9 (10)	7.3 (10)	5.3 (7)	0.8 (8)	2.0 (7)	3.1 (7)
C(7)	7.5 (9)	5.8 (9)	7.5 (9)	−2.0 (7)	0.5 (7)	−1.2 (7)
C(8)	4.6 (6)	7.5 (10)	9.1 (11)	−1.7 (7)	−1.4 (6)	1.3 (9)
C(9)	10.0 (11)	8.5 (11)	4.7 (7)	−1.1 (10)	−0.2 (7)	2.3 (8)
B(1)	5.2 (7)	8.9 (12)	3.4 (6)	−0.4 (8)	−0.4 (5)	0.2 (7)

2. Molecule b

Br(1)	6.7 (1)	10.9 (1)	6.1 (1)	−0.9 (1)	−2.3 (1)	1.8 (1)
P(1)	4.5 (1)	4.6 (1)	3.6 (1)	0.0 (1)	0.2 (1)	0.6 (1)
F(1)	7.0 (4)	12.5 (10)	6.5 (4)	4.0 (6)	−2.0 (4)	−0.4 (6)
F(2)	8.8 (5)	9.8 (7)	5.6 (4)	1.6 (6)	0.6 (4)	−1.7 (5)
F(3)	12.7 (8)	9.9 (9)	7.8 (6)	−6.3 (7)	0.1 (5)	2.5 (6)
F(4)	6.6 (4)	14.2 (10)	6.2 (4)	3.6 (6)	−2.7 (4)	−1.4 (6)
F(5)	11.7 (8)	8.9 (7)	9.2 (7)	−4.6 (7)	1.1 (6)	2.9 (6)
F(6)	11.2 (6)	8.6 (7)	5.0 (4)	4.2 (6)	0.6 (4)	−0.5 (4)
N(1)	3.7 (4)	4.5 (4)	4.1 (4)	0.0 (3)	−0.3 (3)	−0.3 (4)
N(2)	5.9 (5)	4.3 (5)	4.2 (4)	−0.7 (4)	0.5 (4)	0.5 (4)
C(1)	4.2 (5)	4.5 (6)	5.6 (6)	0.5 (5)	−0.8 (4)	0.1 (5)
C(2)	5.6 (6)	4.4 (6)	5.3 (6)	0.1 (5)	−0.7 (5)	0.4 (5)
C(3)	5.0 (5)	4.6 (6)	3.9 (5)	−1.3 (5)	1.0 (4)	−0.4 (4)
C(4)	5.4 (6)	6.2 (7)	5.1 (6)	0.6 (6)	0.4 (5)	−1.1 (6)
C(5)	4.4 (5)	4.9 (6)	5.2 (6)	0.7 (5)	0.5 (4)	−0.6 (5)
C(6)	9.0 (11)	9.8 (14)	5.7 (8)	−3.1 (11)	0.9 (7)	1.1 (9)
C(7)	5.2 (6)	6.2 (8)	7.5 (9)	0.7 (7)	−1.0 (6)	−0.2 (8)
C(8)	9.4 (11)	4.5 (7)	7.8 (9)	0.8 (8)	0.0 (8)	0.7 (7)
C(9)	9.6 (11)	11.6 (15)	4.1 (6)	−5.0 (11)	1.9 (7)	1.4 (8)
B(1)	4.6 (6)	5.0 (7)	4.4 (6)	0.4 (6)	0.1 (5)	0.0 (6)

[a] Esd's in units of the last significant digit.

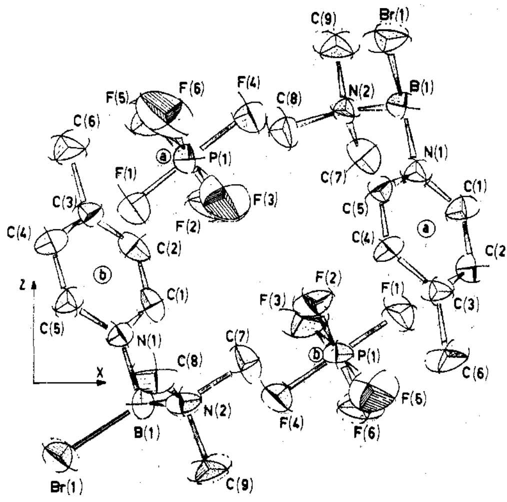


Figure 1.—ORTEP drawing of the thermal ellipsoids for the crystallographically independent unit, projected along the b axis. The two independent ions of each species are labeled as a and b.

