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25

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The Crystal Structure of $POBr_3$: Space Group and Refinement by Least Squares*

By

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Contrary to an earlier report, the X-ray diffraction data for $POBr_3$ are consistent with space group Pnma.

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* Work done under the auspices of the U.S. Atomic Energy Commission.

Olie and Mijlhoff (1969; referred to below as OM) reported a crystal structure for phosphoryl bromide, $POBr_3$, which had been refined in space group $Pn2_1a$, but which deviated from Pnma by no more than 0.08 Å. OM stated that refinement by least squares in Pnma "proved to be disastrous" and that "R did not drop below 36%", whereas (with anisotropic thermal parameters) R was reduced to 11.3% in $Pn2_1a$. We found it incredible that one could not get approximately as good agreement in space group Pnma as in $Pn2_1a$ with such slight deviations from the higher symmetry. Indeed, calculations we have made with the data of OM have reduced R below 11.3% in both space groups. We must conclude that there was some defect in the program used by OM or some error in using it.

Dr. Olie kindly gave us a list of 432 non-zero structure factors. We refined the structure using the CDC-6600 computer and the full-matrix least-squares program of Dr. Allan Zalkin of this laboratory. Scattering factors for neutral atoms were taken from Cromer and Waber (1965) with dispersion corrections for Br and P from Cromer (1965). OM used slightly different scattering factors and apparently neglected the dispersion corrections, but we do not believe that this difference is the origin of the divergence of our results. We assigned equal weights to the reflections for lack of knowledge of the experimental accuracies. The cell dimensions of OM were used: a = 9.467(6), b = 9.938(6), c = 6.192(3) Å.

Starting with coordinates similar to those reported by OM (but naturally with Br(1) and Br(3) equivalent), four cycles of refinement in Pnma with individual isotropic thermal parameters reduced $R = \Sigma|\Delta F| / \Sigma|F_o|$ to 0.192. Further cycles yielded no significant improvement. With individual anisotropic thermal parameters, eight cycles reduced R to 0.110 and $R_2 = (\Sigma(\Delta F)^2 / \Sigma F_o^2)^{1/2}$ to 0.128. The final shifts in no case exceeded 10^{-3} times the respective estimated standard deviation. The resulting parameters are listed in Table 1 and the molecular dimensions are compared in Tables 2 and 3 with those found with the other space group.

In space group $Pn2_1a$ one expects strong correlation between the parameters of Br(1) and Br(3), especially when these atoms are given independent anisotropic thermal parameters, and refinement difficulty would not be unexpected. However, refinement in this space group (with 45 independent parameters rather than the 28 used in Pnma) reduced R to 0.103 and R_2 to 0.119 without incident other than considerably slower convergence than we achieved in Pnma. The resulting coordinates correspond to bond distances and angles less symmetrical than those found in space group Pnma, and the thermal parameters correspond to more asymmetric motion. We regard these results to be unacceptable as a plausible model of the

molecular structure, and we do not report the coordinates because we have no confidence in them.†

An examination of the discrepancies among the observed and calculated structure factors (for Pnma) revealed 11 that were larger than 15 electrons. Refinement in Pnma after removal of these 11 reflections resulted in R = 0.097, R_2 = 0.106, and a bond distance P - O = 1.49(2) Å. This sensitivity of the result to deletion of data suggests that more detailed analysis of this data set is unjustified without more specific knowledge of the accuracy of individual measurements, and that the standard deviations reported in this note are not to be taken too literally. The 11 reflections in question include the 10 which also gave the worst agreement in space group $Pn2_1a$, and therefore their poor agreement in Pnma cannot be taken as evidence for the non-centric group.

We conclude that there is no reason to reject Pnma as the correct space group, and that this description should be used unless and until some better evidence to the contrary is found.

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† To anticipate a likely question, we report that the R test of Hamilton (1965), if applied to the R_2 ratio 0.128/0.119 = 1.08, gives the result that the centric group can be rejected at the 0.005 level. In our opinion the presence of systematic errors and incorrect weights makes this test inappropriate in the present case.

Table 1. Final parameters in space group Pnma

	Br(1)	Br(2)	P	O
x	0.3469(4)	0.4801(6)	0.3102(10)	0.174(3)
y	0.0790(3)	1/4	1/4	1/4
z	0.1799(5)	0.6096(8)	0.3799(14)	0.494(4)
B(11)	7.1(2)	5.0(3)	2.5(4)	4(1)
B(22)	2.6(1)	5.8(2)	2.2(3)	6(2)
B(33)	4.2(1)	3.3(2)	2.4(3)	3(1)
B(12)	-0.5(1)	0	0	0
B(13)	0.8(2)	-1.6(2)	0.5(4)	2(1)
B(23)	-1.2(1)	0	0	0

Table 2. Bond distances (Å)

	Pnma	$Pn2_1a$	
	This work	This work	OM
P - Br(1)	2.131(6)	2.118(21)	2.131(11)
P - Br(2)	2.147(10)	2.148(11)	2.140(6)
P - Br(3)	(2.131)	2.147(17)	2.150(11)
P - O	1.470(29)	1.445(32)	1.442(18)

Table 3. Bond angles (°)

	Pnma	$Pn2_1a$	
	This work	This work	OM
Br(1) - P - Br(2)	105.3(3)	106.2(6)	106.3(4)
Br(1) - P - Br(3)	105.8(2)	105.7(8)	105.1(3)
Br(2) - P - Br(3)	(105.3)	103.5(7)	105.3(4)
Br(1) - P - O	115.0(6)	118.3(28)	115.4(17)
Br(2) - P - O	109.8(12)	109.6(14)	109.5(8)
Br(3) - P - O	(115.0)	112.3(25)	114.6(18)

References

CROMER, D. T. (1965). Acta Cryst. 18, 17.

CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104.

HAMILTON, W. C. (1965). Acta Cryst. 18, 502.

OLIE, K. & MIJLHOFF, F. C. (1969). Acta Cryst. B25, 974.

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