of the other octet. The data are compatible with a model in which only hydrogen tautomerism is taking place and Lewis base exchange, if any, is too slow to be detected. There are, therefore, two types of boron in the ratio of 2:1 which would be expected to have different chemical shift values. These two kinds of boron would be expected to couple to the seven hydrogens by similar (but not identical) amounts. Assuming that both kinds of boron spin couple to the seven hydrogens equally, agreement between the intensities predicted and the intensities observed can be shown (Table I).

TABLE I

PREDICTED *vs.* OBSERVED INTENSITIES

Low-field borons	0.02	0.13	0.40	0.67	0.67	0.40	0.13	0.02	
High-field borons		0.01	0.07	0.20	0.33	0.33	0.20	0.07	0.01
Predicted (calcd) intens	0.02	0.14	0.47	0.87	1.00	0.73	0.33	0.09	0.01
Obsd intens (octet)		0.14[a]	0.49	0.88	1.00	0.71	0.29	0.08[a]	
Predicted (calcd) intens (sextet)			0.37	0.83	1.00	0.67	0.67	0.23	

[a] Weakest peaks rather broad.

Table I also shows the calculated intensities where tautomerism excludes the bridge hydrogens. This model would predict two sextets in place of two octets. A better fit is obtained for the two octets. This result is in agreement with the observed intensities in the B^{11} nmr spectrum of $B_3H_8^-$ [3,5] which show better agreement for a nonet (tautomerism including bridge hydrogens) than for a septet (tautomerism excluding bridge hydrogens).

The spectrum of THF–triborane in THF consisted of an unresolved multiplet which is compatible with that of a single octet with $J = 38$ cps. These data are in agreement with the Phillips, Miller, and Muetterties data on $B_3H_7 \cdot O(C_2H_5)_2$ in diethyl ether.[4]

Two systems have been examined; in one there was Lewis base exchange and tautomerism ($B_3H_7 \cdot$THF in THF) and the other case we interpreted as only hydrogen tautomerism taking place ($B_3H_7 \cdot N(CH_3)_3$ in benzene). It was known that if $B_3H_7 \cdot N(CH_3)_3$ and $N(CH_3)_3$ were mixed further, decomposition of the B_3H_7 moiety would occur. Accordingly, $B_3H_7 \cdot N(CH_3)_3$ was dissolved in diethyl ether and the nmr spectrum was obtained. The same spectrum as $B_3H_7 \cdot N(CH_3)_3$ dissolved in benzene was obtained and we interpret this result as indicating the ether to be too weak to promote Lewis base exchange. From these results it was expected that no Lewis base exchange would occur in $B_3H_7 \cdot$THF dissolved in benzene. However, the nmr spectrum of $B_3H_7 \cdot$THF in benzene appeared to be similar to that of $B_3H_7 \cdot$THF in THF.

This latter result suggests that Lewis base exchange does occur in $B_3H_7 \cdot$THF in benzene, or, at least, that in benzene the THF molecule is able to migrate from one boron atom to another in the same molecule. Since THF is a much weaker base than trimethylamine, the fact that this observation was made for the THF adduct and not for the trimethylamine adduct is not surprising. A similar exchange reaction has been observed for the $(CH_3)_3Ga \cdot N(CH_3)_3$ adduct with both $(CH_3)_3Ga$ and $N(CH_3)_3$ in an inert solvent.[7]

Chemical shifts relative to boron trifluoride etherate as zero are listed in Table II.

TABLE II

CHEMICAL SHIFTS

Compound	Chemical shift, cps
THF·B_3H_7 in THF	10 ± 1
THF·B_3H_7 in benzene (position of max intens)	10 ± 2
$(CH_3)_3N \cdot B_3H_7$ in benzene	
High-field octet	16.2 ± 1
Low-field octet	14.4 ± 1
$(CH_3)_3N \cdot B_3H_7$ in ether	
High-field octet	14.4 ± 1
Low-field octet	13.0 ± 1

In summary we may conclude: Lewis base exchange in $B_3H_7 \cdot$LB is not a prerequisite to hydrogen tautomerism, or at least the rate at which H tautomerism occurs is much greater than Lewis base exchange.