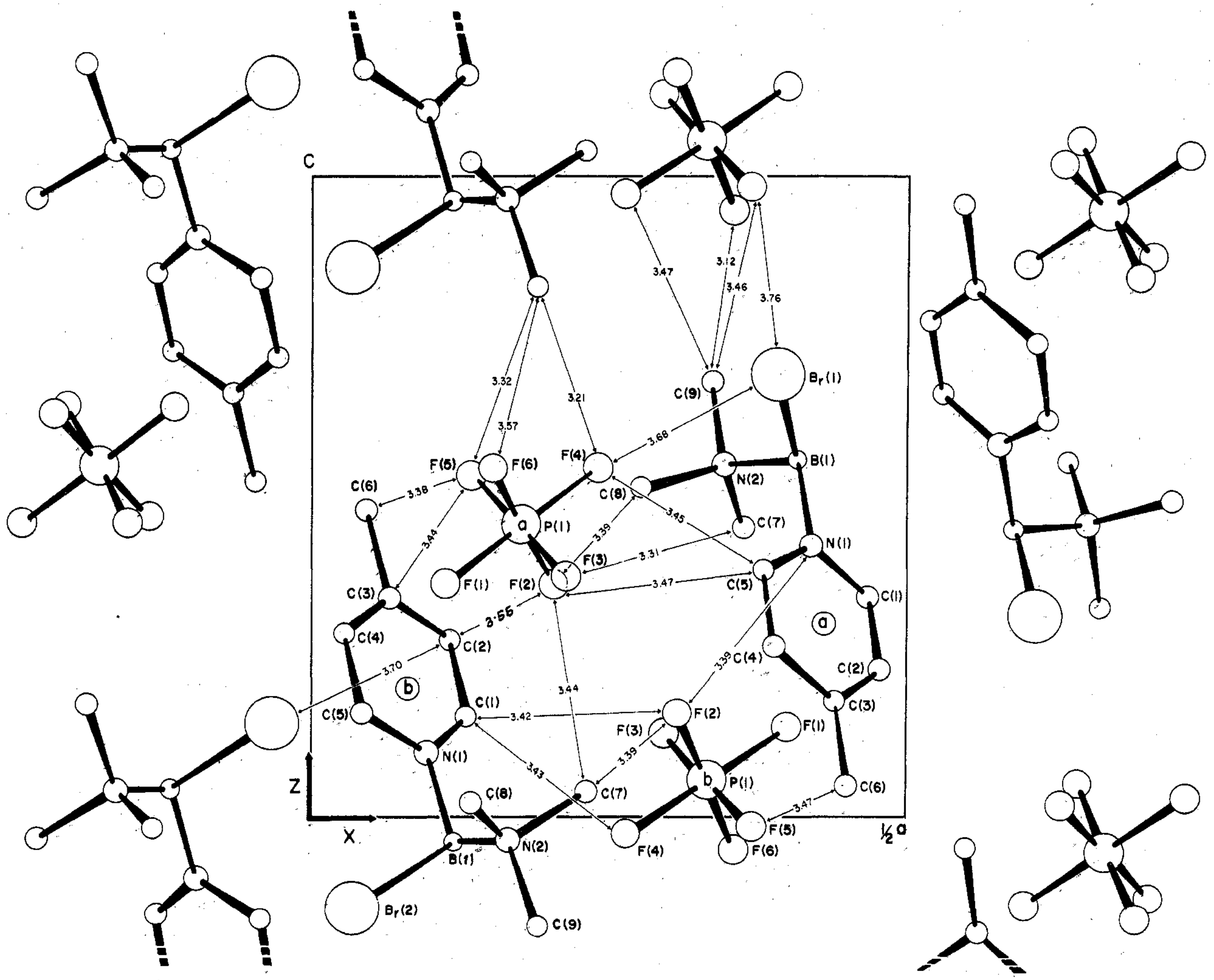


Figure 2.—Molecular packing of I, viewed along the b axis (cf. Figure 1). The shortest interatomic distances among different ions are indicated.

consequently $\mu R = 0.26$ (5), we felt it unnecessary to perform any absorption correction.

Structure Determination and Refinement

The structure was solved by the Patterson method. The heaviest interatomic vectors were seen to lie approximately on the planes with $y = 0$ and $y = {}^1/_2$; accordingly the positions of the two independent bromine atoms were located at nearly equal y coordinates thus giving rise to a quasicentrosymmetric arrangement. As a consequence the Fourier map calculated by phasing the reflections with the bromine atoms revealed the superimposition of two similar images of the structure, corresponding to a pseudosymmetry plane through the bromine atoms. However location of the two phosphorus atoms helped to remove part of the pseudosymmetry. The structure was then solved by three successive Fourier maps calculated after stepwise introduction of all the atoms. The refinement of the atomic parameters was carried out by means of seven cycles of 9×9 block-diagonal least-squares procedure,[3] until the maximum shift in the atomic coordinates and anisotropic thermal factors was less than one-third of the corresponding standard deviation. The weighting scheme adopted throughout the refinement corresponds to that suggested by Cruickshank and Philling

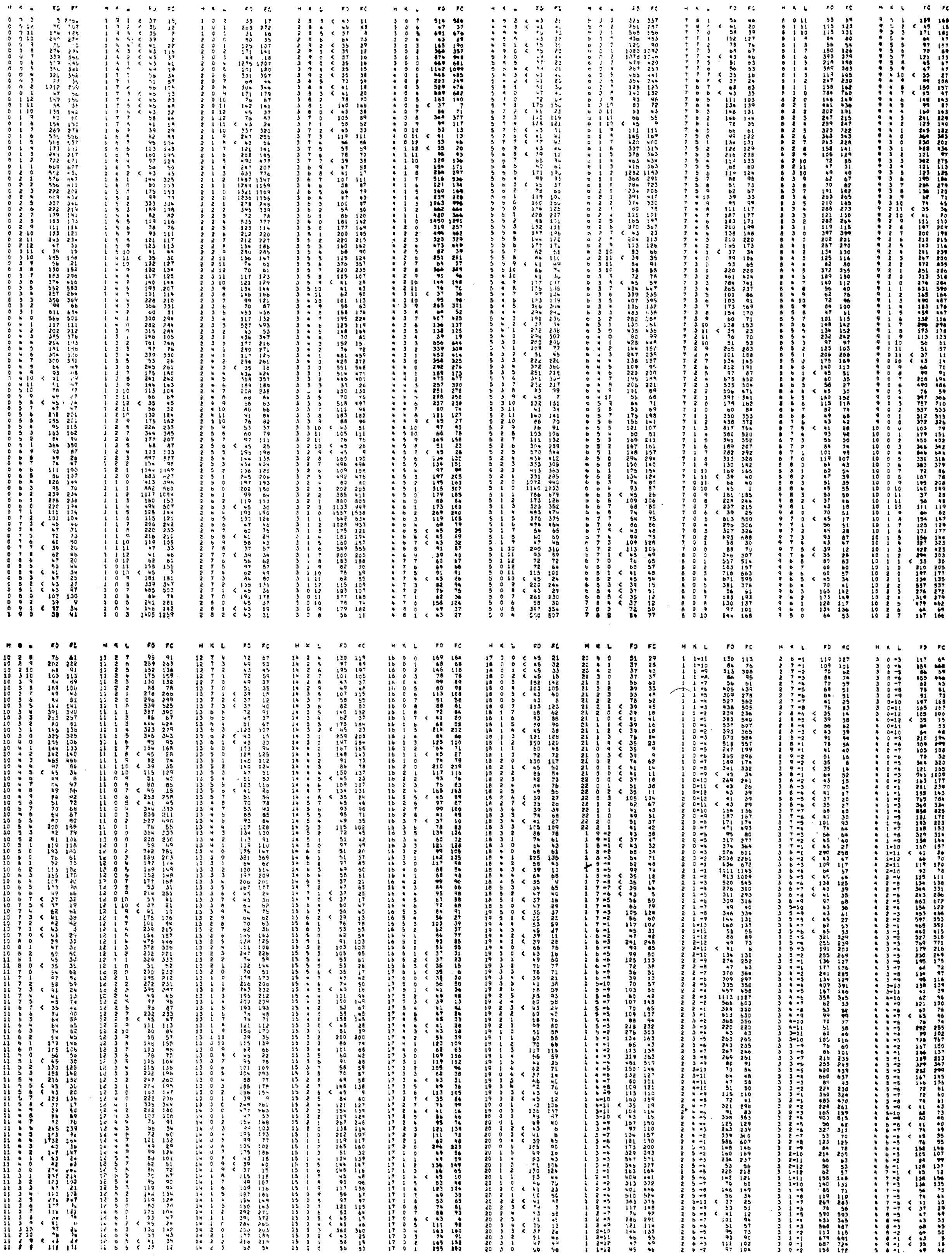
$$w(hkl) = 1/a + bF_o(hkl) + cF_o^2(hkl)$$

---

[3] A complete set of crystallographic programs (FORTRAN IV) written by A. Immirzi was used throughout the determination and refinement of the structure: A. Immirzi, *Ric. Sci.*, **37**, 743, 846, 850 (1967).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS



where, apart from a constant factor, $a = 2F_{\min}$, $b = 1$, and $c = 2/F_{\max}$.[4] At the end of the refinement, neglecting the hydrogen atoms, the disagreement factor R $(=\Sigma||F_o| - |F_c||/|F_o|)$ is 0.102 for 2962 independent measured reflections ($R = 0.089$ if only the 2481 nonzero reflections are taken into account). The final fractional coordinates and thermal factors are reported

---

[4] D. W. T. Cruickshank and D. E. Philling, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, New York, N. Y., 1961, p 32.

