

Table 5 (cont.)

		A	B	C	D
H(4)	1	0.18	103	69	24
	2	0.26	13	84	103
	3	0.16	91	22	109
H(5)	1	0.22	55	43	84
	2	0.26	35	121	124
	3	0.19	91	117	35

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A Neutron Diffraction Study of the Crystal Structure of Sodium Arsenate Heptahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$

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The positions of all 15 independent hydrogen atoms in the crystal structure of disodium hydrogen orthoarsenate heptahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, approximately located in a previous single-crystal X-ray analysis, have been confirmed by neutron diffraction. Anisotropic least-squares refinement of the hydrogen atoms led to a final R value of 0.068 over 476 independent neutron intensities measured on a manually operated diffractometer. No correction was made for absorption but an empirical extinction correction was applied. The neutron analysis, in which hydrogen atom positions were located with coordinate estimated standard deviations of about 0.04 Å, confirms the hydrogen-bonding system deduced from the X-ray analysis. The anionic hydrogen atom, H(1), is carried by the oxygen atom O(4), with the longest As–O bond (1.74 Å compared with an average length of 1.67 Å); while the markedly non-linear hydrogen bond of O(4)–H(1) to the water oxygen atom O(6) is relatively short at 2.68 Å, O(4)–H(1) is not quite the longest O–H distance in the structure. Each of the seven water molecules is closely coplanar with the two oxygen atoms to which it is hydrogen-bonded, although nearly all the hydrogen bonds are significantly bent. In terms of the classification by lone pair orientation, five of the water molecules are of type *A* and two of type *G*. Water H–O–H angles range from 104 to 110°, with an e.s.d. of about 3°.

Introduction

The crystal structure of disodium hydrogen orthoarsenate heptahydrate, or sodium arsenate heptahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, has been determined by single-crystal

X-ray analysis by Ferraris & Chiari (1970*a*) and, together with its phosphorus isomorph, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ independently by Baur & Khan (1970). Each of the two crystallographically independent sodium ions (in layers perpendicular to [010]) is approximately octahe-

drally coordinated to six water oxygen atoms; the formulation $[\text{Na}_2(\text{OH}_2)_7][\text{AsO}_3\text{OH}]$ has been suggested (Baur & Khan, 1970). Hydrogen bonds link those octahedra in chains along $[101]$ with edges and faces of the octahedra being shared alternately. The anions, contained between the sodium-water (101) layers, maintain some degree of isolation.

In an accurate X-ray analysis involving 2384 independent diffractometer reflexions, a three-dimensional Fourier difference synthesis, coupled with bond and angle calculations to eliminate spurious peaks, enabled the approximate sites of all the 15 hydrogen atoms in the anion and in the seven crystallographically independent water molecules to be found (Ferraris & Chiari, 1970*a*). Nearly all the hydrogen bonds appear to be bent. A neutron-diffraction investigation has now been made to enable these atoms to be located more precisely, so that the configuration of the anion and the conformation of the water molecules and associated hydrogen bonds can be established. It forms part of a series of studies on acidic (and chiefly hydrated) arsenates (Ferraris, 1969; Ferraris & Chiari, 1970*a, b*; Ferraris, Jones & Yerkess, 1971) and phosphates (Jones & Cruickshank, 1961; Curry, Denne & Jones, 1968; Curry & Jones, 1970).

Experimental

Crystallographic data

These were taken to be as reported in the X-ray crystal structure analysis by Ferraris & Chiari (1970*a*): monoclinic, space group $P2_1/n$ (C_2^2), $a=10.659$, $b=11.011$, $c=9.394$ Å, $\beta=95^\circ 26'$, $Z=4$. There is satisfactory agreement with the unit-cell data reported by Baur & Khan (1970), in which the a and c axes have been interchanged.

