

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

Distance		Distance	
P—Br(1)	2.16 ± 0.02 Å	Br ⁻ -Br(1)	3.12 ± 0.02 Å
P—Br(2)	2.13 ± 0.03	Br ⁻ -Br(2)	3.19 ± 0.02
P—Br(3)	2.17 ± 0.03	Br ⁻ -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⁻ ion is surrounded by four Br atoms each belonging to a different PBr₄⁺ unit, with distances much smaller than the van der Waals separations.

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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.

The structure of $C_{19}H_{20}O_2N_5Br$ (I) was easily solved by this program after interpretation of the Patterson map, and

the machine time was only about 1.49 hr. The crystal structure of $C_{31}H_{51}O_2Br$ (V), which had spurious peaks due to

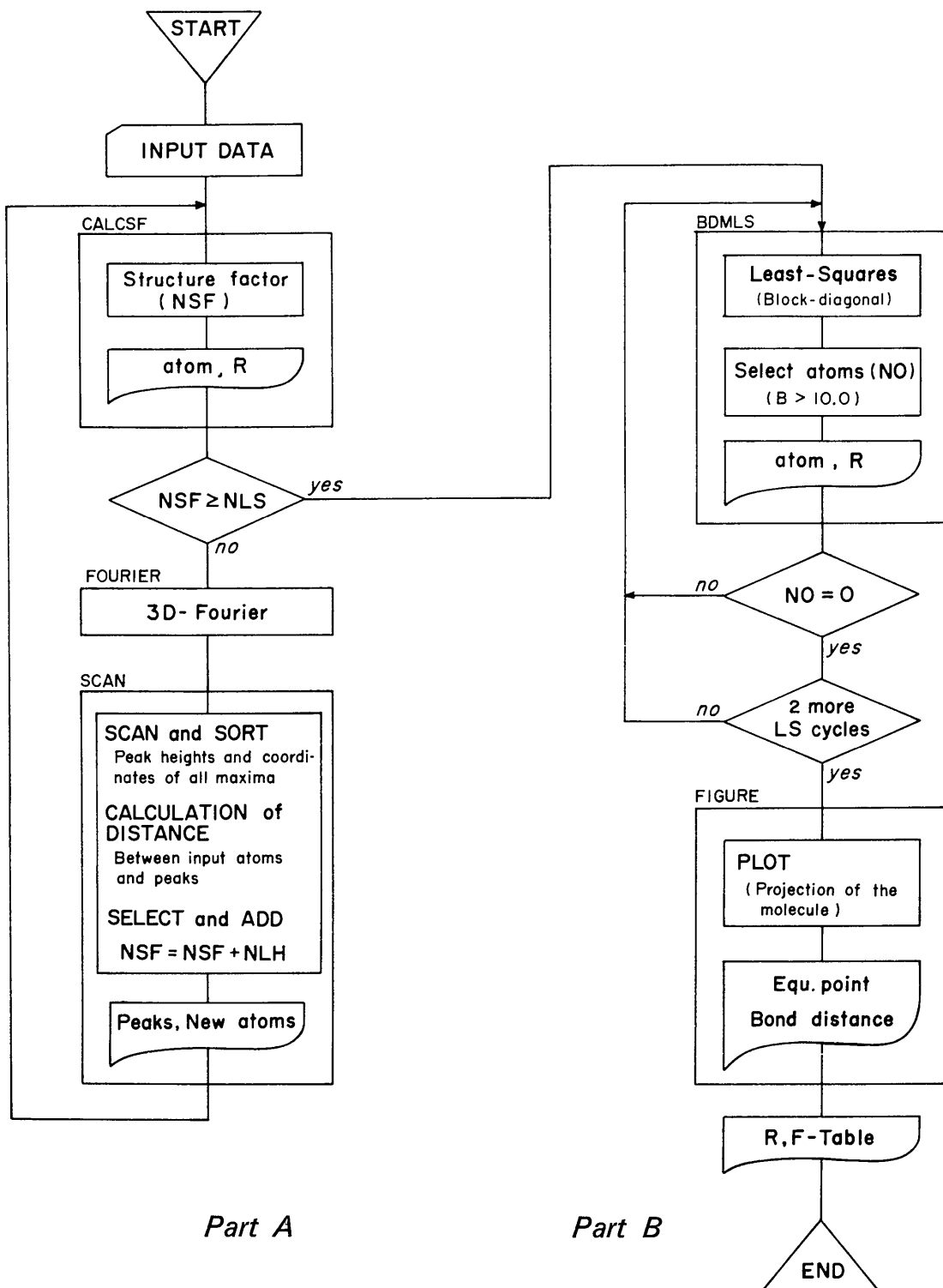


Fig. 1. An outline of the procedures adopted in the analysis of the structure. Notation: NSF=Number of input atoms for the structure factor calculation, NLS=Maximum NSF, NLH=Number of additional atoms for the next structure factor calculation, NO=Number of eliminated atoms ($B > 10.0$) for the next least-squares calculation.

Table 1. Examples of the automatic heavy-atom analysis of some organic compounds

A. Crystal data	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
Formula	$C_{19}H_{20}O_2N_5SBr$	$C_{12}H_{11}O_2Br$	$C_{17}H_{15}BrO_3S$	$C_{17}H_{27}O_5N \cdot HBr$	$C_3H_5O_2Br$	$C_{40}H_{46}O_8NBr$	$C_{40}H_{47}O_{11}Ag$
Mol. wt.	462.4	267.1	379.3	406.3	535.7	750.7	831.8
Space group	$P2_1/c$	$P2_12_12_1$	$C2/c$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
Z	4	4	8	4	2	4	4
a (Å)	12.460	8.264	23.453	17.781	19.138	22.535	23.762
b (Å)	13.510	6.148	8.977	8.786	7.437	12.332	14.591
c (Å)	12.006	21.465	16.338	11.859	9.849	13.917	12.080