TABLE II (*Continued*)

H	K	L	FO	FC
5	8	-2	< 41	27
5	8	-3	< 41	19
5	8	-4	45	27
5	8	-5	45	33
5	7	-7	70	61
5	7	-6	53	49
5	7	-5	< 43	37
5	7	-4	42	37
5	7	-3	53	44
5	7	-2	98	104
5	7	-1	117	122
5	6	-1	117	116
5	6	-2	149	176
5	6	-3	91	100
5	6	-4	< 45	67
5	6	-5	70	51
5	6	-6	74	60
5	6	-7	56	41
5	6	-8	40	33
5	6	-9	< 35	17
5	5	-10	56	56
5	5	-9	47	27
5	5	-8	113	111
5	5	-7	109	127
5	5	-6	< 45	44
5	5	-5	58	69
5	5	-4	132	119
5	5	-3	142	150
5	5	-2	70	34
5	5	-1	175	170
5	4	-1	249	240
5	4	-2	117	127
5	4	-3	151	170
5	4	-4	257	250
5	4	-5	243	240
5	4	-6	253	217
5	4	-7	58	21
5	4	-8	136	129
5	4	-9	< 43	37
5	4	-10	51	16
5	3	-11	< 37	12
5	3	-10	41	25
5	3	-9	115	115
5	3	-8	111	110
5	3	-7	269	260
5	3	-6	321	305
5	3	-5	41	16
5	3	-4	190	179
5	3	-3	446	425
5	3	-2	272	317
5	3	-1	775	751
5	2	-1	156	152
5	2	-2	673	680
5	2	-3	226	201
5	2	-4	391	345
5	2	-5	208	204
5	2	-6	329	323
5	2	-7	224	219
5	2	-8	130	115
5	2	-9	140	134
5	2	-10	60	42
5	2	-11	75	76
5	1	-12	76	73
5	1	-11	< 41	30
5	1	-10	44	43
5	1	-9	220	226
5	1	-8	132	112
5	1	-7	272	275
5	1	-6	253	251
5	1	-5	345	374
5	1	-4	51	30
5	1	-3	432	514
5	1	-2	74	49
5	1	-1	957	896
5	0	-1	504	456
5	0	-2	693	747
5	0	-3	49	70
5	0	-4	202	172
5	0	-5	37	16
5	0	-6	430	392
5	0	-7	397	422
5	0	-8	274	271
5	0	-9	< 45	20
5	0	-10	< 45	51
5	0	-11	< 41	6
5	0	-12	< 35	7
6	0	-11	68	49
6	0	-10	272	291
6	0	-9	< 45	10
6	0	-8	147	169
6	0	-7	210	228
6	0	-6	76	104
6	0	-5	544	568
6	0	-4	97	91
6	0	-3	300	350
6	0	-2	436	358
6	0	-1	481	506
6	1	-1	60	67
6	1	-2	45	36
6	1	-3	313	365
6	1	-4	488	491
6	1	-5	80	81
6	1	-6	580	563
6	1	-7	206	183
6	1	-8	206	202
6	1	-9	97	80
6	1	-10	76	61
6	1	-11	80	82
6	2	-11	41	27
6	2	-10	142	140
6	2	-9	51	52
6	2	-8	241	249
6	2	-7	304	313
6	2	-6	218	221
6	2	-5	218	217
6	2	-4	154	152
6	2	-3	200	213
6	2	-2	191	177
6	2	-1	239	202
6	3	-1	191	181
6	3	-2	220	225
6	3	-3	578	659
6	3	-4	677	646
6	3	-5	597	560
6	3	-6	80	58
6	3	-7	95	77
6	3	-8	72	80
6	3	-9	150	153
6	3	-10	< 41	31
6	3	-11	84	74
6	4	-10	72	64
6	4	-9	< 43	3
6	4	-8	< 45	18
6	4	-7	76	70
6	4	-6	76	82
6	4	-5	286	286
6	4	-4	206	185
6	4	-3	321	339
6	4	-2	189	190
6	4	-1	364	338
6	5	-1	148	153
6	5	-2	125	129
6	5	-3	167	182
6	5	-4	259	243
6	5	-5	265	251
6	5	-6	99	114
6	5	-7	78	70
6	5	-8	< 43	29
6	5	-9	60	42
6	6	-8	78	79
6	6	-7	< 43	20
6	6	-6	78	81
6	6	-5	70	72
6	6	-4	113	100
6	6	-3	105	112
6	6	-2	< 45	0
6	6	-1	156	160
6	7	-1	< 45	19
6	7	-2	< 45	25
6	7	-3	107	117
6	7	-4	62	75
6	7	-5	< 43	17
6	7	-6	56	52
6	7	-7	56	54
6	8	-5	< 35	29
6	8	-4	62	52
6	8	-3	43	30
6	8	-2	62	74
6	8	-1	< 41	29
7	8	-1	< 41	16
7	8	-2	< 41	41
7	8	-3	70	66
7	8	-4	< 37	12
7	7	-7	60	44
7	7	-6	< 39	25
7	7	-5	< 41	17
7	7	-4	82	77
7	7	-3	66	65
7	7	-2	88	78
7	7	-1	72	77
7	6	-1	95	86
7	6	-2	132	112
7	6	-3	74	60
7	6	-4	111	124
7	6	-5	49	45
7	6	-6	49	24
7	6	-7	< 41	32
7	6	-8	< 37	35
7	5	-9	82	68
7	5	-8	91	99
7	5	-7	58	48
7	5	-6	74	57
7	5	-5	43	94
7	5	-4	101	96
7	5	-3	45	57
7	5	-2	169	162
7	5	-1	302	318
7	4	-1	107	94
7	4	-2	385	424
7	4	-3	202	222
7	4	-4	148	118
7	4	-5	56	44
7	4	-6	121	93
7	4	-7	119	126
7	4	-8	64	44
7	4	-9	91	85
7	4	-10	43	7
7	3	-11	45	34
7	3	-10	91	104
7	3	-9	82	68
7	3	-8	187	183
7	3	-7	109	100
7	3	-6	45	20
7	3	-5	60	54
7	3	-4	255	244
7	3	-3	471	495
7	3	-2	311	334
7	3	-1	232	264
7	2	-1	130	121
7	2	-2	502	472
7	2	-3	492	542
7	2	-4	500	547
7	2	-5	173	175
7	2	-6	269	255
7	2	-7	128	139
7	2	-8	76	76
7	2	-9	142	124
7	2	-10	66	61
7	2	-11	47	44
7	1	-11	84	85
7	1	-10	70	63
7	1	-9	93	84
7	1	-8	208	182
7	1	-7	165	155
7	1	-6	150	158
7	1	-5	156	164
7	1	-4	107	121
7	1	-3	555	577
7	1	-2	144	151
7	1	-1	749	691
7	0	-1	163	167
7	0	-2	537	576
7	0	-3	395	442
7	0	-4	329	337
7	0	-5	348	350
7	0	-6	< 39	26
7	0	-7	669	643
7	0	-8	121	100
7	0	-9	144	141
7	0	-10	101	89
7	0	-11	< 39	8
8	0	-11	47	34
8	0	-10	< 43	14
8	0	-9	51	43
8	0	-8	56	47
8	0	-7	150	125
8	0	-6	66	46
8	0	-5	78	71
8	0	-4	173	155
8	0	-3	261	277
8	0	-2	64	59
8	0	-1	611	624
8	1	-1	70	84
8	1	-2	457	441
8	1	-3	51	63
8	1	-4	148	147
8	1	-5	294	302
8	1	-6	333	322
8	1	-7	255	271
8	1	-8	267	241
8	1	-9	154	144
8	1	-10	45	41
8	1	-11	78	86
8	2	-11	< 37	31
8	2	-10	72	76
8	2	-9	93	78
8	2	-8	134	119
8	2	-7	197	184
8	2	-6	302	316
8	2	-5	304	285
8	2	-4	202	222
8	2	-3	99	135
8	2	-2	179	177
8	2	-1	539	502
8	3	-1	313	281
8	3	-2	150	170
8	3	-3	93	98
8	3	-4	160	145
8	3	-5	395	390
8	3	-6	152	147
8	3	-7	259	235
8	3	-8	62	25
8	3	-9	< 43	30
8	3	-10	43	25
8	4	-10	< 37	11
8	4	-9	< 41	17
8	4	-8	88	88
8	4	-7	< 45	17
8	4	-6	220	192
8	4	-5	286	270
8	4	-4	134	117
8	4	-3	510	527
8	4	-2	56	61
8	4	-1	86	84
8	5	-1	117	103
8	5	-2	152	161
8	5	-3	105	105
8	5	-4	51	62
8	5	-5	78	77
8	5	-6	152	155
8	5	-7	109	89
8	5	-8	49	15
8	5	-9	70	62
8	6	-8	58	47
8	6	-7	47	21
8	6	-6	101	85
8	6	-5	53	40
8	6	-4	56	39
8	6	-3	84	89
8	6	-2	109	110
8	6	-1	179	168
8	7	-1	72	70
8	7	-2	< 45	16
8	7	-3	< 43	6
8	7	-4	51	25
8	7	-5	64	51
8	7	-6	45	42
8	8	-4	60	54
8	8	-3	< 37	7
8	8	-2	58	50
8	8	-1	51	28
9	8	-1	< 39	12
9	8	-2	< 37	24
9	8	-3	47	41
9	7	-6	< 35	17
