The crystal structure of arsenic triiodide, AsI₃

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With 1 figure

Auszug

Die Gitterkonstanten des rhomboedrischen AsJ_3 sind $a_H = 7{,}208$ Å, $c_H = 21{,}436$ Å, $Z = 6$; $a_R = 8{,}269$ Å, $\alpha = 51°41'$, $Z = 2$; Raumgruppe $R3$. Die Struktur wurde aus Fourier- und Differenz-Projektionen parallel c und a bestimmt bis zu den Endwerten $R_{h0\cdot l} = 0{,}11$ und $R_{hk\cdot 0} = 0{,}16$. Die Jod-Atome bilden annähernd eine hexagonale dichteste Kugelpackung; AsJ_3 hat jedoch nicht die BiJ_3-Struktur. Die As-Atome sind aus den Mittelpunkten der J-Oktaeder herausgerückt, so daß die Struktur als eine Molekülstruktur angesehen werden kann. Die Molekülgrößen $As—J = 2{,}556 \pm 0{,}004$ Å, $J—As—J = 102{,}0°$ $\pm 0{,}1°$ sind nicht sehr verschieden von denen im Dampfzustand. Der intermolekulare Abstand $As \cdots J = 3{,}50$ Å weist auf Anziehungskräfte zwischen den Molekülen hin.

Abstract

Crystals of arsenic triiodide, AsI_3, are rhombohedral, $a_H = 7.208$ Å, $c_H = 21.436$ Å, $Z = 6$; $a_R = 8.269$ Å, $\alpha = 51°41'$, $Z = 2$; space group $R3$. The structure was determined from Fourier and difference projections along the crystallographic axes, the final discrepancy factors being $R(h0\cdot l) = 0.11$, $R(hk\cdot 0) = 0.16$. The iodine atoms are in an approximately hexagonal close-packed array, but the compound does *not* have the bismuth iodide structure, as reported previously. The arsenic atoms are significantly displaced from the centres of iodine octahedra, and have only three near-neighbour iodine atoms, so that the structure may be considered as built up from discrete AsI_3 molecules. The dimensions of the molecules are $As—I = 2.556 \pm 0.004$ Å, $I—As—I = = 102.0° \pm 0.1°$, not significantly different from the values in the vapour state. The intermolecular $As \cdots I$ distances are 3.50 Å, indicative of some intermolecular attractive forces.

Introduction

It is reported that arsenic triiodide, AsI_3, has the bismuth iodide structure, with arsenic atoms located at the centers of octahedra of iodine atom[1,2]. Examination of the original analyses however

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[1] Strukturbericht **2**, 25, 294.

[2] Structure Reports **11**, 272.

suggests that the arsenic atom position has not been determined with any precision or even reliability, and the present paper describes a reinvestigation of the structure.

Experimental

Crystals of arsenic triiodide are red hexagonal plates, with $(00 \cdot 1)$ developed and smaller $(10 \cdot 0)$ faces. The unit-cell parameters were determined from large-angle reflections on an $h0 \cdot l$ Weissenberg film ($CuK\alpha_1$ and $CuK\alpha_2$ radiations), with extrapolation by the method of Farquhar and Lipson[3] using the Nelson-Riley function[4]. The extrapolations suggested possible errors of only 0.001 Å in the cell-edge measurements, but since the film was placed in the Weissenberg goniometer in the usual front-reflection mounting, the measurements are probably not as accurate as this. The values of the lattice parameters given previously[1,2] are significantly too small as a result of absorption errors. The space group was determined from $hK \cdot l$ Weissenberg films ($K = 0 \rightarrow 5$) and $hk \cdot 0$ and $h0 \cdot l$ precession films.

Crystal data

$$[\lambda(CuK\alpha_1) = 1.54051 \text{ Å}, \ \lambda(CuK\alpha_2) = 1.54433 \text{ Å}]$$

Arsenic triiodide, AsI_3; M.W. $= 455.7$; m.p. $= 146 °C$.

