

$\beta^2 = 24.4 \text{ oe}^2$  when the protons are situated on F-F lines. Proton deviation from F-F directions (the magnitude of the intramolecular distance  $r(\text{F-H})$  being preserved) lessen the theoretical values for  $\beta^2$  so that with H-F-F angles exceeding  $20^\circ$   $\beta^2$  becomes less than the lower limit of its possible values. To summarize, it may be said that, according to the n.m.r. data, the protons in solid HF are situated at a distance of  $(0.95 \pm 0.03) \text{ \AA}$  from the F atoms, involving a possible deviation from the F-F line not exceeding  $10^\circ$ .

It is also worthy of mention that according to the empirical formula of Pimentel & McClellan (1960), with F-F equal to  $2.49 \text{ \AA}$ , the F-H bond length should approximately equal  $1.02 \text{ \AA}$ , which is in agreement with our  $r(\text{H-F})$  value in solid hydrogen fluoride.

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### References

- ATOJI, M. & LIPSCOMB, W. H. (1954). *Acta Cryst.* **7**, 173.  
 EL SAFFAR, Z. M. (1966). *J. Chem. Phys.* **45**, 4643.  
 PAKE, G. (1948). *J. Chem. Phys.* **16**, 327.  
 PEDERSEN, B. (1964). *J. Chem. Phys.* **41**, 122.  
 PEDERSEN, B. (1968). *Acta Chem. Scand.* **22**, 444.  
 PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond*. San Francisco: Freeman.  
 SUTTON, L. E. (1958). *Interatomic Distances*, Special Publication No. 11. London: The Chemical Society.  
 VAN VLECK J. F. (1948). *Phys. Rev.* **74**, 1168.

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**The crystal structure of POBr<sub>3</sub>: space group and refinement by least squares.\*** By LIESELOTTE K. TEMPLETON and DAVID H. TEMPLETON, *Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.*

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Contrary to an earlier report, the X-ray diffraction data for POBr<sub>3</sub> are consistent with space group *Pnma*.

Olie & Mijlhoff (1969) (referred to below as OM) reported a crystal structure for phosphoryl bromide, POBr<sub>3</sub>, which had been refined in space group *Pn2<sub>1</sub>a*, but which deviated from *Pnma* by no more than  $0.08 \text{ \AA}$ . OM stated that refinement in *Pnma* (with a block-diagonal least-squares program) '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<sub>1</sub>a*. We found it incredible that one could not get approximately as good agreement in space group *Pnma* as in *Pn2<sub>1</sub>a* 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 & 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 this difference certainly is not 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:  $a = 9.467(6)$ ,  $b = 9.938(6)$ ,  $c = 6.192(3) \text{ \AA}$ .

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  $R = \sum |AF| / \sum |F_o|$  to 0.192. Further cycles yielded no significant improvement. With

individual anisotropic thermal parameters, eight cycles reduced R to 0.110 and  $R_2 = [\sum (\Delta F)^2 / \sum F_o^2]^{1/2}$  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. Observed and calculated structure factors (multiplied by 6) are listed in Table 4.

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)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
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

\* The temperature factor is  $\exp(-\sum_i \sum_j h_i h_j b_i b_j B_{ij}/4)$ .

Table 2. Bond distances

	<i>Pnma</i>	<i>Pn2<sub>1</sub>a</i>	OM
P-Br(1)	This work	This work	OM
P-Br(1)	2.131 (6) Å	2.118 (21) Å	2.131 (11) Å
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)
O---Br*	3.065 (27)	3.092 (29)	3.08 (2)

\* Atom in adjacent molecule.