9	7	-5	58	53
9	7	-4	86	83
9	7	-3	< 43	26
9	7	-2	74	64
9	7	-1	121	88
9	6	-1	103	103
9	6	-2	64	43
9	6	-3	88	80
9	6	-4	66	57
9	6	-5	< 45	32
9	6	-6	62	49
9	6	-7	< 39	29
9	6	-8	62	38
9	5	-9	< 35	18
9	5	-8	< 41	36
9	5	-7	56	44
9	5	-6	74	69
9	5	-5	< 45	20
9	5	-4	181	155
9	5	-3	181	204
9	5	-2	70	46
9	5	-1	< 43	26
9	4	-1	158	128
9	4	-2	230	218
9	4	-3	171	183
9	4	-4	169	166
9	4	-5	222	206
9	4	-6	< 45	72
9	4	-7	51	43
9	4	-8	78	74
9	4	-9	64	58
9	4	-10	< 35	15
9	3	-10	84	75
9	3	-9	56	30
9	3	-8	70	56
9	3	-7	58	64
9	3	-6	119	129
9	3	-5	113	120
9	3	-4	319	354
9	3	-3	169	202
9	3	-2	253	229
9	3	-1	198	173
9	2	-1	134	126
9	2	-2	179	159
9	2	-3	224	241
9	2	-4	191	199
9	2	-5	348	338
9	2	-6	140	147
9	2	-7	121	125
9	2	-8	99	91
9	2	-9	84	83
9	2	-10	68	82
9	2	-11	76	78
9	1	-11	39	64
9	1	-10	132	123
9	1	-9	62	48
9	1	-8	175	160
9	1	-7	56	41
9	1	-6	358	359
9	1	-5	296	270
9	1	-4	306	324
9	1	-3	313	305
9	1	-2	290	255
9	1	-1	97	73
9	0	-1	58	61
9	0	-2	206	183
9	0	-3	424	417
9	0	-4	185	174
9	0	-5	183	207
9	0	-6	60	70
9	0	-7	247	222
9	0	-8	53	36
9	0	-9	232	230
9	0	-10	72	61
9	0	-11	43	31
10	0	-11	< 35	12
10	0	-10	95	85
10	0	-9	< 45	21
10	0	-8	169	152
10	0	-7	121	132
10	0	-6	280	245
10	0	-5	47	42
10	0	-4	169	206
10	0	-3	171	148
10	0	-2	448	473
10	0	-1	206	195
10	1	-1	395	375
10	1	-2	274	267
10	1	-3	434	455
10	1	-4	51	64
10	1	-5	82	78
10	1	-6	103	86
10	1	-7	356	359
10	1	-8	175	167
10	1	-9	99	86
10	1	-10	82	66
10	1	-11	< 35	30
10	2	-10	70	74
10	2	-9	< 43	13
10	2	-8	175	162
10	2	-7	210	197
10	2	-6	243	236
10	2	-5	134	130
10	2	-4	160	177
10	2	-3	232	222
10	2	-2	391	392
10	2	-1	370	366
10	3	-1	284	270
10	3	-2	76	78
10	3	-3	325	334
10	3	-4	101	109
10	3	-5	70	73
10	3	-6	60	60
10	3	-7	111	93
10	3	-8	< 45	39
10	3	-9	105	101
10	3	-10	51	31
10	4	-9	< 39	32
10	4	-8	113	105
10	4	-7	107	88
10	4	-6	< 45	45
10	4	-5	150	127
10	4	-4	130	143
10	4	-3	49	66
10	4	-2	150	145
10	4	-1	132	123
10	5	-1	360	343
10	5	-2	58	48
10	5	-3	76	74
10	5	-4	47	50
10	5	-5	< 45	9
10	5	-6	62	55
10	5	-7	60	41
10	5	-8	< 39	36
10	6	-7	< 37	16
10	6	-6	< 41	25
10	6	-5	< 43	36
10	6	-4	< 45	24
10	6	-3	< 45	48
10	6	-2	91	85
10	6	-1	144	147
10	7	-1	< 43	37
10	7	-2	64	56
10	7	-3	53	25
10	7	-4	< 41	17
10	7	-5	< 37	24
10	7	-6	49	41
10	8	-3	< 35	15
10	8	-2	< 35	30
10	8	-1	43	46
11	8	-1	< 35	16
11	7	-5	45	23
11	7	-4	58	51
11	7	-3	< 41	24
11	7	-2	< 41	36
11	7	-1	51	45
11	6	-1	56	24
11	6	-2	< 45	33
11	6	-3	< 45	52
11	6	-4	60	50
11	6	-5	43	77
11	6	-6	45	48
11	6	-7	< 35	34
11	5	-8	< 37	32
11	5	-7	45	52
11	5	-6	111	74
11	5	-5	51	24
11	5	-4	72	64
11	5	-3	72	67
11	5	-2	< 45	31
11	5	-1	140	105
11	4	-1	309	302
11	4	-2	253	248
11	4	-3	< 45	58
11	4	-4	74	74
11	4	-5	128	117
11	4	-6	76	82
11	4	-7	86	81
11	4	-8	< 41	23
11	4	-9	< 37	14
11	3	-10	< 35	17
11	3	-9	41	21
11	3	-8	72	63
11	3	-7	84	77
11	3	-6	160	183
11	3	-5	80	86
11	3	-4	146	127
11	3	-3	179	179
11	3	-2	171	163
11	3	-1	97	107
11	2	-1	292	297
11	2	-2	125	136
11	2	-3	62	68
11	2	-4	117	111
11	2	-5	175	172
11	2	-6	< 45	34
11	2	-7	204	200
11	2	-8	53	18
11	2	-9	49	28
11	2	-10	< 37	2
11	1	-10	< 39	39
11	1	-9	< 43	51
11	1	-8	74	76
11	1	-7	143	156
11	1	-6	142	125
11	1	-5	173	180
11	1	-4	165	171
11	1	-3	41	20
11	1	-2	298	294
11	1	-1	257	223
11	0	-1	125	119
11	0	-2	44	62
11	0	-3	51	58
11	0	-4	42	72
11	0	-5	130	149
11	0	-6	78	77
11	0	-7	286	270
11	0	-8	50	52
11	0	-9	121	121
11	0	-10	45	44
12	0	-10	< 37	21
12	0	-9	78	65
12	0	-8	212	197
12	0	-7	47	14
12	0	-6	317	311
12	0	-5	138	116
12	0	-4	214	254
12	0	-3	< 39	26
12	0	-2	98	100
12	0	-1	158	140
12	1	-1	97	80
12	1	-2	< 39	30
12	1	-3	309	330
12	1	-4	53	56
12	1	-5	193	190
12	1	-6	253	262
12	1	-7	44	87
12	1	-8	91	98
12	1	-9	62	45
12	1	-10	62	62
12	2	-10	68	60
12	2	-9	101	97
12	2	-8	74	58
12	2	-7	< 45	6
12	2	-6	101	66
12	2	-5	51	65
12	2	-4	253	263
12	2	-3	< 41	60
12	2	-2	123	145
12	2	-1	210	199
12	3	-1	167	147
12	3	-2	79	127
12	3	-3	263	291
12	3	-4	93	90
12	3	-5	179	167
12	3	-6	< 45	43
12	3	-7	49	15
12	3	-8	70	63
12	3	-9	< 39	35
12	4	-9	64	51
12	4	-8	< 39	43
12	4	-7	53	53
12	4	-6	66	61
12	4	-5	< 45	52
12	4	-4	113	140
12	4	-3	93	84
12	4	-2	232	226
12	4	-1	247	238
12	5	-1	< 45	32
12	5	-2	68	62
12	5	-3	97	107
12	5	-4	47	32
12	5	-5	49	48
12	5	-6	45	47
12	5	-7	49	23
12	5	-8	< 35	21
12	6	-6	41	40
12	6	-5	47	31
12	6	-4	82	98
12	6	-3	105	102
12	6	-2	66	51
12	6	-1	70	38
12	7	-1	< 41	10
12	7	-2	< 39	20
12	7	-3	< 39	17
12	7	-4	62	65
13	7	-4	< 33	24
13	7	-3	39	21
13	7	-2	39	38
13	7	-1	76	65
13	6	-1	138	130
13	6	-2	< 43	15
13	6	-3	< 43	41
13	6	-4	< 41	13
13	6	-5	74	49
13	6	-6	49	27
13	5	-7	66	50
13	5	-6	< 41	34
13	5	-5	58	39
13	5	-4	62	38
13	5	-3	< 45	49
13	5	-2	84	84
13	5	-1	60	37
13	4	-1	144	150
13	4	-2	86	88
13	4	-3	138	114
13	4	-4	72	57
13	4	-5	66	74
13	4	-6	58	50
13	4	-7	< 41	40
13	4	-8	68	55
13	3	-9	39	41
13	3	-8	49	61
13	3	-7	60	52
13	3	-6	< 45	38
13	3	-5	66	68
13	3	-4	80	69
13	3	-3	64	87
13	3	-2	197	195
13	3	-1	93	94
13	2	-1	350	327
13	2	-2	84	69
13	2	-3	107	109