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On the Crystal Structures of the Red, Yellow, and Orange Forms of Mercuric Iodide

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HgI_2 has three modifications, the well-known red and yellow forms,[1] stable above and below 126°, respectively, and a metastable orange form.[2,3] No detailed single-crystal structure studies have been reported. Early powder work[4] on the red form determined the single variable positional parameter which was such that the iodine atoms are distorted somewhat from ideal close packing. The parameters of the yellow form have been inferred[1] to be similar to those of $HgBr_2$ and the structure of the orange form is unknown. In this Note we give the results of a three-dimensional single-crystal structure refinement of the parameters for the red and yellow forms and some preliminary crystal data for the orange form.

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[1] W. G. Wyckoff, "Crystal Structures," Vol. 1, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1963.

[2] H. W. Kohlscüter, *Kolloidchem. Beih.*, **24**, 319 (1927).

[3] V. S. Gorskii, *Physik. Z. Sowjetunion*, **6**, 515 (1934).

[4] J. M. Bijvoet, A. Claassen, and A. Karssen, *Proc. Acad. Sci. Amsterdam*, **29**, 529 (1926).

TABLE I

Observed and Calculated Structure Factors of Yellow HgI_2

k	ℓ	F_{obs}	F_{cal}	A_{cal}	B_{cal}
h=0					
0	2	114	129	129	-1
0	4	40	48	-48	1
0	6	127	144	144	-4
0	8	180	203	202	-11
0	10	11	11	10	-3
0	12	41	37	-36	4
0	14	68	73	73	-3
0	16	58	68	67	-10
2	0	17	20	20	0
2	1	14*	9	2	-8
2	2	53	56	-55	10
2	3	209	235	0	-235
2	4	89	106	-105	15
2	5	157	169	-0	-169
2	6	24	27	-21	15
2	7	33	32	8	31
2	8	26	24	17	16
2	9	28	24	8	-22
2	10	52	42	-37	19
2	11	126	130	-2	-130
2	12	59	48	-45	17
2	13	48	46	-2	-46
2	14	16*	12	6	11
2	15	43	41	8	40
4	0	160	164	-164	-0
4	1	113	136	1	136
4	2	66	55	-54	-5
4	3	19	17	9	-14
4	4	44	33	29	-16
4	5	29	21	20	7
4	6	90	78	-76	-18
4	7	139	122	26	120
4	8	131	113	-112	-13
4	9	87	71	23	67
4	10	27*	19	-7	-17
4	11	34	32	17	-26
4	12	28	27	16	-21
4	13	21	20	17	11
4	14	58	53	-52	-13
4	15	69	65	19	62
4	16	39	44	-44	-4
6	0	48	45	-45	-0
6	1	12*	8	-8	-3
6	2	60	63	63	-8
6	3	44	53	-16	51
6	4	122	145	145	-10
6	5	47	41	-18	37
6	6	33	27	26	-8
6	7	31	28	-27	-9
6	8	34	31	-29	-10
h=0					
6	9	31	34	-32	10
6	10	88	71	69	-17
6	11	53	49	-26	41
6	12	88	90	88	-17
6	13	23	26	-21	15
h=1					
1	0	66	73	-73	-0
1	1	121	130	-70	109
1	2	171	159	-69	143
1	3	125	116	-51	104
1	4	64	70	-63	-30
1	5	100	117	79	86
1	6	143	136	-58	-123
1	7	68	80	43	67
1	8	50	51	-41	30
1	9	72	76	-50	57
1	10	76	79	-25	74
1	11	46	44	-7	43
1	12	50	50	-24	-44
1	13	52	57	51	24
1	14	49	60	-23	-55
1	15	19	18	9	15
1	16	29	35	-9	34
1	17	30	33	-29	16
3	0	101	106	106	2
3	1	105	119	-118	20
3	2	94	105	100	-30
3	3	110	105	-103	20
3	4	94	89	89	-4
3	5	102	90	89	13
3	6	76	83	81	14
3	7	33	30	27	11
3	8	73	70	68	-14
3	9	121	123	-121	18
3	10	72	55	50	-24
3	11	52	50	-48	14
3	12	37	38	38	0
3	13	69	55	55	2
3	14	28	31	31	4
3	15	13*	8	-8	2
3	16	27	24	21	-12
5	0	19	16	-15	5
5	1	89	68	-20	-65
5	2	103	99	-16	-97
5	3	77	72	-9	-71
5	4	52	45	-13	43
5	5	82	72	25	-67
5	6	127	128	-7	127
5	7	61	57	12	-55
5	8	15	10	-10	1