β (°)	93°27'	-	112°38'	-	94°04'	-	-
V (Å ³)	2017.4	1090.6	3174.7	1852.7	1398.3	3867.6	4188.3
D_m (g·cm ⁻³)	1.519	1.599	1.582	1.440	1.268	1.281	1.297
D_c (g·cm ⁻³)	1.522	1.626	1.588	1.455	1.272	1.289	1.319
B. Problem	molecular-conformation	molecular-conformation	molecular-conformation	structure-unknown	molecular-conformation	structure-unknown	structure-unknown
C. Procedure of "SEARCH"							
after 1 cycle	149.0 ^{ch}	65.5 ^{ch}	12 ^{atoms}	193.5 ^{ch}	10 ^{atoms}	453.5 ^{ch}	28 ^{atoms}
2	43.0	15	111.0 ^{ch}	12 ^{atoms}	16	174.5	33
3	43.0	15	79.0	20	22	167.5	33
4	43.0	15	69.0	22	24	136.0	34
Total time	149.0 ^{ch}	108.5 ^{ch}	259.0 ^{ch}	483.5 ^{ch}	931.5 ^{ch}	122.5	50
D. Refinement	full-matrix	full-matrix	full-matrix	full-matrix	full-matrix	block-diagonal	block-diagonal
Temp. factor	all aniso.	all aniso.	all aniso.	all aniso.	all aniso.	all aniso.	all aniso.
R	0.053	0.083	0.060	0.092	0.077	0.110	0.065
Obs. reflexion	2117	1193	1813	1436	1570	2200	2066
E. Experiment							
λ	Mo-K α	Mo-K α	Mo-K α	Mo-K α	Mo-K α	Mo-K α	Mo-K α
Scan-range	$\theta \leq 27.5^\circ$	$\theta \leq 27.5^\circ$	$\theta \leq 27.5^\circ$	$\theta \leq 27.5^\circ$	$\theta \leq 27.0^\circ$	$\theta \leq 24.5^\circ$	$\theta \leq 23.5^\circ$
Scan-technique	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Filter	Zr	Zr	Zr	Zr	Zr	Zr	Zr
(I) p-Bromophenyl N-carbamoylthiamine anhydride				(V) Adiantol B bromoacetate			
(II) Methyl benzobicyclo[2.1.1]hexene-exo-8-bromo-endo-2-carboxylate				(VI) Isozygospirin A mono-p-bromobenzoate			
(III) anti-9-Benzonorbornenyl p-bromobenzenesulfonate				(VII) Silver polyetherin A			
(IV) Stemonine hydrobromide monohydrate							

pseudosymmetry in the electron density distribution, was also solved without any human intervention after four cycles, taking 9.3 hr.