13	2	-4	158	165
13	2	-5	49	46
13	2	-6	97	80
13	2	-7	109	103
13	2	-8	< 43	36
13	2	-9	< 39	48
13	1	-10	37	55
13	1	-9	49	57
13	1	-8	< 43	54
13	1	-7	169	163
13	1	-6	49	49
13	1	-5	97	82
13	1	-4	< 43	31
13	1	-3	72	83
13	1	-2	306	296
13	1	-1	154	142
13	0	-1	226	222
13	0	-2	109	84
13	0	-3	298	299
13	0	-4	47	55
13	0	-5	187	199
13	0	-6	76	72
13	0	-7	111	95
13	0	-8	47	19
13	0	-9	58	51
13	0	-10	< 35	26
14	0	-9	< 39	7
14	0	-8	< 43	39
14	0	-7	82	71
14	0	-6	99	104
14	0	-5	117	118
14	0	-4	< 45	18
14	0	-3	< 43	22
14	0	-2	64	53
14	0	-1	144	120
14	1	-1	< 41	39
14	1	-2	51	34
14	1	-3	58	36
14	1	-4	93	75
14	1	-5	58	52
14	1	-6	76	64
14	1	-7	123	113
14	1	-8	86	75
14	1	-9	< 39	30
14	2	-9	45	30
14	2	-8	< 41	15
14	2	-7	60	39
14	2	-6	93	90
14	2	-5	97	92
14	2	-4	185	216
14	2	-3	136	155
14	2	-2	148	149
14	2	-1	189	175
14	3	-1	228	211
14	3	-2	103	98
14	3	-3	64	76
14	3	-4	138	130
14	3	-5	99	96
14	3	-6	101	96
14	3	-7	74	52
14	3	-8	< 39	21
14	4	-8	41	24
14	4	-7	53	64
14	4	-6	51	57
14	4	-5	70	52
14	4	-4	101	114
14	4	-3	119	130
14	4	-2	66	71
14	4	-1	107	117
14	5	-1	189	196
14	5	-2	78	79
14	5	-3	< 45	25
14	5	-4	68	64
14	5	-5	72	60
14	5	-6	49	52
14	5	-7	37	42
14	6	-5	39	42
14	6	-4	< 39	41
14	6	-3	< 41	13
14	6	-2	56	45
14	6	-1	< 43	11
14	7	-1	45	28
14	7	-2	< 35	7
15	6	-1	64	52
15	6	-2	53	33
15	6	-3	53	35
15	6	-4	< 37	34
15	5	-6	< 37	16
15	5	-5	< 39	16
15	5	-4	< 41	40
15	5	-3	60	61
15	5	-2	105	95
15	5	-1	128	92
15	4	-1	86	88
15	4	-2	72	51
15	4	-3	< 45	50
15	4	-4	80	85
15	4	-5	56	21
15	4	-6	< 41	27
15	4	-7	< 37	20
15	3	-8	< 37	6
15	3	-7	53	44
15	3	-6	60	59
15	3	-5	< 45	13
15	3	-4	105	118
15	3	-3	107	122
15	3	-2	243	236
15	3	-1	53	50
15	2	-1	80	71
15	2	-2	103	72
15	2	-3	136	147
15	2	-4	76	92
15	2	-5	91	89
15	2	-6	103	112
15	2	-7	< 43	32
15	2	-8	74	77
15	1	-9	< 35	33
15	1	-8	< 41	35
15	1	-7	56	61
15	1	-6	74	48
15	1	-5	117	103
15	1	-4	148	141
15	1	-3	80	84
15	1	-2	76	83
15	1	-1	208	192
15	0	-1	72	79
15	0	-2	45	34
15	0	-3	158	167
15	0	-4	163	172
15	0	-5	93	97
15	0	-6	62	58
15	0	-7	105	116
15	0	-8	47	52
15	0	-9	39	53
16	0	-8	51	56
16	0	-7	< 43	32
16	0	-6	123	119
16	0	-5	105	115
16	0	-4	132	132
16	0	-3	66	43
16	0	-2	148	135
16	0	-1	173	155
16	1	-1	220	227
16	1	-2	243	224
16	1	-3	47	52
16	1	-4	66	60
16	1	-5	49	39
16	1	-6	51	52
16	1	-7	< 41	26
16	1	-8	53	46
16	2	-8	45	12
16	2	-7	60	59
16	2	-6	62	65
16	2	-5	99	115
16	2	-4	< 45	28
16	2	-3	119	120
16	2	-2	< 45	67
16	2	-1	107	100
16	3	-1	239	222
16	3	-2	115	115
16	3	-3	109	138
16	3	-4	49	78
16	3	-5	53	48
16	3	-6	53	51
16	3	-7	43	31
16	4	-7	70	67
16	4	-6	47	40
16	4	-5	49	37
16	4	-4	45	34
16	4	-3	47	53
16	4	-2	79	65
16	4	-1	84	60
16	5	-1	< 43	42
16	5	-2	< 43	28
16	5	-3	56	59
16	5	-4	< 39	31
16	5	-5	< 37	31
16	6	-3	< 35	38
16	6	-2	< 37	11
16	6	-1	51	25
17	6	-1	< 35	19
17	5	-4	39	39
17	5	-3	43	26
17	5	-2	< 39	28
17	5	-1	< 41	38
17	4	-1	< 43	18
17	4	-2	70	67
17	4	-3	< 43	19
17	4	-4	105	92
17	4	-5	47	30
17	4	-6	45	42
17	3	-7	< 35	15
17	3	-6	< 39	18
17	3	-5	56	30
17	3	-4	165	166
17	3	-3	47	28
17	3	-2	62	72
17	3	-1	117	105
17	2	-1	121	115
17	2	-2	84	71
17	2	-3	97	100
17	2	-4	53	54
17	2	-5	66	54
17	2	-6	56	55
17	2	-7	51	38
17	1	-8	< 35	6
17	1	-7	82	80
17	1	-6	< 43	44
17	1	-5	121	117
17	1	-4	58	57
17	1	-3	91	101
17	1	-2	97	90
17	1	-1	78	65
17	0	-1	136	123
17	0	-2	< 45	16
17	0	-3	64	48
17	0	-4	< 45	28
17	0	-5	49	36
17	0	-6	70	74
17	0	-7	< 41	15
17	0	-8	< 35	44
18	0	-7	51	37
18	0	-6	51	39
18	0	-5	< 43	33
18	0	-4	60	55
18	0	-3	146	131
18	0	-2	93	95
18	0	-1	< 45	13
18	1	-1	74	56
18	1	-2	86	101
18	1	-3	76	96
18	1	-4	183	182
18	1	-5	74	67
18	1	-6	< 41	39
18	1	-7	< 37	28
18	2	-7	< 35	38
18	2	-6	< 39	20
18	2	-5	< 41	30
18	2	-4	64	53
18	2	-3	88	91
18	2	-2	< 45	61
18	2	-1	84	79
18	3	-1	70	76
18	3	-2	72	49
18	3	-3	47	49
18	3	-4	76	60
18	3	-5	< 39	11
18	3	-6	37	29
18	4	-5	< 35	9
18	4	-4	< 39	33
18	4	-3	45	31
18	4	-2	< 41	25
18	4	-1	95	95
18	5	-1	41	23
18	5	-2	60	53
18	5	-3	68	66
19	5	-1	< 35	23
19	4	-1	56	54
19	4	-2	43	23
19	4	-3	< 37	42
19	4	-4	37	26
19	3	-5	< 35	40
19	3	-4	47	30
19	3	-3	43	37
19	3	-2	56	45
19	3	-1	72	51
19	2	-1	47	60
19	2	-2	125	118
19	2	-3	45	55
19	2	-4	43	41
19	2	-5	43	37
19	2	-6	41	32
19	1	-6	< 37	22
19	1	-5	58	62
19	1	-4	62	45
19	1	-3	< 43	25
19	1	-2	66	55
19	1	-1	121	126
19	0	-1	58	63
19	0	-2	47	21
19	0	-3	66	62
19	0	-4	49	33
19	0	-5	93	83
19	0	-6	< 37	20
20	0	-5	103	98
20	0	-4	< 39	40
20	0	-3	< 41	40
20	0	-2	56	74
20	0	-1	51	24
20	1	-1	< 43	21
20	1	-2	< 43	22
20	1	-3	< 41	24
20	1	-4	< 39	44
20	1	-5	< 37	16
20	2	-5	45	26
20	2	-4	< 37	31
20	2	-3	< 39	41
20	2	-2	47	42
20	2	-1	51	66
20	3	-1	< 39	26
20	3	-2	56	51
20	3	-3	< 37	18
20	3	-4	60	44
20	4	-2	56	41
20	4	-1	41	40
21	3	-2	< 35	25
21	3	-1	39	56
21	2	-1	< 39	22
21	2	-2	< 37	30
21	2	-3	49	50
21	2	-4	62	61
21	1	-4	41	52
21	1	-3	62	52
21	1	-2	< 39	27
21	1	-1	41	65
21	0	-1	< 41	27
21	0	-2	72	89
21	0	-3	< 39	21
21	0	-4	< 37	9
22	0	-3	< 35	4
22	0	-2	58	66
22	0	-1	< 37	26
22	1	-1	45	47
22	1	-2	45	28
22	2	-1	43	47