h=1					
5	9	60	50	-14	-48
5	10	56	41	-13	-39
5	11	54	45	-0	-45
5	12	73	68	-4	68
5	13	51	41	18	-36
5	14	67	76	2	76
7	0	38	41	-40	-6
7	1	57	63	58	25
7	2	60	69	-37	-58
7	3	50	63	59	23
7	4	33	31	-31	0
7	5	45	43	-34	25
7	6	40	47	-35	31
7	7	28	26	-4	26
7	9	81	85	83	19
7	10	59	64	-34	-53
7	11	44	46	43	16
9	0	16	18	17	-5
9	1	38	41	40	8
9	2	35	36	21	30
9	3	26	28	23	16
9	4	22	27	24	-12
h=2					
0	0	251	250	250	0
0	2	84	90	90	-3
0	4	47	41	-41	1
0	6	108	113	113	-1
0	8	149	168	168	-10
0	10	22*	7	6	-4
0	12	46	36	-35	5
0	14	68	68	68	-2
0	16	62	64	63	-10
2	0	22	16	16	3
2	1	20*	5	4	-2
2	2	47	46	-44	11
2	3	185	179	3	-179
2	4	72	83	-81	16
2	5	129	135	-0	-135
2	6	19	20	-13	16
2	7	26	29	6	28
2	8	21	21	15	15
2	9	20	18	9	-16
2	10	41	39	-35	18
2	11	134	115	-1	-115
2	12	41	42	-39	17
2	13	52	42	-2	-42
2	14	22	13	8	10
2	15	40	42	7	41
4	0	120	127	-127	-5
4	1	98	103	8	102
h=2					
4	2	45	48	-47	-7
4	3	22	20	11	-16
4	4	31	31	26	-17
4	5	25	21	19	9
4	6	64	63	-59	-21
4	7	104	107	26	104
4	8	98	100	-99	-15
4	9	64	60	24	55
4	10	33*	19	-10	-16
4	11	34	31	16	-26
4	12	36	28	18	-21
4	13	32	21	16	13
4	14	49	49	-47	-14
4	15	57	61	19	58
6	0	49	39	-39	-1
6	1	21*	15	-12	-9
6	2	72	55	55	-8
6	3	52	43	-20	38
6	4	135	124	123	-12
6	5	35	44	-20	39
6	6	32	23	21	-10
6	7	57*	27	-26	-4
6	8	36	28	-26	-9
6	9	32	33	-33	3
6	10	76	69	67	-16
6	11	50	47	-28	38
6	12	74	83	81	-18
h=3					
1	0	53	42	-42	-0
1	1	83	69	-39	57
1	2	103	91	-37	83
1	3	74	67	-31	59
1	4	53	39	-33	-21
1	5	82	72	51	51
1	6	107	89	-36	-82
1	7	51	49	30	39
1	8	42	35	-28	21
1	9	52	51	-36	36
1	10	59	56	-15	54
1	11	37	31	-6	30
1	12	44	38	-14	-35
1	13	44	44	41	16
1	14	44	49	-18	-46
1	15	9	12	7	9
3	0	61	61	61	5
3	1	74	79	-79	10
3	2	63	63	59	-20
3	3	67	70	-69	14
3	4	55	53	53	-7
3	5	71	58	58	9
h=3					
3	6	52	52	51	10
3	7	20	17	17	4
3	8	53	46	46	-7
3	9	90	90	-90	11
3	10	40	39	34	-19
3	11	41	38	-36	12
3	12	27	26	25	-1
3	13	55	47	47	1
3	14	24	23	22	5
5	0	12	11	-6	9
5	1	40	43	-16	-39
5	2	68	63	-10	-62
5	3	44	44	-0	-44
5	4	31	34	-11	32
5	5	51	51	21	-46
5	6	96	95	-4	95
5	7	43	39	4	-39
5	8	8	5	-4	3
5	9	37	36	-12	-33
5	10	34	34	-11	-32
5	11	32	33	4	-33
5	12	43	53	-5	53
7	0	30	28	-25	-13
7	1	44	47	43	18
7	2	50	52	-26	-45
7	3	50	53	50	14
7	4	38	23	-22	4
7	5	29	29	-23	16
7	6	37	32	-24	21
7	7	21	22	-5	21
h=4					
0	0	110	119	119	0
0	2	44	39	38	-5
0	4	36	29	-29	1
0	6	59	57	57	3
0	8	87	94	94	-7
0	10	12*	5	-2	-5
0	12	65*	30	-30	5
2	0	19	11	10	2
2	1	14*	8	5	5
2	2	31	23	-23	5
2	3	95	90	4	-89
2	4	58	43	-42	10
2	5	78	71	-2	-71
2	6	15*	10	-3	10
2	7	21	22	2	22
2	8	15*	13	10	8
2	9	14*	9	8	-3
2	10	28	24	-22	10
2	11	60	73	0	-73
2	12	22	26	-24	11
4	0	81	67	-66	-5
4	1	71	51	8	51
4	2	31	26	-26	-3
4	3	18	17	8	-15
4	4	31	22	20	-10
4	5	20*	9	9	4
4	6	46	33	-30	-15
4	7	74	65	15	63
4	8	61	62	-62	-8
4	9	36	34	16	30
4	10	12*	9	-5	-7
4	11	31*	23	9	-20
6	0	24	29	-29	-1
6	1	20	15	-9	-11
6	2	27	32	32	-2
6	3	34	25	-16	19
h=5					
1	0	17	18	-18	-0
1	1	22	26	-17	19
1	2	32	41	-13	39
1	3	21	29	-16	24
1	4	13	14	-9	-11
1	5	32	33	25	21
1	6	41	45	-15	-42
1	7	15	21	16	13
1	8	12	19	-14	13
1	9	22	24	-20	14
3	0	26	24	24	4
3	1	33	40	-40	1
3	2	27	26	24	-10
3	3	29	36	-35	9
3	4	21	20	19	-5
3	5	34	32	32	5
3	6	18	21	20	7
5	0	10	6	0	6
5	1	19	18	-10	-15
5	2	35	33	-4	-32
5	3	16	17	2	-17