Neutron diffraction measurements

Crystals well developed on $\{\bar{1}01\}$ were grown in a few hours by seeding just above room temperature an aqueous solution of commercial $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ saturated at 70–80°C. From these, a crystal of dimensions $8 \times 5 \times 4$ mm and weight 0.29 g, with b -axis elongation indicated by X-ray photographs, was selected and set up about the ϕ -rotation axis of a manually operated 'Badger' diffractometer at the DIDO reactor, Atomic Energy Research Establishment, Harwell. Possible loss of water during irradiation was minimized by enclosing the crystal in an approximately conical eggshell soda-glass cover.

The procedure for neutron data collection and data reduction generally followed that described by Ferraris, Jones & Yerkess (1971) for pharmacolite, $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$, except where otherwise specified. Counting times were 7–8 seconds per 0.1° step in 2θ for θ - 2θ scanning with a fission-chamber monitor count of 2×10^4 . Individual background counts, typically 400–600 counts per step, were obtained for each reflexion and found to be about ten times higher than for

pharmacolite. Despite some slight variation in background with χ , attributed to variation in the extent to which the tapered glass crystal cover was exposed to the rectangular neutron beam, intensities appeared to be unaffected. From the 2300 hkl and $\bar{h}kl$ reflexions with $2\theta < 80^\circ$ accessible with neutron wavelength $\lambda = 1.04$ Å, measurements were sought from the 1015 (44%) which calculations from the X-ray coordinates for all atoms indicated should have intensity exceeding 4×10^{-24} cm². Intensities of 489 reflexions were actually recorded, ranging from 350 counts (integrated) for the reflexions 681 and 044, to 63,000 for 323; of these, 13 were rejected because of very low intensity to leave 476 (21% of those accessible) which were used in the final refinement. The lower limits of measurement depend on the background, which is chiefly due to hydrogen incoherent scattering. Hydrogen constitutes about 42% of the neutron scattering power of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, estimated as $\sum_{\text{H atoms}} |b| / \sum_{\text{all atoms}} |b|$. The unit-cell hydrogen content is nearly three times, the weight of the crystal ten times, and the background count (including the effect of the glass cover) about 15 times greater in $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ than the corresponding values in pharmacolite (Ferraris, Jones & Yerkess, 1970), for which the monitor count was $2\frac{1}{2}$ times that used here. With $\mu = 0.16$ cm⁻¹ absorption was neglected; extinction is discussed later.

Structure refinement

The following neutron scattering lengths were used: As, 0.63; Na, 0.351; O, 0.577; H, -0.378×10^{-12} cm. With atomic positional parameters as derived from the X-ray analysis (Ferraris & Chiari, 1970*a*) and with the isotropic temperature factor B set at 3.0 Å for the hydrogen atoms, the R value was 0.19. This fell to 0.097 after three cycles of isotropic least-squares refinement of the hydrogen atoms by the *ORFLS* program of the *X-ray 63 System* on the ATLAS computer, in which structure factor differences (rather than their squares) were used, with weighting $1/\sigma$; σ was derived from the data reduction program written by W. A. Denne. Two cycles of anisotropic least-squares refinement, again with the heavy-atom parameters fixed at the values derived from the X-ray analysis, left some hydrogen principal temperature coefficients apparently negative, but all were positive definite after a further cycle in which only the anisotropic temperature factors were varied.

At this stage of the refinement, with $R=0.093$, the effect of extinction was tested by plotting F_o/F_c against measured intensity. This led to an extinction correction, ranging from $F_{\text{corr}} = F_{\text{obs}}/0.97$ for $I_{\text{meas}} = 10,000$ to $F_{\text{corr}} = F_{\text{obs}}/0.89$ for $I_{\text{meas}} = 63,000$, which caused R to drop slightly to 0.090. A further improvement to 0.083 resulted from checking the experimental measurements for unusually poor agreements and changing the background for some of these reflexions. Two further aniso-

tropic least-squares cycles gave convergence, with $R=0.068$ and all shifts less than standard deviations. Table 1 gives the final values of F_o and F_c . For the hydrogen atoms, Table 2 lists the final fractional atomic coordinates (estimated standard deviations in parentheses), together with coefficients, B_{ij} , in the expression

$$\exp \left[-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_j^* a_j \right]$$
. Parameters for the Na, As, and O atoms are not reported, since the values derived by Ferraris & Chiari (1970a) from X-ray data have been retained. The designations of the atoms are also those adopted by Ferraris & Chiari (1970a).