in Table I together with their corresponding standard deviations; Figure 1 shows an ORTEP drawing of the thermal ellipsoids. A list of the observed and calculated structure factors is also given in Table II, while Table III lists bond lengths, bond angles, and some relevant dihedral angles for the independent unit of the structure.

Discussion of the Structure

The presence of two chemically identical but crystallographically independent formula units in the unit cell, a and b in Figures 1 and 2, is rather unusual. However, as can be seen from the figures, a pseudocentrosymmetric arrangement of the ions exists around the points with approximate fractional coordinates ($^1/_4$, -0.06, $^1/_4$), ($^1/_4$, -0.06, $^3/_4$), and the symmetry-related ones. While the PF_6^- ions are in good agreement with such pseudosymmetry, the cations depart from it as far as the positions in space of the bromine atoms are concerned. This departure results from the presence of optically active cations having all the same chirality, as it is unambiguously derived from the spatial distribution of the three Fourier-detectable substituents attached to the boron atoms (the hydrogen atom must necessarily occupy the remaining tetrahedral site). A virtually complete centrosymmetry could be achieved only through the exchange of Br with H in the coordination sites around the boron atom in either of the two independent cations, producing a racemic mixture. We believe that the present structure represents an interesting example in which the tendency toward the retention of a center of symmetry—which in most cases is a favorable condition of good packing—associated with the presence of chiral isomorphous molecules, is the driving force toward the occurrence of two independent molecules in the asymmetric unit.