Observed and Calculated Structure Factors of Red HgI_2

h	ℓ	F_{obs}	F_{cal}
k=0			
0	6	105	-175
0	8	146	168
0	10	17*	9
0	12	19*	11
0	14	87	-86
1	3	104	-125
1	4	57	53
1	5	101	-105
1	6	104	-113
1	7	90	84
1	8	77	-71
1	9	73	-66
1	10	66	54
1	11	52	49
1	12	67	59
1	13	40	-35
1	14	28*	-17
k=0			
1	15	40*	25
1	16	38	-40
2	0	248	-247
2	2	74	80
2	4	31	22
2	6	122	132
2	8	120	-130
2	10	20*	-9
2	12	22*	-6
2	14	73	70
3	1	66	-71
3	2	91	-94
3	3	74	80
3	4	33	-31
3	5	72	66
3	6	78	67
3	7	51	-46
k=0			
3	8	47	44
3	9	43	41
3	10	33	-35
3	11	39	-35
3	12	38	-42
4	0	117	119
4	2	44	-40
4	4	17*	-9
4	6	74	-68
4	8	75	69
4	10	11*	7
4	12	26*	3
4	14	43	-37
5	1	44*	25
5	2	42	42
5	3	41	42
5	4	14	14
k=0			
5	5	29	31
5	6	31	-31
5	7	23*	-14
5	8	48*	20
5	9	50*	19
6	0	63*	-46
k=1			
1	4	237	241
1	6	25	-25
1	8	11	-7
1	10	116	-118
1	12	81	70
2	1	101	-104
2	2	108	-124
2	3	92	89
2	4	46	-40
2	5	77	-79
k=1			
2	6	84	87
2	7	71	68
2	8	58	56
2	9	54	-51
2	10	51	-44
2	11	43	37
2	12	47	-51
2	13	25	28
3	0	17	17
3	2	89	88
3	4	127	-144
3	6	35*	16
3	8	9*	4
3	10	74	78
3	12	52	-48
4	1	64	-59
4	2	62	60
k=1			
4	3	48	38
4	4	22	20
4	5	45	38
4	6	40	-46
4	7	45	-43
4	8	28	-31
4	9	53*	27
5	0	22*	-8
5	2	45	-39
5	4	72	66
5	6	25*	-6
5	8	13*	-2
k=2			
2	0	193	192
2	2	75	-62
2	4	31*	-17
2	6	104	-105
k=2			
2	8	98	105
2	10	22*	10
2	12	12*	3
2	14	55	-57
3	1	71	-60
3	2	56	76
3	3	71	-63
3	4	31	-31
3	5	58	53
3	6	56	-56
3	7	41	39
3	8	40	-38
3	9	42	33
3	10	34	31
3	11	50*	-27
4	0	94	-100
4	2	32	34
k=2			
4	4	18*	9
4	6	59	58
4	8	56	-59
4	10	24*	-6
5	2	39	-35
5	3	42	35
5	4	23*	-12
5	5	50*	26
k=3			
3	2	70	-59
3	4	96	96
3	6	19*	-10
3	8	21*	-5
3	10	46	-54
3	12	25	32
4	1	38	-38
4	2	47	-43
k=3			
4	3	31	29
4	4	17*	-14
4	5	25	27
4	6	27	33
4	7	28	-27
4	8	41*	21
5	2	51*	28
5	4	48	-45
k=4			
4	0	48	58
4	2	27	-20
4	4	20*	-4