Table 1. Final list of observed and calculated structure factors
The significant figures of the estimated standard deviations are given in parentheses

M	K	L	F _o	F _c	M	K	L	F _o	F _c	M	K	L	F _o	F _c	M	K	L	F _o	F _c	M	K	L	F _o	F _c
2	0	0	6.30	6.07	7	5	1	6.64	6.90	8	2	4	2.72	-3.18	9	0	8	8.71	8.23	10	0	8	8.71	8.23
4	0	0	0.98	-0.89	8	5	1	4.71	-4.94	11	2	4	4.0*	-1.83	12	0	8	5.19	-1.81	13	0	8	5.19	-1.81
6	0	0	0.90	0.65	9	6	1	3.82	3.14	14	3	2	2.32	2.38	15	0	8	8.92	-7.21	16	0	8	8.92	-7.21
8	0	0	4.41	-4.03	10	6	1	4.22	-4.22	17	3	2	2.00	-2.26	18	0	8	5.92	-3.86	19	0	8	5.92	-3.86
10	0	0	0.93	1.03	11	6	1	4.54	-3.93	20	3	3	3.89	0.76	21	0	8	2.00	-2.00	22	0	8	2.00	-2.00
12	1	0	8.13	-7.44	12	6	1	1.92	-0.99	23	3	3	3.19	-1.43	24	0	8	7.10	-6.65	25	0	8	7.10	-6.65
14	1	0	3.12	-3.49	13	6	1	2.34	2.45	26	3	3	3.07	1.15	27	0	8	4.08	-3.86	28	0	8	4.08	-3.86
16	1	0	3.09	3.92	14	6	1	1.84	-0.81	28	3	3	3.19	-1.35	29	0	8	4.39	-4.39	30	0	8	4.39	-4.39
18	1	0	3.02	4.35	15	6	1	4.20	-4.17	30	3	4	4.76	-4.34	31	0	8	6.03	-5.52	32	0	8	6.03	-5.52
20	1	0	0.79	0.11	16	6	1	1.52	0.70	32	3	4	3.96	-3.44	33	0	8	3.19	-2.70	33	0	8	3.19	-2.70
22	1	0	0.79	0.11	17	6	1	1.52	0.70	34	3	4	3.41	3.47	34	0	8	6.50	-5.88	34	0	8	6.50	-5.88
24	1	0	1.77	1.80	18	6	1	3.81	3.54	35	3	5	3.30	2.06	35	0	8	6.79	6.26	35	0	8	6.79	6.26
26	1	0	0.32	0.42	19	6	1	1.54	1.48	36	3	5	3.02	-1.44	36	0	8	3.19	-2.70	36	0	8	3.19	-2.70
28	1	0	2.22	-2.05	20	6	1	1.93	-1.88	37	3	5	3.01	-1.41	37	0	8	6.50	-6.00	37	0	8	6.50	-6.00
30	1	0	0.43	0.42	21	6	1	1.92	-1.88	38	3	5	3.19	-1.43	38	0	8	4.40	-3.92	38	0	8	4.40	-3.92
32	1	0	1.01	-1.05	22	6	1	1.40	-1.70	39	3	5	3.49	-3.11	39	0	8	5.31	-4.82	39	0	8	5.31	-4.82
34	1	0	0.10	0.11	23	6	1	1.31	-1.31	40	3	5	3.55	-3.20	40	0	8	6.42	-5.91	40	0	8	6.42	-5.91
36	1	0	0.10	0.11	24	6	1	1.40	-1.70	41	3	5	3.12	-2.95	41	0	8	4.22	-3.71	41	0	8	4.22	-3.71