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

Table 3. Bond angles

	<i>Pnma</i>		<i>Pn2<sub>1</sub>a</i>	
	This work	This work	This work	OM
Br(1)-P-Br(2)	105·3 (3)°	105·8 (2)	106·2 (6)°	106·3 (4)°
Br(1)-P-Br(3)	105·8 (3)	105·7 (8)	105·7 (8)	105·1 (3)
Br(2)-P-Br(3)	105·5 (2)	105·5 (7)	105·5 (7)	105·3 (4)
Br(1)-P-O	115·0 (6)	118·3 (28)	118·3 (28)	115·4 (17)
Br(2)-P-O	109·8 (12)	109·6 (14)	109·6 (14)	109·5 (8)
Br(3)-P-O	(115·0)	112·3 (25)	112·3 (25)	114·6 (18)

Table 4. Observed and calculated structure factors ( $\times 6$ )

hkl	Observed	Calculated	hkl	Observed	Calculated
0 0 1	100	100	1 1 1	100	100
0 0 2	200	200	1 1 2	100	100
0 0 3	300	300	1 1 3	100	100
0 0 4	400	400	1 1 4	100	100
0 0 5	500	500	1 1 5	100	100
0 0 6	600	600	1 1 6	100	100
0 0 7	700	700	1 1 7	100	100
0 0 8	800	800	1 1 8	100	100
0 0 9	900	900	1 1 9	100	100
0 0 10	1000	1000	1 1 10	100	100
0 0 11	1100	1100	1 1 11	100	100
0 0 12	1200	1200	1 1 12	100	100
0 0 13	1300	1300	1 1 13	100	100
0 0 14	1400	1400	1 1 14	100	100
0 0 15	1500	1500	1 1 15	100	100
0 0 16	1600	1600	1 1 16	100	100
0 0 17	1700	1700	1 1 17	100	100
0 0 18	1800	1800	1 1 18	100	100
0 0 19	1900	1900	1 1 19	100	100
0 0 20	2000	2000	1 1 20	100	100
0 0 21	2100	2100	1 1 21	100	100
0 0 22	2200	2200	1 1 22	100	100
0 0 23	2300	2300	1 1 23	100	100
0 0 24	2400	2400	1 1 24	100	100
0 0 25	2500	2500	1 1 25	100	100
0 0 26	2600	2600	1 1 26	100	100
0 0 27	2700	2700	1 1 27	100	100
0 0 28	2800	2800	1 1 28	100	100
0 0 29	2900	2900	1 1 29	100	100
0 0 30	3000	3000	1 1 30	100	100
0 0 31	3100	3100	1 1 31	100	100
0 0 32	3200	3200	1 1 32	100	100
0 0 33	3300	3300	1 1 33	100	100
0 0 34	3400	3400	1 1 34	100	100
0 0 35	3500	3500	1 1 35	100	100
0 0 36	3600	3600	1 1 36	100	100
0 0 37	3700	3700	1 1 37	100	100
0 0 38	3800	3800	1 1 38	100	100
0 0 39	3900	3900	1 1 39	100	100
0 0 40	4000	4000	1 1 40	100	100
0 0 41	4100	4100	1 1 41	100	100
0 0 42	4200	4200	1 1 42	100	100
0 0 43	4300	4300	1 1 43	100	100
0 0 44	4400	4400	1 1 44	100	100
0 0 45	4500	4500	1 1 45	100	100
0 0 46	4600	4600	1 1 46	100	100
0 0 47	4700	4700	1 1 47	100	100
0 0 48	4800	4800	1 1 48	100	100
0 0 49	4900	4900	1 1 49	100	100
0 0 50	5000	5000	1 1 50	100	100
0 0 51	5100	5100	1 1 51	100	100
0 0 52	5200	5200	1 1 52	100	100
0 0 53	5300	5300	1 1 53	100	100
0 0 54	5400	5400	1 1 54	100	100
0 0 55	5500	5500	1 1 55	100	100
0 0 56	5600	5600	1 1 56	100	100
0 0 57	5700	5700	1 1 57	100	100
0 0 58	5800	5800	1 1 58	100	100
0 0 59	5900	5900	1 1 59	100	100
0 0 60	6000	6000	1 1 60	100	100
0 0 61	6100	6100	1 1 61	100	100
0 0 62	6200	6200	1 1 62	100	100
0 0 63	6300	6300	1 1 63	100	100
0 0 64	6400	6400	1 1 64	100	100
0 0 65	6500	6500	1 1 65	100	100
0 0 66	6600	6600	1 1 66	100	100
0 0 67	6700	6700	1 1 67	100	100
0 0 68	6800	6800	1 1 68	100	100
0 0 69	6900	6900	1 1 69	100	100
0 0 70	7000	7000	1 1 70	100	100
0 0 71	7100	7100	1 1 71	100	100
0 0 72	7200	7200	1 1 72	100	100
0 0 73	7300	7300	1 1 73	100	100
0 0 74	7400	7400	1 1 74	100	100
0 0 75	7500	7500	1 1 75	100	100
0 0 76	7600	7600	1 1 76	100	100
0 0 77	7700	7700	1 1 77	100	100
0 0 78	7800	7800	1 1 78	100	100
0 0 79	7900	7900	1 1 79	100	100
0 0 80	8000	8000	1 1 80	100	100
0 0 81	8100	8100	1 1 81	100	100
0 0 82	8200	8200	1 1 82	100	100
0 0 83	8300	8300	1 1 83	100	100
0 0 84	8400	8400	1 1 84	100	100
0 0 85	8500	8500	1 1 85	100	100
0 0 86	8600	8600	1 1 86	100	100
0 0 87	8700	8700	1 1 87	100	100
0 0 88	8800	8800	1 1 88	100	100
0 0 89	8900	8900	1 1 89	100	100
0 0 90	9000	9000	1 1 90	100	100
0 0 91	9100	9100	1 1 91	100	100
0 0 92	9200	9200	1 1 92	100	100
0 0 93	9300	9300	1 1 93	100	100
0 0 94	9400	9400	1 1 94	100	100
0 0 95	9500	9500	1 1 95	100	100
0 0 96	9600	9600	1 1 96	100	100
0 0 97	9700	9700	1 1 97	100	100
0 0 98	9800	9800	1 1 98	100	100
0 0 99	9900	9900	1 1 99	100	100
0 0 100	10000	10000	1 1 100	100	100