* indicates unobserved reflections, estimated as half minimum observed intensity.

Experimental Section

Both the red and orange forms cocrystallized from acetone solution at room temperature, as small ($\sim$0.1 mm)[3] cubes and pyramids, respectively. The orange crystals were rare and sometimes not observed. The yellow crystals were prepared by sublimation of the red powder to form small rhombs. X-Ray diffraction data were taken on all three forms at room temperature, the orange and yellow requiring care to avoid a physical disturbance that would initiate the transformation to the stable red form. Unit cell dimensions were measured from NaCl calibrated Weissenberg films and from diffractometer measurements. The intensity data were recorded on multiple-film integrated Weissenberg photographs with both Cu Kα and Mo Kα radiation about the *b* axis for the red form, and *a* and *b* axes for the yellow form. The total numbers of independent reflections measured were 144 and 285 for the red and yellow forms, respectively. The absorption corrections were made using an IBM 1620 modification[5] of an IBM 7090 program;[6] the interfilm interlayer correlations and Lp corrections were made with IBM 1620 programs.[7]

An inspection of the Patterson synthesis for the *red form* confirmed space group $P4_2/nmc$ (No. 137)[8] with Hg atoms in positions (2a) and I atoms in (4d) with *z* close to the value 0.39 (with origin at $\bar{1}$) previously determined.[4] An anisotropic least-squares refinement was carried out using an IBM 7070 program,[9] giving an agreement index of 0.07 for all reflections (Table I). The Cruickshank weighting scheme[10] was used, *i.e.*, $w = (A + BF + CF^2)^{-1}$, with $A = 2F_{\min}$, $B = 1.0$, $C = 2/F_{\max}$. The atomic scattering factors given were corrected for anomalous dispersion.[11] The final crystal structural data are given in

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(5) B. M. Craven, Technical Report No. 45, Crystallography Laboratory, University of Pittsburgh, 1963.

(6) D. J. Wehe, W. R. Busing, and H. A. Levy, Oak Ridge National Laboratory Report ORNL-TM-229, 1962.

(7) P. T. Beurskens, Technical Report, Crystallography Laboratory, University of Pittsburgh, 1964.

(8) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

(9) G. B. Carpenter, Advanced Research Projects Agency Technical Report C2, Brown University, 1963.

(10) D. W. J. Cruickshank and D. E. Pilling, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon Press Inc., New York, N. Y., 1961.

(11) "International Tables for X-ray Crystallography," Vol. II and III, The Kynoch Press, Birmingham, England, 1962.

