Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1960). **13**, 446

Cell dimensions and space group of 1,1-diphenyl-2-picrylhydrazine.*

By R. D. Ellison and R. W. Holmberg, *Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.*

(*Received* 23 *July* 1959 *and in revised form* 7 *December* 1959)

The cell dimensions and space group of 1,1-diphenyl-2-picrylhydrazine were determined for crystals of this compound grown from a benzene solution. The crystals, which contained benzene of crystallization, were sufficiently stable to allow powder diffraction patterns to be taken on a diffractometer without decomposition, but special care was required to preserve small single crystals for a time period long enough to obtain single crystal diffrac-

Table 1. *Interplanar spacings for* 1,1-*diphenyl*-2-*picrylhydrazine*

h	k	l	d_c (Å)	d_o (Å)	I_0	
0	0	1	11·068	11·07	*s*−	*
1	0	0	8·731	8·76	*m*	*
1	0	−1	8·517	8·50	*m*	*
0	1	1	7·722	7·71	*s*	*
1	1	0	6·784	6·73*b*	*m*	
1	1	−1	6·683			
1	0	1	5·895	5·93	tr.	
1	0	−2	5·700	5·70	*w*	*
0	0	2	5·534	5·53	*w*−	
0	2	0	5·390	5·37*b*	*w*−	
1	1	1	5·172	5·19	*w*− −	
1	1	−2	5·039	5·04	*w*	
0	1	2	4·923	4·93	*m*	*
0	2	1	4·846	4·84	*s*+	*
2	0	−1	4·680	4·69	*w*−	*
1	2	0	4·586	4·58	*m*+ +	
1	2	−1	4·554			
2	0	0	4·365	4·37	*s*−	*
2	1	−1	4·293			
2	0	−2	4·258	4·26	*m*	*
1	0	2	4·057	4·08*b*	*w*	
2	1	0	4·046			
1	2	1	3·978	3·96	*s*	
2	1	−2	3·960			
1	0	−3	3·950			
1	2	−2	3·916			
0	2	2	3·861	3·86	*s*−	*
1	1	2	3·797	3·80	*w*−	*
1	1	−3	3·709	3·71	*s*−	
0	0	3	3·689			
2	0	1	3·636	3·62	*w*	*
2	2	−1	3·534			
2	0	−3	3·514			
0	1	3	3·491	3·49	*s*	*
2	1	1	3·445	3·44	tr.	
0	3	1	3·417			
2	2	0	3·392			
2	2	−2	3·341	3·34 to 3·31*b*	*m*−	
2	1	−3	3·341			
1	3	0	3·323			
1	3	−1	3·310			
1	2	2	3·241	3·24	*w*	*
1	2	−3	3·186	3·18	*m*−	*
3	0	−1	3·105			
3	0	−2	3·075			
1	3	1	3·068			
0	2	3	3·044	3·04	m^{++}	
1	3	−2	3·040			
1	0	3	3·028			
2	2	1	3·014			
0	3	2	3·014			
3	1	−1	2·983			
1	0	−4	2·965			
3	1	−2	2·957	3·95*b*	*m*	
2	0	2	2·947			
2	2	−3	2·944			
1	1	3	2·915			
3	0	0	2·910			
1	1	−4	2·859			
2	3	−1	2·850	2·85	*w*+	
2	0	−4	2·850			
2	1	2	2·843			
3	0	−3	2·839			
3	1	0	2·810	2·82	*w*+	
2	3	0	2·774			
0	0	4	2·767			
2	1	−4	2·755			
2	3	−2	2·746	2·75	*m*−	
3	1	−3	2·745			
0	4	0	2·695	2·69	*w*	
3	2	−1	2·690			
1	3	2	2·690			
0	1	4	2·680			
3	2	−2	2·671			
1	3	−3	2·658	2·66	*w*−	
1	2	3	2·640			
0	4	1	2·618			
1	2	−4	2·598	2·60	*w*	
3	0	1	2·593			
2	2	2	2·586			
1	4	0	2·575			
0	3	3	2·574			
1	4	−1	2·569	2·57	*w*	
3	2	0	2·561			
2	3	1	2·556			
3	1	1	2·521			
2	2	−4	2·519			
2	3	−3	2·512	2·51	*w*+	
3	2	−3	2·512			
3	0	−4	2·510			

b indicates a broad line.

* indicates an observation that was used in the least-squares refinement of the cell.

---

* Work performed for the U.S. Atomic Energy Commission at the Oak Ridge National Laboratory, operated by the Union Carbide Corporation, Oak Ridge, Tennessee.

tion patterns. Because the crystals were attacked to some degree by all of the greases and adhesives commonly used for mounting, polyvinyl alcohol in aqueous solution was used to glue the crystals to glass wool fibers. The mounted crystals were enclosed in thin-wall capillary tubes that contained an atmosphere saturated with benzene. Precession camera data for two zones were then obtained in addition to powder diffraction data.