Rhombohedral.

Hexagonal cell, $a_H = 7.208$, $c_H = 21.436$ Å
$\qquad V_H = 964.5 \text{ Å}^3$, $Z = 6$.

Rhombohedral cell, $a_R = 8.269$ Å, $\alpha_R = 51°41'$
$\qquad V_R = 321.5 \text{ Å}^3$, $Z = 2$.

$D_m = 4.75^2$, $D_x = 4.706 \text{ g cm}^{-3}$.

Absorption coefficients for x-rays, $\lambda = 1.5418$ Å, $\mu = 1220 \text{ cm}^{-1}$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad \lambda = 0.7107$ Å, $\mu = 200 \text{ cm}^{-1}$.

$F(000) = 1152$ (hexagonal cell).

Laue group, $\bar{3}$.

Absent reflections: $hk \cdot l$ absent when $-h + k + l \neq 3n$ (hexagonal indices). Space group is $R3$—C_3^4 or $R\bar{3}$—C_{3i}^2. $R\bar{3}$ was confirmed by the structure analysis.

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[3] M. C. M. Farquhar and H. Lipson, The accurate determination of cell dimensions from single-crystal x-ray photographs. Proc. Physic. Soc. [London] 58 (1946) 200—206.

[4] J. B. Nelson and D. P. Riley, An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals. Proc. Physic. Soc. [London] 57 (1945) 160—177.

The intensities of the $h0 \cdot l$ and $hk \cdot 0$ reflections were recorded on multiple-exposure precession films with $MoK\alpha$ radiation, and estimated visually. Lorentz and polarization factors were applied, and the structure amplitudes derived. The crystal used was a hexagonal plate with edge 0.1 mm and thickness 0.02 mm, and absorption corrections were not considered necessary. The intensities of all the $hk \cdot l$ reflections were recorded on equi-inclination Weissenberg films of a crystal rotating about the a axis; $CuK\alpha$ radiation was used for these films, and since absorption errors are more severe these data were used only for qualitative comparison, the detailed structure determination being carried out using the $MoK\alpha$ zonal data.

Structure analysis

Preliminary examination of the $h0 \cdot l$ structure factors indicated that the iodine atoms were situated close to $\frac{1}{3}, \frac{1}{3}, \frac{1}{12}$ in space group $R\bar{3}$, as previously found[1,2] but that better agreement between F_0 and

Table 1. *Measured and calculated structure factors*
(The F_c values were calculated from the final parameters; F_c' were calculated with $z_{As} = \frac{1}{6}$).

h 0 l

h 0 l	F_o	F_c	F_c'
0 0 3	104	-132	-165
6	693	-704	-606
9	77	-11	-160
12	380	408	569
15	137	104	-28
18	272	-292	-204
21	<49	-9	-56
24	101	115	133
27	<47	5	1
1 0 1	74	57	90
4	84	89	-35
7	60	-101	69
10	35	75	-82
13	62	-71	37
16	43	43	-10
19	<47	7	22
22	<49	-25	-21
25	<50	15	7
28	<45	-5	-1
$\bar{1}$ 0 2	192	-188	-136
5	139	152	75
8	59	-70	-27
11	44	41	51
14	<40	-7	-56
17	<44	-36	23
20	<47	44	-6
23	<50	-19	13
26	<47	3	-10
2 0 2	44	-39	2

h 0 l	F_o	F_c	F_c'
2 0 5	170	130	66
8	133	-146	-109
11	<39	30	38
14	<42	46	3
17	<46	-27	25
20	<49	13	-32
23	<49	-19	8
26	<47	14	1
$\bar{2}$ 0 1	54	46	73
4	72	-31	-135
7	86	-90	53
10	108	139	3
13	41	-56	38
16	<44	-4	-52
19	<48	2	15
22	<49	-1	2
3 0 0	652	648	648
3	85	-73	-92
6	433	-433	-374
9	29	-7	-102
12	269	270	376
15	66	71	-19
18	211	-201	-140
21	<49	-6	-39
24	70	79	92
$\bar{3}$ 0 3	85	-73	-92
6	433	-433	-374
9	29	-7	-102
12	269	270	376