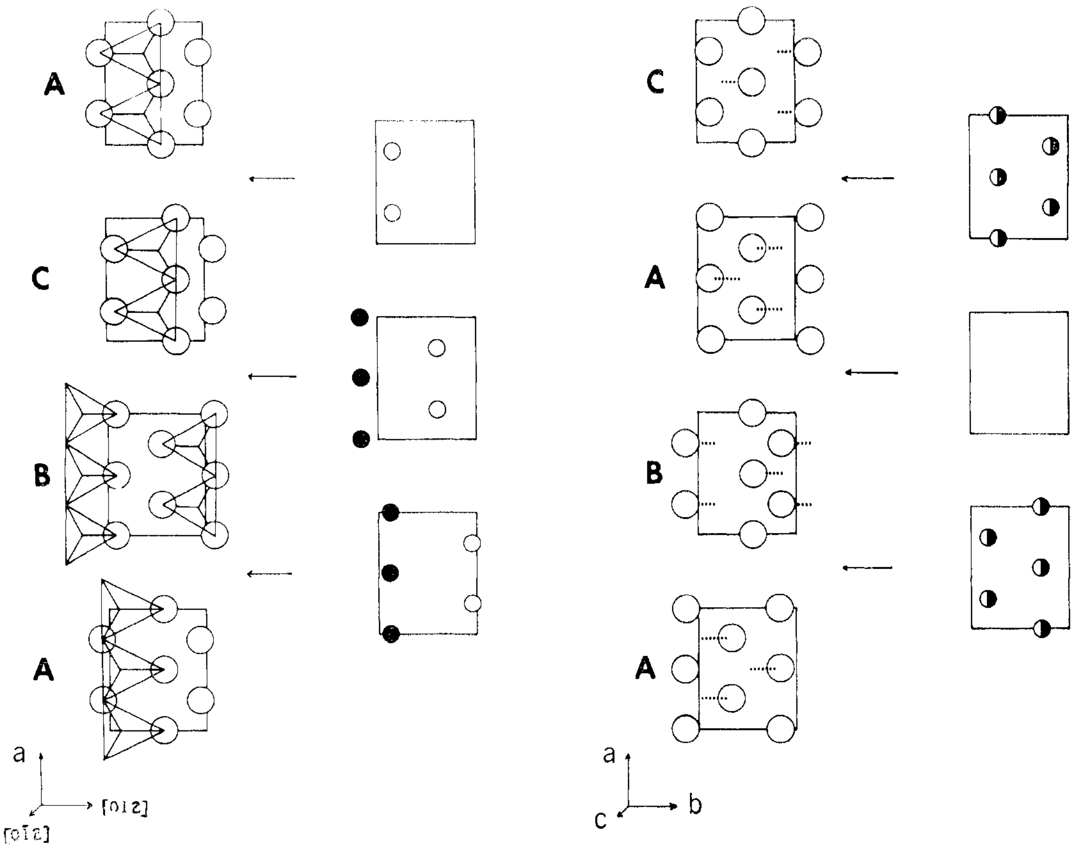

Figure 1.—Distorted hexagonal layer packing sequences in red and yellow HgI_2. Left side, red HgI_2: large open circles, I; small open circles, Hg in tetrahedra pointing downward; small filled circles, Hg in tetrahedra pointing upward. Right side, yellow HgI_2: large open circles, I; small half-filled circles, Hg in distorted octahedra; dotted lines indicated primary bond directions of HgI_2 molecules.

Table II. They differ only in additional accuracy from those derived in 1926 from powder data.[4] Owing to the very large absorption coefficients ($\mu r \approx 9$ and 32 for Mo Kα and Cu Kα, respectively), the absolute significance of the temperature factors is very doubtful, other than to permit the determination of the best value of z_I from the single-crystal measurements.

Inspection of the Patterson synthesis for the *yellow form* confirmed space group $Cmc2_1$ (No. 36)[8] and the location of the atoms similar to those found in $HgBr_2$,[12] *i.e.*, the Hg atoms in (4a) and the I atoms in two sets of (4a), with six variable positional parameters. An anisotropic least-squares refinement using the same procedure as for the red form gave the parameters shown in Table II and an agreement index of 0.10.

