Fifty-three lines were observed for $BiBr_3$, and the pattern could be interpreted in terms of the same space group as $BiCl_3$. The lattice parameter is 9·23 Å. Agreement with the data of Urazov & Sokolova is rather poor but some correspondence is recognizable.

Thermal analysis revealed $BiBr_3$ to undergo a transition at 158°. However, the X-ray pattern failed to reveal a change of structure up to 195 °C. It may be that the transition is the beginning of free rotation of the molecules without a change of crystal symmetry.

Table 1 lists the completely indexed patterns of $BiCl_3$ and $BiBr_3$, giving both calculated and observed spacings and observed intensities.

The authors wish to thank Mr A. J. Darnell of this department for making pure anhydrous $BiCl_3$ available for this work and for preparing some of the diffractometer samples.

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The crystal structure of sodium polymetaarsenite $(NaAsO_2)_x$.

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A certain amount of confusion exists in the literature regarding the formulation of alkali metal arsenites. Thus the formulae Na_2HAsO_3 and $NaAsO_2$ are used synonomously for sodium arsenite. It has been shown in our laboratories that the data on A.S.T.M. cards numbered 1–0905 (Na_2HAsO_3) and 7–9 ($NaAsO_2$) are very similar to the powder pattern of a commercial arsenite which analyses as $As_2O_3 . 0·62\ Na_2O$. The powder pattern on card No. 2–0373 (Na_2HAsO_3) is almost identical with that reported in Table 1 which we have obtained for a pure compound $NaAsO_2$, the formula of which was established by chemical analysis. Schreinemakers & de Baat (1917) and Nelson (1941), who studied the $Na_2O–As_2O_3–H_2O$ system, have also demonstrated the existence of this compound. All data in the A.S.T.M. X-ray Powder Data File (1957) for sodium arsenite are therefore incorrect. The compound $NaAsO_2$, for which the name sodium polymetaarsenite is suggested, is the subject of the present note.

Table 1. *Powder diffraction data for sodium polymetaarsenite*

d (Å)	*I*	*hkl*	*d* (Å)	*I*	*hkl*
7·18	18	200	2·036	5	022
4·93	67	210	1 985	19	412, 231
3·58	92	400	1·912	44	430
3·55	54	211	1·824	32	621
3·40	4	020	1·792	20	800, 431
3·17	100	410	1·740	5	602
2·822	45	021	1·731	< 1	810
2·689	66	411	1·694	8	040
2·627	10	221	1·642	4	630
2·547	16	002	1·606	5	041, 213
2·386	16	600	1·582	< 1	820
2·251	5	610	1·530	16	440, 432
2·213	< 1	421	1·513	17	821
2·154	< 1	230	1·496	4	413
2·072	< 1	402	1·465	5	802, 441

Sodium polymetaarsenite may be prepared either by the reaction of stoichiometric amounts of sodium hydroxide and arsenious oxide, or by crystallization of solutions of arsenious oxide in sodium hydroxide in the appropriate region of the ternary phase diagram (Nelson, 1941).

Single crystals of sodium polymetaarsenite were obtained in the form of thin cleavage flakes by crushing a solidified melt. Unit-cell dimensions were obtained from diffractometer measurements on powder and single crystals and from back-reflection photographs of the 0*kl* reflections. The crystals are orthorhombic with unit-cell dimensions (Cu $K\alpha_1 \lambda = 1·54050$, Cu $K\alpha_2 \lambda = 1·54434$ Å)

$$a = 14·314,\quad b = 6·779,\quad c = 5·086\ \text{Å}\ .$$

These dimensions are considered to be accurate to within ±0·005 Å. Assuming eight formula units, $NaAsO_2$, per unit cell, the calculated density is 3·49 g.cm.$^{-3}$. The calculated density is slightly higher than that determined by pycnometer, 3·40 g.cm.$^{-3}$ probably because of incomplete displacement of air from the crystals. Only finely divided, highly imperfect crystals were available in sufficient quantity for the determination.

The extinctions observed establish the space group uniquely as *Pbca*. An inclination Weissenberg photograph of an (100) cleavage flake of sodium polymeta-

Table 2. *Final parameters from Fourier syntheses*

Atom	*x*	*y*	*z*
As	0·080	0·103	0·250
O_1	0·127	0·322	0·405
O_2	0·154	0·568	0·810
Na^+	0·306	0·102	0·250