In space group *Pn2<sub>1</sub>a* 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*<sub>2</sub> to 0·119 without incident except considerably slower convergence than we achieved in *Pnma*. We started with the coordinates of OM and the thermal parameters listed in Table 1. The resulting co-ordinates 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*<sub>2</sub>=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<sub>1</sub>a*, 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.

*Note added by Dr Olie, 3 May 1971:* The refinement of our data by the Templetons shows that the conclusions drawn with respect to the molecular structure and intermolecular interactions are independent of the choice of *Pn2<sub>1</sub>a* or *Pnma* as the proper space group. Based on the information we have at present, we have no valid criterion for making a choice; therefore, the conclusion in the final lines of the Templetons' paper may be inverted to: 'We conclude that there is no reason to accept *Pnma* as the correct space group, and that this description should not be used unless and until some better evidence ... is found'.

In the case of POCl<sub>3</sub> (Olie, 1971), which has an analogous structure, we found, using photographic data weighting according to Cruickshank (1961) that the centric group could still be rejected on a 5% level.

\* To anticipate a likely question, we report that the *R* test of Hamilton (1965), if applied to the *R*<sub>2</sub> 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 (cf. Ford & Rollett, 1970).

## References

- CROMER, D. T. (1965). *Acta Cryst.* **18**, 77.  
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.  
 CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Oxford: Pergamon Press.  
 FORD, G. C. & ROLLETT, J. S. (1970). *Acta Cryst.* **A26**, 162.  
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.  
 OLIE, K. (1971). *Acta Cryst.* **B27**, 1459.  
 OLIE, K. & MILHOFF, F. C. (1969). *Acta Cryst.* **B25**, 974.