

structure. The  $C$  value for this model, although quite high, was not the highest. It therefore seems that the  $R$  index is a more reliable criterion than  $C$ .

$E$ -maps for both structures were easily interpretable. All atoms were located without any ambiguity.

The tangent program was written in FORTRAN code for a 32 K microsecond computer by the authors of this paper. It is capable of calculating 150 phases for one model (6 cycles) in 40 seconds and 400 phases for one model (4 cycles) in 2.4 minutes.

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## References

- COOPER, A., NORTON, D. A. & HAUPTMAN, H. (1969). *Acta Cryst.* **B25**, 814.  
 GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **B24**, 91.  
 HAUPTMAN, H. & KARLE, J. (1956). *Acta Cryst.* **9**, 45.  
 KARLE, I. L. & KARLE, J. (1964). *Acta Cryst.* **17**, 835.  
 KARLE, I. L. & KARLE, J. (1966). *Acta Cryst.* **21**, 860.  
 KARLE, I. L. & KARLE, J. (1968). *Acta Cryst.* **B24**, 81.  
 KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.  
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.  
 OH, Y. L. & MASLEN, E. N. (1968). *Acta Cryst.* **B24**, 883.

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**Refinement of the crystal structure of phosphorus pentabromide,  $\text{PBr}_5$ .** By W. GABES and K. OLIE, *Laboratory of Inorganic Chemistry, University of Amsterdam, Nieuwe Achtergracht 123, The Netherlands*

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The crystal structure of  $\text{PBr}_5$  has been refined from 607 reflexions. The cell dimensions are:  $a = 5.663 \pm 0.003$ ,  $b = 17.031 \pm 0.005$ ,  $c = 8.247 \pm 0.005$  Å. The final structure consists of regular tetrahedral  $\text{PBr}_4^+$  ions, within the range of error, and  $\text{Br}^-$  ions. The average P-Br distance is 2.15 Å.

Independent X-ray studies of  $\text{PBr}_5$  by Powell & Clark (1940) and van Driel & MacGillavry (1941) showed this compound to be orthorhombic with space group  $Pbcm (D_{2h}^{11})$ . According to these authors the structure consists of irregular tetrahedral  $\text{PBr}_4^+$  ions and  $\text{Br}^-$  ions. The Raman spectrum of  $\text{PBr}_5$  showed however that the deformation of the  $\text{PBr}_4^+$  group is small. In order to gain more information we refined the structure. The unit-cell dimensions were determined from Cu  $K\alpha$  Weissenberg camera photographs, calibrated with Al:  $a = 5.663 \pm 0.003$ ,  $b = 17.031 \pm 0.005$ ,  $c = 8.247 \pm 0.005$  Å; the errors are three times the standard deviations. The intensity data for the refinement were collected on a Nonius diffractometer with Cu  $K\alpha$  radiation. The 607 reflexions with an intensity greater than the minimum value were used in the least-squares program of Rutten-Keulemans (1966). The final parameters of van Driel & MacGillavry (1941) were used as a starting point. The atomic scattering factors used were those for P, Br and  $\text{Br}^-$  from *International Tables for X-ray Crystallography* (1962). With isotropic temperature factors the disagreement index  $R$  decreased from 38.5 to 23.3 within 5 cycles. Owing to

Table 1. Final parameters of the asymmetric unit in fractions of cell edges

Standard deviations are given in parentheses.

	$x$	$y$	$z$
P	0.036 (0.002)	0.1340 (0.0006)	0.2500 0
Br(1)	0.2591 (0.0006)	0.1274 (0.0002)	0.0384 (0.0005)
Br(2)	-0.2093 (0.0009)	0.0390 (0.0003)	0.2500 0
Br(3)	-0.1564 (0.0009)	0.2440 (0.0003)	0.2500 0
$\text{Br}^-$	0.603 (0.001)	0.4050 (0.0003)	0.2500 0

the size of the crystal (0.50 × 0.58 × 0.25 mm) an absorption correction was necessary (Eikelenboom, 1970). The linear absorption coefficient used was  $\mu_{\text{Cu } K\alpha} = 328 \text{ cm}^{-1}$ . After this absorption correction  $R$  reduced to 18.5 in three cycles

Table 2. Vibration parameters of the asymmetric unit ( $\text{Å}^{-2}$ )

Standard deviations are given in parentheses.

$$T = \exp [(-h^2a^*2U_{11} - k^2b^*2U_{22} - l^2c^*2U_{33} - hka^*b^*2U_{12} - klb^*c^*2U_{23} - hla^*c^*2U_{13})2\pi^2].$$