Table 3. *Calculated and observed structure factors for sodium polymetaarsenite*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
020	65	82	10,0,0	37	50	470	110	98	002	278	−271
040	177	−181	10,2,0	(13)	8	610	47	42	004	157	145
060	115	−103	10,4,0	39	−43	630	(11)	3	006	77	−97
080	32	23	10,6,0	(11)	−23	650	(13)	−18	020	66	79
200	50	49	12,0,0	71	76	670	(12)	4	022	125	−85
220	(6)	5	12,2,0	31	36	810	66	68	024	69	49
240	42	−36	12,4,0	61	−57	830	107	99	040	134	−167
260	17	−20	12,6,0	40	−52	850	(14)	7	042	141	136
280	22	13	14,0,0	57	63	870	55	−49	044	117	−94
400	209	−166	14,2,0	(11)	17	10,1,0	47	40	060	82	−85
420	(8)	−14	14,4,0	53	−40	10,3,0	85	82	062	85	89
440	44	53	16,0,0	(9)	0	10,5,0	(14)	−2	064	64	−66
460	32	24	16,2,0	(9)	−10	10,7,0	47	−63	080	(16)	17
480	14	3	16,4,0	(6)	0	12,1,0	30	27	021	241	−202
600	119	−112	18,0,0	34	−60	12,3,0	26	30	023	209	185
620	19	−19	210	125	−118	12,5,0	(11)	−10	025	108	−111
640	97	86	230	46	−64	14,1,0	22	−31	041	78	−85
660	46	50	250	35	39	14,3,0	52	−57	043	44	49
680	41	−35	270	53	50	14,5,0	(8)	5	045	50	−53
800	129	−109	410	173	−163	16,1,0	32	−33	061	87	85
820	53	−49	430	213	−208	16,3,0	38	−44	063	50	−61
840	94	81	450	(12)	1	18,1,0	11	−20	081	64	60
860	70	65									

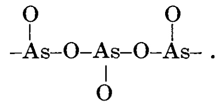
Figures in brackets denote reflections which were not observed experimentally.
These reflections were allocated half the minimum intensity observable.

arsenite was used to record 0*kl* reflections. Further cleavage, parallel to [010], gave crystals suitable for rotation about the *c* axis, which were used to record *hk*0 reflections. Rotation photographs showed approximate halving of the *a* axis. Intensity measurements of 0*kl* and *hk*0 reflections were made by visual comparison of spots on a calibrated scale with multiple-film Weissenberg photographs. The intensities of *hk*0 reflections were corrected for absorption using the graphical method of Rogers & Moffett (1956).

Arsenic atoms were located from Patterson projections while the remainder of the atoms were located using Fourier projections and spatial relationships. Parameters were refined using $F_o - F_c$ syntheses. The final parameters are listed in Table 2. The percentage discrepancy between the observed and calculated structure amplitudes (Table 3) was 12·0 for the 0*kl* reflections and 15·0 for the *hk*0 reflections. An anisotropic temperature factor, $\exp\left[-(B_x \cos^2 \omega + B_y \sin^2 \omega)(\sin \theta/\lambda)^2\right]$ with $B_x = 1{\cdot}85$, $B_y = 1{\cdot}07$ Å^2 was used for the *hk*0 reflections, and $\exp\left[-(B_y \cos^2 \omega + B_z \sin^2 \omega)(\sin \theta/\lambda)^2\right]$ with $B_y = 2{\cdot}02$, $B_z = 1{\cdot}07$ Å^2 was used for the 0*kl* reflections. In both cases ω is the angle between the *b* axis and the normal to the planes (*hkl*).

The accuracy of the atomic parameters is considered to be low except for the arsenic atoms. This is a natural consequence of the fact that the contribution of the arsenic atoms to the structure factors largely outweighs the contribution from the other atoms. In addition, copper radiation was used so that relatively few reflections were accessible for measurement and absorption effects were large. Also, in the two projections studied, the sodium atoms were obscured, in one case by arsenic atoms, in the other case by one set of oxygen atoms.

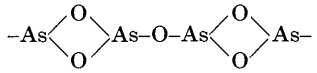
Nevertheless the main features of the structure may be described with some confidence. Each arsenic atom is at the apex of a triangular pyramid having three oxygen atoms forming the base. AsO_3 groups are linked together in polymeric chains by shared oxygen atoms:



$$-\overset{\overset{\textstyle O}{|}}{As}-O-\underset{\underset{\textstyle O}{|}}{As}-O-\overset{\overset{\textstyle O}{|}}{As}-\,.$$

Four chains run through the unit cell parallel to the *c* axis, bound together in two sets by the electrostatic attraction of sheets of sodium ions.

Sodium polymetaarsenite appears to be structurally related to the monoclinic form of arsenious oxide rather than to the cubic modification. Although both polymorphs are built up of pyramidal AsO_3 groups, the cubic modification has a compact molecule, As_4O_6 (Bozorth, 1923), while the monoclinic modification is polymeric,



(Bötticher, Plieth, Reuber–Kürbs & Stranski, 1951). In this connection it is worth noting that the monoclinic form crystallises from potassium hydroxide solutions of arsenious oxide.

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