h 0 l	F_o	F_c	F_c'
3 0 15	66	71	-19
18	211	-201	-140
21	<49	-6	-39
24	70	79	92
4 0 1	<42	24	38
4	122	111	55
7	<43	-44	36
10	<44	-14	-93
13	<46	-40	16
16	49	55	25
19	<49	7	15
22	<49	-28	-26
$\bar{4}$ 0 2	172	-154	-132
5	75	67	32
8	<44	26	47
11	<46	25	29
14	<47	-42	-67
17	<49	-24	9
20	<49	45	16
23	<47	-7	9
5 0 2	<46	22	37
5	81	50	26
8	82	-85	-70
11	<48	10	13
14	<49	38	20
17	<49	-10	13
20	<49	-3	-23
$\bar{5}$ 0 1	<46	16	26
4	80	-46	-83

h 0 l	F_o	F_c	F_c'
$\bar{5}$ 0 7	33	-35	19
10	77	82	28
13	<48	-21	18
16	<49	-18	-38
19	<49	0	5
6 0 0	204	196	196
3	<48	-22	-27
6	138	-133	-115
9	<49	-1	-32
12	99	89	124
15	<48	25	-6
18	63	-66	-46
$\bar{6}$ 0 3	<48	-22	-27
6	138	-133	-115
9	<49	-1	-32
12	99	89	124
15	<48	25	-6
18	63	-66	-46
7 0 1	<48	7	10
4	59	52	37
7	<48	-10	10
10	<48	-20	-42
13	<47	-11	3
16	<46	25	17
$\bar{7}$ 0 2	68	-63	-57
5	<48	17	7
8	<47	26	32
11	<47	8	9
14	<46	-23	-30

h k 0

h k 0	F_o	F_c		h k 0	F_o	F_c		h k 0	F_o	F_c		h k 0	F_o	F_c
3 0 0	652	648		7 1 0	<46	-19		6 3 0	84	65		5 5 0	<46	-10
6 0 0	204	196		2 2 0	104	-139		1 4 0	73	-90		3 6 0	84	65
1 1 0	206	-222		5 2 0	<47	-43		4 4 0	<47	-27		1 7 0	<46	-19
4 1 0	73	-90		3 3 0	311	284		2 5 0	<47	-43				

F_c values for reflections with $l \neq 6 \ n$ was obtained for z_{As} about 1/5, rather than the previous value[1,2] of 1/6. A Fourier series was summed with only those reflections whose signs were independent of the arsenic position, and the resulting electron-density map confirmed the new arsenic position, and gave revized coordinates for the iodine atoms. Positional and thermal parameters were refined by $h0 \cdot l$ $(F_o - F_c)$ syntheses, the scattering factors of the *International Tables*[5], corrected
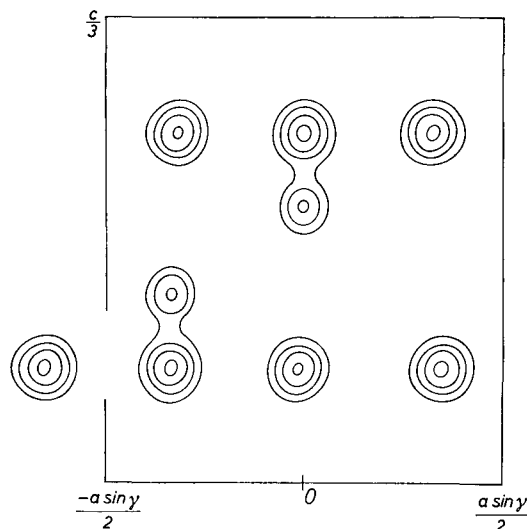