All the crystals of the *orange form* examined were multiple-growth twins when viewed through a polarizing microscope with a first-order red plate. The Laue symmetry was 4/mmm with $c = a = 24.85$ A, and the observed systematic extinctions were hkl absent when $l = 2n$ and h or $k = 4n$, or h, k, and l all equal $8n$, hhl with $h = 2n$, and $h00$ and $0k0$ with h or $k = 8n$, which did not permit a unique space group determination. The zero-layer Weissenberg photographs about both c and a axes were identical with those about the c axis of the red form. The higher layers and rotation photographs showed weak additional spectra indicating a superstructure relationship such that $a_{\text{orange}} \approx 4/2a_{\text{red}}$ and $c_{\text{orange}} \approx 2c_{\text{red}}$. Attempts to interpret the diffraction data from these twinned crystals indicated a close similarity in the iodine lattice to that of the red form but failed to establish the Hg positions.

TABLE II

CRYSTAL AND STRUCTURAL DATA ON HgI_2[a]

	Red	Yellow	Orange
a, A	4.361 (5)	4.702 (5)	24.85 (5)
b, A		7.432 (5)	
c, A	12.450 (7)	13.872 (7)	24.85 (5)
SG	$P4_2nmc$ (No. 137)	$Cmc2_1$ (No. 36)	
D_m, g/cc	6.30	6.23	
Z	2	4	128
D_x, g/cc	6.38	6.27	6.30

Red Form

Hg in (a), $x = 0.75$, $y = 0.25$, $z = 0.75$ (origin at $\bar{1}$)
I_2 in (d), $x = 0.25$, $y = 0.25$, $z = 0.3893$ (2)

	β_{11}	β_{22}	β_{33}	β_{ij}[b]
Hg	0.034 (8)	0.034 (8)	0.005 (1)	0.000
I	0.052 (8)	0.025 (1)	0.003 (1)	0.000

Yellow Form

Hg in (a), $x = 0$, $y = 0.3433$ (6), $z = 0.9989$ (5)
I_I in (a), $x = 0$, $y = 0.0916$ (7), $z = 0.1311$ (4)
I_{II} in (a), $x = 0$, $y = 0.4059$ (6), $z = 0.3667$ (3)

	β_{11}	β_{12}	β_{33}	β_{23}	other $\beta_{ij} = 0$
Hg	0.047	0.015	0.006	0.016	
I_I	0.037	0.004	0.002	0.005	
I_{II}	0.028	0.005	0.002	0.008	

[a] Standard deviations in parentheses apply to last figures.
[b] β_{ij} are defined by: $f^t = f^0 \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{31}lh)$.

Discussion

Both red and yellow HgI_2 have the iodine atoms in distorted close-packed arrangements, the former being distorted cubic, c, the latter distorted hc. In the red form, the Hg atoms occupy one-fourth of the tetrahedrally coordinated voids between each iodine layer.

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(12) H. Braekken, *Z. Krist.*, **81**, 152 (1932).

In the yellow form, they occupy all of the octahedrally coordinated voids between alternate iodine layers, giving a layer structure with respect to the Hg–I primary bonds. These stacking relationships are illustrated in Figure 1 and the first neighbor distances between like and unlike atoms are shown in Table III.

TABLE III

INTERATOMIC NEAREST NEIGHBOR DISTANCES (A) IN RED AND YELLOW MERCURIC IODIDE

Yellow HgI_2		Red HgI_2	
Hg–I	2.615[a]	4Hg–I	2.783
Hg–I	2.620[a]	4I–I	4.142
2Hg–I	3.507	4I–I	4.361
2Hg–I	3.510	4I–I	4.635
I–I	4.017[b]	4Hg–Hg	4.361
2I–I	4.256	4Hg–Hg	6.167
2I–I	4.356	($\sigma \approx 0.003$ A)	
4I–I	4.397		
2I–I	4.702		
I–I	5.208		
I–I	5.235[a]		
2Hg–Hg	4.397		
4Hg–Hg	4.702		
($\sigma \approx 0.006$ A)			

[a] Within the HgI_2 molecule, with I–Hg–I = 178.3°. [b] Between the $(HgI_2)_n$ layers.