From the single crystal data, it was found that diphenyl picrylhydrazine, as grown from benzene solution, is monoclinic. The powder patterns were indexed on the basis of the cell obtained from the single crystal data and were used in a least-squares refinement of the cell size. Patterns taken on a diffractometer with Cu $K\alpha$ radiation were used in a preliminary refinement, the final refinement being a least-squares fit of the cell parameters to data from a Debye–Scherrer pattern taken with Cr $K\alpha$ radiation. Since all of the observable lines are in the forward reflection region, and because no corrections were made for the displacement of lines by absorption, it is felt that the internal consistency of the data set is not a fair measure of accuracy; the limits of error given below are approximately twice that indicated by this internal consistency. The cell dimensions are:

$$a = 9{\cdot}37 \pm 0{\cdot}02,\ b = 10{\cdot}78 \pm 0{\cdot}04,\ c = 11{\cdot}87 \pm 0{\cdot}02\ \text{Å}\ ,\quad \beta = 111^\circ\ 14' \pm 10'.$$

The observed interplanar spacings are compared with those calculated on the basis of this cell in Table 1.

The systematic absence of the $0k0$ reflections for odd values of k, together with a readily observable pyroelectric effect indicates the non-centrosymmetric space group $P2_1$.

The benzene of crystallization was determined by heating freshly crystallized material in a vacuum at 60 °C. to constant weight. A weight loss of 16·7% was found. The value calculated for one benzene per diphenyl picrylhydrazine is 16·5%. The density, calculated on the basis of two molecules of diphenyl picrylhydrazine plus two benzenes of crystallization per unit cell, is 1·406 g.cm.$^{-3}$, in good agreement with pycnometric density measurements of 1·40 g.cm.$^{-3}$.

Acta Cryst. (1960). **13**, 447

The crystal structures of some plutonium borides.

By B. J. McDonald and W. I. Stuart, *U.K.A.E.A. Production Group, Windscale and Calder Works, Technical Section, Sellafield, Seascale, Cumberland, U.K.*

(*Received* 7 *January* 1960)

A study of the plutonium–boron system has led to the identification of four plutonium borides, the structures being consistent with compounds of chemical formulae PuB, PuB_2, PuB_4, and PuB_6.

All the borides were prepared by heating powder-mixtures of elemental boron and plutonium in argon at 0·25 atmospheres. Preparations were carried out at 1200 °C. using a range of Pu:B ratios equivalent to 40–95 at.% boron; and also at 800 °C. in the more limited range 60–65 at.% boron. X-ray powder-photographs showed that the products of reaction contained unidentified phases, in addition to the borides already mentioned.

Plutonium monoboride was formed at 1200 °C. and in the composition range 40–70 at.% boron. The amount of monoboride formed decreased as the percentage of boron increased. This phase has a cubic NaCl-type structure (similar to that of TiB, ZrB and HfB) with lattice parameter 4·92 Å; the Pu–B distance is 2·46 Å. The existence of uranium and thorium monoborides has not been reported.

Plutonium diboride was formed in preparations at 800 °C., but not at 1200 °C. At 800 °C. the effect of changes in Pu:B ratio has not yet been fully investigated, but in the limited composition range studied (60–65 at.% B), PuB_2 was the only boride phase formed. It is simple hexagonal and is isomorphous with uranium diboride. Lattice parameters are $a = 3{\cdot}18$ and $c = 3{\cdot}90$ Å, with Pu atoms at (0, 0, 0) and boron atoms at (1/3, 2/3, 1/2) and (2/3, 1/3, $\bar{1}$/2). The structure is the AlB_2-type, in which boron atoms form two-dimensional hexagonal networks with planar layers of metal atoms interposed. Thus plutonium, uranium and several transition metals (Post, Glaser & Moskowitz, 1954) form a series of isocrystalline

Table 1. *Interatomic distances for some diborides* (Å)

Compound	Metal atomic radius	Lattice parameters		Metal-boron dist. expl.	Metal–boron dist. contact	Expl.-contact	Boron–boron distance in planes expl.	Expl.-contact (*B* diam.)
		a	*c*					
CrB_2	1·27	2·97	3·07	2·30	2·23	0·07	1·73	0
VB_2	1·34	3·00	3·06	2·31	2·24	0·07	1·73	0
TiB_2	1·47	3·03	3·23	2·38	2·32	0·06	1·75	0·01
MoB_2	1·39	3·05	3·08	2·32	2·28	0·04	1·76	0·02
TaB_2	1·46	3·08	3·27	2·41	2·35	0·06	1·78	0·04
NbB_2	1·46	3·09	3·30	2·43	2·35	0·08	1·78	0·04
HfB_2	1·59	3·14	3·47	2·51	2·44	0·07	1·81	0·07
ZrB_2	1·60	3·17	3·53	2·54	2·46	0·08	1·83	0·09
UB_2	1·52	3·14	4·00	2·70	2·36	0·34	1·81	0·07
PuB_2	1·60	3·18	3·90	2·68	2·47	0·21	1·83	0·09