Fig. 1. Electron-density projection along a_H. Contours at intervals of 20, 40, 60, 80 $e\text{Å}^{-2}$ for I, and 20, 30, 40 $e\text{Å}^{-2}$ for As

for anomalous dispersion, being used. The final values of R, the usual discrepancy factor, were 0.11 for the $h0 \cdot l$ reflections, and 0.16 for the $hk \cdot 0$ reflections. With z_{As} taken as 1/6, and all the other parameters at their final values, $R(h0 \cdot l)$ increases to 0.38.

Measured and calculated structure factors are listed in Table 1, and the $h0 \cdot l$ electron-density projection is shown in Fig. 1.

Atomic coordinates and interatomic distances

The final positional and thermal parameters are given in Table 2, and the standard deviations, calculated from CRUICKSHANK's formulae[6] in Table 3. The interatomic distances and angles are given in Table 4.

[5] International tables for x-ray crystallography. Vol. III. Kynoch Press, Birmingham, 1962.

[6] D. W. J. CRUICKSHANK, The accuracy of electron-density maps in x-ray analysis with special reference to dibenzyl. Acta Crystallogr. 2 (1949) 65—82.

Table 2. *Final atomic parameters*

	x	y	z	B
Hexagonal axes				
6 As in 6c	0	0	0.1985	4.5 Å²
18 I in 18f	0.3485	0.3333	0.0822	4.8
Rhombohedral axes				
2 As in 2c	0.1985	0.1985	0.1985	4.5
6 I in 6f	0.4307	0.0670	−0.2511	4.8

Table 3. *Standard deviations of hexagonal coordinates*

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
As	0	0	0.0094 Å
I	0.0013 Å	0.0013 Å	0.0040 Å

Table 4. *Interatomic distances and angles, and standard deviations*

Intramolecular		Intermolecular	
As—I	2.556 ± 0.004 Å	As · · · I	3.50 Å
I—As—I	102.0° ± 0.1°	I · · · I	4.26 (4) Å
I · · · I	3.97 Å		4.21, 4.30, 4.30 Å
			4.29, 4.38, 4.38 Å

Discussion

The present analysis indicates that the iodine atoms in arsenic triiodide are in an approximately hexagonal close-packed array, but the crystal does *not* have the bismuth iodide structure[1,2], the arsenic atom having $z = 0.1985$, rather than $^1/_6$. The arsenic atoms are thus displaced from the centres of iodine octahedra, and have only three near-neighbour iodine atoms (at 2.556 Å, with three further off at 3.502 Å); the structure may therefore be considered as built up from discrete AsI_3 molecules.

The dimensions of the AsI_3 molecules are As—I = 2.556 ± 0.004 Å, I—As—I = 102.0° ± 0.1°, identical with the dimensions in the vapour state, 2.55 ± 0.03 Å, 101° ± 1.5°[7]. The As · · · I intermolecular

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[7] Tables of interatomic distances and configuration in molecules and ions, Chem. Soc. Spec. Publ., no. 11, 1958.

distances are 3.502 $\pm$ 0.007 Å; this is less than the sum of the van der Waals radii, 4.15 Å, indicative of some intermolecular attraction, which probably involves $d\pi - p\pi$ bonding with donation of iodine $5p$ electrons to vacant $4d$ orbitals on the arsenic atom of a neighbouring molecule. Each iodine atom has six iodine neighbours in a plane parallel to (00·1); two of these are in the same AsI_3 molecule and are at 3.97 Å, and the other four are at 4.26 Å. In addition there are six other near neighbours, three below the plane at 4.21, 4.30, 4.30 Å, and three above at 4.29, 4.38, 4.38 Å. All these intermolecular I · · · I contacts correspond to normal van der Waals interactions.