38	1	0	0.32	0.42	25	6	1	1.31	-1.31	42	3	5	3.19	-1.43	42	0	8	6.50	-6.00	42	0	8	6.50	-6.00
40	1	0	0.79	0.11	26	6	1	1.40	-1.70	43	3	5	3.02	-1.44	43	0	8	4.40	-3.92	43	0	8	4.40	-3.92
42	1	0	1.77	1.80	27	6	1	1.54	1.48	44	3	5	3.19	-1.43	44	0	8	5.31	-4.82	44	0	8	5.31	-4.82
44	1	0	0.32	0.42	28	6	1	1.93	-1.88	45	3	5	3.49	-3.11	45	0	8	6.42	-5.91	45	0	8	6.42	-5.91
46	1	0	0.10	0.11	29	6	1	1.31	-1.31	46	3	5	3.55	-3.20	46	0	8	6.50	-6.00	46	0	8	6.50	-6.00
48	1	0	0.10	0.11	30	6	1	1.40	-1.70	47	3	5	3.12	-2.95	47	0	8	4.22	-3.71	47	0	8	4.22	-3.71
50	1	0	0.32	0.42	31	6	1	1.31	-1.31	48	3	5	3.19	-1.43	48	0	8	6.50	-6.00	48	0	8	6.50	-6.00
52	1	0	0.79	0.11	32	6	1	1.40	-1.70	49	3	5	3.02	-1.44	49	0	8	4.40	-3.92	49	0	8	4.40	-3.92
54	1	0	1.77	1.80	33	6	1	1.54	1.48	50	3	5	3.19	-1.43	50	0	8	5.31	-4.82	50	0	8	5.31	-4.82
56	1	0	0.32	0.42	34	6	1	1.93	-1.88	51	3	5	3.49	-3.11	51	0	8	6.42	-5.91	51	0	8	6.42	-5.91
58	1	0	0.10	0.11	35	6	1	1.31	-1.31	52	3	5	3.55	-3.20	52	0	8	6.50	-6.00	52	0	8	6.50	-6.00
60	1	0	0.10	0.11	36	6	1	1.40	-1.70	53	3	5	3.12	-2.95	53	0	8	4.22	-3.71	53	0	8	4.22	-3.71
62	1	0	0.32	0.42	37	6	1	1.31	-1.31	54	3	5	3.19	-1.43	54	0	8	6.50	-6.00	54	0	8	6.50	-6.00
64	1	0	0.79	0.11	38	6	1	1.40	-1.70	55	3	5	3.02	-1.44	55	0	8	4.40	-3.92	55	0	8	4.40	-3.92
66	1	0	1.77	1.80	39	6	1	1.54	1.48	56	3	5	3.19	-1.43	56	0	8	5.31	-4.82	56	0	8	5.31	-4.82
68	1	0	0.32	0.42	40	6	1	1.93	-1.88	57	3	5	3.49	-3.11	57	0	8	6.42	-5.91	57	0	8	6.42	-5.91
70	1	0	0.10	0.11	41	6	1	1.31	-1.31	58	3	5	3.55	-3.20	58	0	8	6.50	-6.00	58	0	8	6.50	-6.00
72	1	0	0.10	0.11	42	6	1	1.40	-1.70	59	3	5	3.12	-2.95	59	0	8	4.22	-3.71	59	0	8	4.22	-3.71
74	1	0	0.32	0.42	43	6	1	1.31	-1.31	60	3	5	3.19	-1.43	60	0	8	6.50	-6.00	60	0	8	6.50	-6.00
76	1	0	0.79	0.11	44	6	1	1.40	-1.70	61	3	5	3.02	-1.44	61	0	8	4.40	-3.92	61	0	8	4.40	-3.92
78	1	0	1.77	1.80	45	6	1	1.54	1.48	62	3	5	3.19	-1.43	62	0	8	5.31	-4.82	62	0	8	5.31	-4.82