A consequence of the alternation of Hg sites between the I layers is a greater distortion from ideal packing, and this is apparent in the interatomic distances. Thus in the yellow form, the 12 first-neighbor I–I distances range from 4.017 to 5.234 A, while in the red form, where the Hg atoms are more uniformly distributed between the iodines, the range is only over 0.5 A. In the HgI_4 tetrahedra of the red form, the bonds are equal by symmetry but the angles are distorted to 103.14 and 112.72°. The Hg–I distances of 2.783 A are 0.02 A longer than the sum of the tetrahedral radii $r[Hg(4)] = 1.48$ A and $r[I(4)] = 1.28$ A, recently reported.[13] The HgI_6 octahedra of the yellow form are much more distorted with two short Hg–I distances of 2.617 A and four long distances of 3.508 A, the internal angles at the Hg atom varying from 85 to 95°. The structure approaches closely therefore to that of a molecular arrangement of HgI_2 molecules, with Hg–I bonds equal to the sum of the covalent radii, $r[Hg(2)] = 1.28$ A and $r[I(2)] = 1.33$ A, and is in agreement with measurements in the vapor phase from electron diffraction studies.[14,15] The I–Hg–I angle is 178.3° with an estimated standard deviation of 0.3°, indicating a small but significant deviation from linearity. The HgI_2 molecules lie parallel to a direction at 1.5° to the [012] axis, *i.e.*, inclined at 45.5° to the [*c*] and in the (200) planes. The Hg–I molecular bonds are indicated by dotted lines in Figure 1. The four long Hg–I distances are about 0.1 A shorter than the sum of the usually accepted van der Waals radii (*i.e.*, 1.50 + 2.15 A). The shortest of the 12 first-neighbor I–I distances is that between the HgI_2 layers and is about 0.3 A less than the van der Waals diameter.

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CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC AND
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Some Reactions of Chlorosilazanes[1]

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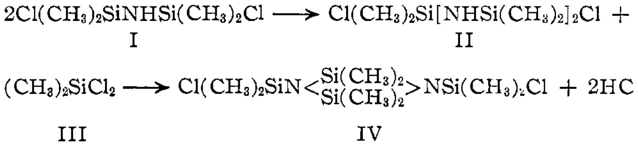
The preparation of 1,3-dichlorotetramethyldisilazane, $Cl(CH_3)_2SiNHSi(CH_3)_2Cl$ (I), has recently been described.[2]

It has been shown that on refluxing a linear or cyclic dimethylpolysilazane with dimethyldichlorosilane, 1,3-dichlorotetramethyldisilazane is obtained.

Further investigation of this reaction revealed that only by refluxing the polysilazane with an excess of dimethyldichlorosilane, 1,3-dichlorotetramethyldisilazane is formed as the favored product, but the formation of 1,3-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (IV) is favored when stoichiometric amounts of reactants are refluxed for several hours. However, 1,3-dichlorotetramethyldisilazane is initially formed also in the latter case. It then disproportionates to yield the unstable compound (II) from which [by reaction with dimethyldichlorosilane (III) previously liberated] 1,3-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (IV) is formed



$$\underset{\text{I}}{2Cl(CH_3)_2SiNHSi(CH_3)_2Cl} \longrightarrow \underset{\text{II}}{Cl(CH_3)_2Si[NHSi(CH_3)_2]_2Cl} + \underset{\text{III}}{(CH_3)_2SiCl_2}$$

$$\longrightarrow \underset{\text{IV}}{Cl(CH_3)_2SiN{<}\genfrac{}{}{0pt}{}{Si(CH_3)_2}{Si(CH_3)_2}{>}NSi(CH_3)_2Cl} + 2HC$$

The structure of IV has also been confirmed by two other authors,[2a,3] who obtained this material by allowing octamethylcyclotetrasilazane to react with dimethyldichlorosilane or 1,3-dichlorotetramethyldisilazane with sodium bis(trimethylsilyl)amide. Compound II is unstable, as on gas chromatographic analysis it disproportionates upon the column to yield a mixture containing compounds I, II, III, and IV. The formula for 1,5-dichlorohexamethyltrisilazane was assigned to it, since the constant chlorine content of this fraction

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[1] A part of this work is taken from a Ph.D. thesis to be submitted by J. Fuchs to the Senate of the Hebrew University.

[2] (a) U. Wannagat, *Angew. Chem. Intern. Ed. Engl.*, **4**, 605 (1965); (b) J. Silbiger and J. Fuchs, *Inorg. Chem.*, **4**, 1371 (1965).

[3] P. Geymeyer and E. G. Rochow, *Angew. Chem. Intern. Ed. Engl.*, **4**, 592 (1965).