The geometrical parameters (bond lengths, bond angles, and dihedral angles) of the four independent ionic species are reported in Table III. Neither of the two pairs of independent ions shows any substantial differences in geometry: in Figure 3 the average dimensions of the cation are reported. As for the hexafluorophosphate anion, its geometry can be described as a slightly distorted octahedron (*cf.* Table III), with a d_{P-F} average value of 1.57 ± 0.04 Å.[5] The two chemically different B–N bond lengths do not show apprecia-

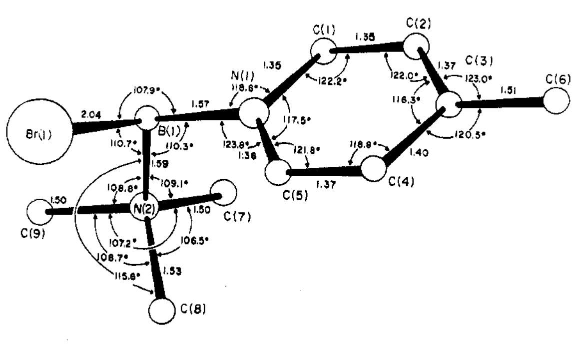


Figure 3.—Molecular geometry of the cation; the parameters are averaged over the two crystallographically independent individuals. For the esd and the dihedral angles, *cf.* Table III.

---

(5) In the present paper the deviations associated with any average value indicate the range of the individual values.

TABLE III

MOLECULAR DIMENSIONS[a]

	Molecule a	Molecule b
A. Bond Lengths, Å		
Br(1)-B(1)	2.03 (2)	2.05 (2)
P(1)-F(1)	1.55 (1)	1.59 (1)
P(1)-F(2)	1.56 (2)	1.59 (1)
P(1)-F(3)	1.55 (2)	1.56 (1)
P(1)-F(4)	1.60 (1)	1.57 (1)
P(1)-F(5)	1.56 (2)	1.55 (1)
P(1)-F(6)	1.52 (2)	1.61 (1)
N(1)-B(1)	1.58 (2)	1.56 (2)
N(1)-C(1)	1.34 (2)	1.36 (2)
N(1)-C(5)	1.37 (2)	1.36 (2)
N(2)-B(1)	1.59 (2)	1.59 (2)
N(2)-C(7)	1.49 (2)	1.52 (2)
N(2)-C(8)	1.52 (2)	1.55 (2)
N(2)-C(9)	1.51 (2)	1.50 (2)
C(1)-C(2)	1.34 (2)	1.36 (2)
C(2)-C(3)	1.41 (2)	1.34 (2)
C(3)-C(4)	1.40 (2)	1.41 (2)
C(4)-C(5)	1.37 (2)	1.38 (2)
C(3)-C(6)	1.49 (2)	1.53 (2)
B. Bond Angles, Deg		
F(1)-P(1)-F(2)	88.9 (4)	90.3 (3)
F(1)-P(1)-F(3)	86.0 (4)	87.9 (3)
F(1)-P(1)-F(4)	177.8 (4)	177.1 (4)
F(1)-P(1)-F(5)	91.3 (4)	91.6 (3)
F(1)-P(1)-F(6)	92.1 (4)	90.7 (3)
F(2)-P(1)-F(3)	87.7 (5)	89.7 (3)
F(2)-P(1)-F(4)	90.4 (3)	91.7 (3)
F(2)-P(1)-F(5)	94.1 (4)	91.4 (4)
F(2)-P(1)-F(6)	177.3 (4)	178.4 (4)
F(3)-P(1)-F(4)	92.0 (4)	90.0 (3)
F(3)-P(1)-F(5)	176.6 (4)	178.8 (4)
F(3)-P(1)-F(6)	89.8 (5)	89.0 (3)
F(4)-P(1)-F(5)	90.8 (4)	90.5 (4)
F(4)-P(1)-F(6)	88.5 (5)	87.3 (3)
F(5)-P(1)-F(6)	88.3 (5)	89.9 (3)
Br(1)-B(1)-N(1)	108.8 (3)	107.1 (3)
Br(1)-B(1)-N(2)	111.7 (6)	109.7 (5)
N(1)-B(1)-N(2)	111.4 (5)	109.3 (5)
B(1)-N(2)-C(7)	108.7 (6)	109.5 (6)
B(1)-N(2)-C(8)	113.7 (6)	118.0 (7)
B(1)-N(2)-C(9)	108.7 (7)	109.0 (6)
B(1)-N(1)-C(1)	120.8 (5)	116.4 (5)
B(1)-N(1)-C(5)	120.9 (6)	126.7 (6)
C(7)-N(2)-C(8)	107.4 (6)	105.7 (6)
C(7)-N(2)-C(9)	110.7 (6)	103.7 (5)
C(8)-N(2)-C(9)	107.6 (6)	109.9 (6)
N(1)-C(1)-C(2)	122.3 (7)	122.2 (6)
C(1)-C(2)-C(3)	123.4 (6)	120.7 (6)
C(2)-C(3)-C(4)	112.6 (6)	120.1 (7)
C(3)-C(4)-C(5)	123.2 (6)	116.4 (6)
C(4)-C(5)-N(1)	120.0 (5)	123.7 (6)
C(5)-N(1)-C(1)	118.3 (6)	116.7 (6)
C(2)-C(3)-C(6)	122.9 (7)	123.2 (7)
C(4)-C(3)-C(6)	124.3 (7)	116.7 (7)
C. Internal Rotation Angles, Deg (Trans Conformation 180°)		
N(1)-B(1)-N(2)-C(7)	59	65
N(1)-B(1)-N(2)-C(8)	−60	−56
N(1)-B(1)-N(2)-C(9)	180	178
Br(1)-B(1)-N(2)-C(7)	179	178
Br(1)-B(1)-N(2)-C(8)	61	61
Br(1)-B(1)-N(2)-C(9)	−58	−66
C(1)-N(1)-B(1)-Br(1)	140	138
C(5)-N(1)-B(1)-Br(1)	−42	−38
C(1)-N(1)-B(1)-N(2)	−97	−104
C(5)-N(1)-B(1)-N(2)	81	81

[a] Esd's in units of the last significant digit.