	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{23}$	$2U_{13}$
P	0.0257 (0.0057)	0.0141 (0.0044)	0.0480 (0.0066)	-0.0005 (0.0086)	0	0
Br(1)	0.0392 (0.0016)	0.0378 (0.0015)	0.0512 (0.0019)	0.0024 (0.0029)	0.0033 (0.0031)	0.0022 (0.0033)
Br(2)	0.0371 (0.0026)	0.0397 (0.0021)	0.0681 (0.0036)	-0.0014 (0.0041)	0	0
Br(3)	0.0402 (0.0024)	0.0258 (0.0019)	0.0593 (0.0031)	0.0085 (0.0041)	0	0
$\text{Br}^-$	0.0357 (0.0030)	0.0320 (0.0026)	0.0590 (0.0035)	0.0157 (0.0048)	0	0

Table 3. Bond distances and angles with three times the standard deviations

Distance		Distance	
P—Br(1)	2.16 ± 0.02 Å	Br <sup>-</sup> -Br(1)	3.12 ± 0.02 Å
P—Br(2)	2.13 ± 0.03	Br <sup>-</sup> -Br(2)	3.19 ± 0.02
P—Br(3)	2.17 ± 0.03	Br <sup>-</sup> -Br(3)	3.06 ± 0.02
Distance		Angle	
Br(1)-Br(3)	3.54 ± 0.02	Br(1)-P-Br(2)	110.0 ± 1.0°
Br(1)-Br(2)	3.51 ± 0.02	Br(1)-P-Br(1)	107.9 ± 1.6
Br(1)-Br(1)	3.49 ± 0.02	Br(1)-P-Br(3)	109.8 ± 1.0
Br(2)-Br(3)	3.50 ± 0.02	Br(2)-P-Br(3)	109.2 ± 1.6

with individual isotropic temperature factors. A further decrease to 15.5 occurred after removing 20 reflexions probably affected by extinction. A final value of  $R=12.4$  was obtained in three cycles using anisotropic temperature factors.

Final positional parameters are given in Table 1 and vibration parameters in Table 2.

### Discussion

According to the results in Table 3 the P-Br distances are equal and the angles are very near the tetrahedral value. All deviations are within three times the standard deviation.

Every Br<sup>-</sup> ion is surrounded by four Br atoms each belonging to a different PBr<sub>4</sub><sup>+</sup> unit, with distances much smaller than the van der Waals separations.

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### References

- DRIEL, M. VAN & MACGILLAVRY, C. H. (1941). *Rec. Trav. Chim. Pays Bas*, **60**, 869.  
 EIKELBOOM, J. C. (1970). Groningen: Program based on those of BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180 and WELLS, M. (1960). *Acta Cryst.* **13**, 722.  
*International Tables for X-ray Crystallography* (1962). Vol. III, Table 3.3.1A. Birmingham: Kynoch Press.  
 POWELL, H. M. & CLARK, D. (1940). *Nature, Lond.* **145**, 971.  
 RUTTEN-KEULEMANS, E. W. M. (1966). *Acta Cryst.* **21**, A293.

*Acta Cryst.* (1970). B26, 444

**Automatic heavy-atom analysis of some organic compounds.** By H. KOYAMA, *Shionogi Research Laboratory, Shionogi & Co. Ltd., Fukushima-ku, Osaka, Japan*, and K. OKADA and C. ITOH, *Electronic Computing Service Co. Ltd., Honcho, Nihonbashi, Chuo-ku, Tokyo, Japan*

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A computer program *SEARCHER* for automatic structure analysis of organic compounds containing a heavy atom is described. From the automatic diffractometer data the computer determines the position of all atoms starting from the heavy-atom position without any chemical assumption.

A computer program *SEARCHER* has been written for automatic structure analysis of organic compounds, each containing one heavy-atom. It is intended for use by organic chemists rather than professional crystallographers.

The program is written mostly in FORTRAN-63 for the CDC 3600 computer and consists of several crystallographic routines. When the heavy-atom coordinates are weighted the program carries out the sequence of calculations listed in Fig. 1. The first part (part *A*) of this program selects from the list of peak positions a set of atomic sites to be included in the subsequent Fourier calculations. The coordinates and peak height of the centre of a Fourier peak are calculated, by use of a suitable second-order polynomial, from twenty-seven values in three neighbouring sections of the three-dimensional electron density distribution. The second part (part *B*) of the program selects, from the peak

positions picked up in *A*, a set of atomic sites to be inserted in the next cycle of *SEARCHER*. Selection of the atomic sites in *A* is based on 'reasonable' interatomic distances (1.1–1.7 Å) between neighbouring light-atom peaks, and that of the atomic sites in *B* is based on the temperature factor only. The process can be recycled until all the atoms of the molecule are located. The output of *SEARCHER* is a projection of the molecules in a unit cell along one of the crystal axes (1 Å = 2.5 cm). At the initial stage, all light atoms are treated as carbon atoms ( $B=3.5$ ) in the structure-factor calculations. The program will solve structures based on all the triclinic, monoclinic, and orthorhombic space groups.

By the *SEARCHER* program, the crystal structures of the seven organic compounds listed in Table 1 have been successfully solved. The crystal data and the experimental details are also given in the Table.