The seven organic compounds which were solved by this program contain up to 60 atoms in one asymmetric unit. The use of this program will become more convenient by

the advent of machines (CDC 6600) with computing times in the nanosecond range. A more detailed description of the method will be published elsewhere.

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Cell dimensions of rare earth orthorhodontes. By R. D. SHANNON, *Central Research Department, E.I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware 19898, U.S.A.*

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The cell dimensions of the perovskites, MRhO_3 ($M = \text{Lu, Tm, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd and Pr}$), have been determined from X-ray data.

Marezio, Remeika & Dernier (1968) and Eibschütz (1965) have recently shown for the rare earth orthogallates and orthoferrites, respectively, the variation in cell dimensions

as a function of atomic number of the rare earth ion. The a and c parameters decrease smoothly with atomic number whereas the b parameter goes through a maximum at Gd.

Table 1. Cell dimensions of the perovskites MRhO_3

Compound	a	b	c	V
LuRhO_3	$5.1861 \pm 2 \text{ \AA}$	$5.6700 \pm 2 \text{ \AA}$	$7.5125 \pm 3 \text{ \AA}$	220.9 \AA^3
TmRhO_3	5.2028 ± 5	5.6974 ± 5	7.5428 ± 8	223.6
ErRhO_3	5.2160 ± 2	5.7117 ± 2	7.5610 ± 4	225.3
HoRhO_3	5.2299 ± 4	5.7257 ± 5	7.5823 ± 7	227.0
DyRhO_3	5.2449 ± 4	5.7314 ± 5	7.6002 ± 7	228.5
TbRhO_3	5.2541 ± 4	5.7492 ± 4	7.6226 ± 6	230.3
GdRhO_3	5.2774 ± 4	5.7605 ± 4	7.6584 ± 5	232.8
EuRhO_3	5.2985 ± 6	5.7607 ± 6	7.6802 ± 8	234.4
SmRhO_3	5.3211 ± 3	5.7613 ± 3	7.7083 ± 4	236.3
NdRhO_3	5.3778 ± 6	5.7551 ± 6	7.7745 ± 9	240.6
PrRhO_3	5.4143 ± 2	5.7473 ± 2	7.8026 ± 3	242.8

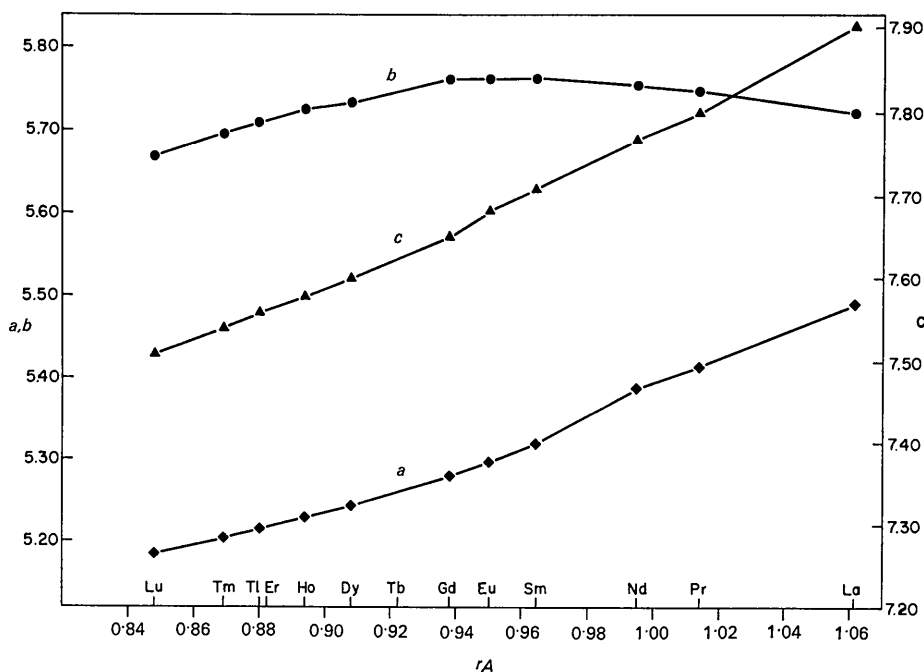


Fig. 1. Cell dimension of MRhO_3 perovskites vs. the effective ionic radius of M^{3+} .