ble difference, and their average value (1.579 ± 0.015 Å) is in the range of values quoted in the literature for B–N bond lengths involving tetrahedral boron atoms.[6] To the best of our knowledge, the B–Br distance (average 2.038 ± 0.008 Å) is the first reported bond length of this type involving a B atom with sp^3 hybridization, and it is appreciably longer than the B–Br distance reported for the gaseous BBr_3 molecule (1.87 ± 0.02 Å).[7] The N–B–N and N–B–Br bond angles are all close to the tetrahedral value (within ±2.5°), in agreement with the sp^3 hybridization on the boron atom. The systematic increase of 1–2° of these bond angles in ion b compared to a is probably significant (the average esd on the angles is 0.4°) and is to be attributed to packing effects. In both cations, the observed compression of the Br–B–N (picolinic) angle is apparently due to the steric interactions involving the bulky $-N(CH_3)_3$ group. One would expect that the nonbonded interactions around the boron atom would give rise to some increase of the N–B–N and N–B–Br angles with respect to the tetrahedral value. The observed values, however, do not differ on the average. This may be rationalized as follows. Since B–H is certainly the shortest of the four B–X bonds, the repulsion between the bonding electron pairs around the boron atom is responsible for some compression effect, which leads to the observed geometry (Sidgwick and Powell's rule).[8] The rotation around the $B-N(CH_3)_3$ bond (*cf.* Table III and Figure 4) obtains a nearly staggered arrangement of the substituents around the B and N atoms. The CH_3-N-CH_3 bond angles are slightly smaller than the tetrahedral

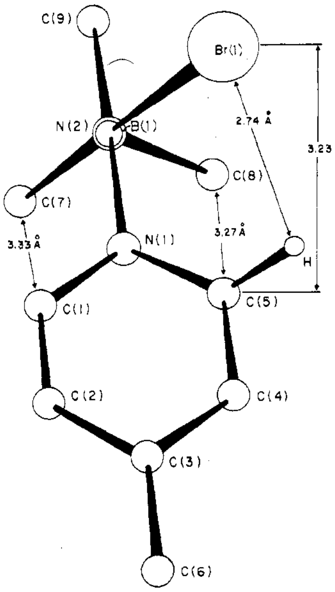


Figure 4.—View of the cation (average geometry) along the B(1)–N(2) bond. The shortest intramolecular distances between atoms separated by more than three bonds are indicated. Only one hydrogen atom has been represented (see text).

---

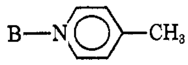
(6) S. Geller and J. L. Hoard, *Acta Crystallogr.*, **4**, 399 (1951); J. L. Hoard, S. Geller, and T. B. Owen, *ibid.*, **4**, 405 (1951).

(7) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Chemical Society, Burlington House, W.1, London, 1958, p 53.

(8) N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc., Ser. A*, **176**, 153 (1940).

value (107.5 ± 3.5°), only one of the six independent measurements being larger than 109.5° (see Table III). The C(8)–N–B angle (average 116.0 ± 2.1°) is significantly larger than the other two corresponding angles (average 108.9 ± 0.8°), apparently because of the larger steric repulsions involving the C(8) group, which is in "gauche" orientation with respect to both of the bulky substituents on the boron atom.

The



group is planar within experimental error. The msd's from the average plane are 0.018 and 0.027 Å for cations a and b, respectively; the equations of the corresponding planes, in terms of fractional coordinates, are $0.6388x + 0.6753y + 0.3640z - 1.1072 = 0$, for a, and $0.6611x + 0.6389y + 0.3885z - 6.7044 = 0$, for b. The dihedral angles between the picolinic group and the Br–B–N(1) and N(2)–B–N(1′) planes are (average) 40.0 ± 2.5 and 81.0 ± 0.3°, respectively; the larger dihedral angle involving the bulkier $-N(CH_3)_3$ group is very likely due to larger steric repulsions. As it is shown in Figure 4, the pyridine ring is nearly orthogonal to the N–B–N plane (average value of the dihedral angle 82 ± 1°); the departure from the 90° value seems to be due to the necessity of increasing the intramolecular Br···H distance (2.7 Å, see Figure 4; the distance has been evaluated assuming the H atom in the normal stereochemical position), which still falls short of the sum of the van der Waals radii (3.1 Å).[9]

The geometry of the pyridine ring of the picolinic residue does not differ, within experimental error, from that established for pyridine by microwave measurements.[10] As expected in an ionic structure, ions with the same charge tend to avoid close contacts. As reported in Figure 2, where hydrogen atoms are neglected, the shortest interatomic distance between different cations is 3.70 Å (Br···C); as for the PF_6^- ions the F···F distances are never shorter than 4 Å. On the other hand, interatomic contact between ions of opposite charge can be as close as 3.12 Å ($F\cdots CH_3$) and 3.39 Å (F···N of the picolinic ring).

Acknowledgment.—We wish to thank Professor Ryschkewitsch, who kindly supplied the compound. We also thank Professor M. Goodman for his interest in this work and gratefully acknowledge the support of research grants from the National Science Foundation (GB 7558) and the National Institutes of Health (GM 08974).

---

[9] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

[10] B. Bank, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, **22**, 2013 (1954).

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

The Crystal and Molecular Structure of Dimeric Tetramethyl-1,3-diisothiocyanatodistannoxane, $[((CH_3)_2SnNCS)_2O]_2$

BY YEH MEI CHOW

Received October 27, 1969

The crystal structure of dimeric tetramethyl-1,3-diisothiocyanatodistannoxane has been determined from three-dimensional X-ray diffraction data. It forms monoclinic crystals in space group $C2/m$ with a = 21.73 (4) Å, b = 7.88 (1) Å, c = 10.96 (2) Å, and β = 134.7 (2)°. The intensities of 546 independent reflections were obtained by visual estimation of film data. The structure was solved by Patterson and Fourier syntheses and refined by the least-squares method to a conventional R factor of 8.0%. The dimeric molecule has $2/m$ symmetry with a central planar four-membered $Sn(2)_2O_2$ ring. Secondary bonding (2.84 (4) Å) between the isothiocyanate nitrogens of these tin atoms and the exocyclic tins forms two additional planar Sn(2)OSn(1)···N(2) rings. The endocyclic tin is thus pentacoordinate, approximately trigonal bipyramidal. Still further weak Sn(1)···S(2) linkage (3.33 (3) Å) between dimers results in distorted octahedral hexacoordination for the exocyclic tin atom and infinite chains parallel to [001]. Distances are Sn(1)–O = 2.05(5), Sn(1)–N(1) = 2.06 (4), Sn(1)–CH_3(1) = 2.07 (3), Sn(2)–O = 1.99 (3), Sn(2)–O = 2.15 (4), Sn(2)–N(2) = 2.39 (8), and Sn(2)–CH_3(2) = 2.15 (3) Å. Both NCS groups are linear with distances N(1)–C(1) = 1.17 (7), C(1)–S(1) = 1.61 (6), N(2)–C(2) = 1.10 (7), and C(2)–S(2) = 1.64 (5) Å.

Introduction

The crystal structure reported here is a part of a general investigation of donor–acceptor interactions between pseudohalogens and heavy atoms in the solid state. Many tetraalkyldistannoxane derivatives $(XR_2Sn)_2O$ and the related hydroxides $XR_2SnOSnR_2OH$ are known (X = halogen, pseudohalogen, carboxylate, nitrate, alkoxide, or phenoxide). Pfeiffer and Brack[1] in 1914 assumed that the compound $(XR_2Sn)_2O$ had the structure I; however, Harada[2] argued the case for a cyclic structure II where the tin atoms have coordination numbers of 4 and 5; on rather insecure evidence he

---

[1] P. Pfeiffer and O. Brack, *Z. Anorg. Allg. Chem.*, **87**, 229 (1914).

[2] R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).