80	1	0	0.32	0.42	46	6	1	1.93	-1.88	63	3	5	3.49	-3.11	63	0	8	6.42	-5.91	63	0	8	6.42	-5.91
82	1	0	0.10	0.11	47	6	1	1.31	-1.31	64	3	5	3.55	-3.20	64	0	8	6.50	-6.00	64	0	8	6.50	-6.00
84	1	0	0.10	0.11	48	6	1	1.40	-1.70	65	3	5	3.12	-2.95	65	0	8	4.22	-3.71	65	0	8	4.22	-3.71
86	1	0	0.32	0.42	49	6	1	1.31	-1.31	66	3	5	3.19	-1.43	66	0	8	6.50	-6.00	66	0	8	6.50	-6.00
88	1	0	0.79	0.11	50	6	1	1.40	-1.70	67	3	5	3.02	-1.44	67	0	8	4.40	-3.92	67	0	8	4.40	-3.92
90	1	0	1.77	1.80	51	6	1	1.54	1.48	68	3	5	3.19	-1.43	68	0	8	5.31	-4.82	68	0	8	5.31	-4.82
92	1	0	0.32	0.42	52	6	1	1.93	-1.88	69	3	5	3.49	-3.11	69	0	8	6.42	-5.91	69	0	8	6.42	-5.91
94	1	0	0.10	0.11	53	6	1	1.31	-1.31	70	3	5	3.55	-3.20	70	0	8	6.50	-6.00	70	0	8	6.50	-6.00
96	1	0	0.10	0.11	54	6	1	1.40	-1.70	71	3	5	3.12	-2.95	71	0	8	4.22	-3.71	71	0	8	4.22	-3.71
98	1	0	0.32	0.42	55	6	1	1.31	-1.31	72	3	5	3.19	-1.43	72	0	8	6.50	-6.00	72	0	8	6.50	-6.00
100	1	0	0.79	0.11	56	6	1	1.40	-1.70	73	3	5	3.02	-1.44	73	0	8	4.40	-3.92	73	0	8	4.40	-3.92
102	1	0	1.77	1.80	57	6	1	1.54	1.48	74	3	5	3.19	-1.43	74	0	8	5.31	-4.82	74	0	8	5.31	-4.82
104	1	0	0.32	0.42	58	6	1	1.93	-1.88	75	3	5	3.49	-3.11	75	0	8	6.42	-5.91	75	0	8	6.42	-5.91
106	1	0	0.10	0.11	59	6	1	1.31	-1.31	76	3	5	3.55	-3.20	76	0	8	6.50	-6.00	76	0	8	6.50	-6.00
108	1	0	0.10	0.11	60	6	1	1.40	-1.70	77	3	5	3.12	-2.95	77	0	8	4.22	-3.71	77	0	8	4.22	-3.71
110	1	0	0.32	0.42	61	6	1	1.31	-1.31	78	3	5	3.19	-1.43	78	0	8	6.50	-6.00	78	0	8	6.50	-6.00
112	1	0	0.79	0.11	62	6	1	1.40	-1.70	79	3	5	3.02	-1.44	79	0	8	4.40	-3.92	79	0	8	4.40	-3.92
114	1	0	1.77	1.80	63	6	1	1.54	1.48	80	3	5	3.19	-1.43	80	0	8	5.31	-4.82	80	0	8	5.31	-4.82
116	1	0	0.32	0.42	64	6	1	1.93	-1.88	81	3	5	3.49	-3.11	81	0	8	6.42	-5.91	81	0	8	6.42	-5.91
118	1	0	0.10	0.11	65	6	1	1.31	-1.31	82	3	5	3.55	-3.20	82	0	8	6.50	-6.00	82	0	8	6.50	-6.00
120	1	0	0.10	0.11	66	6	1	1.40	-1.70	83	3	5	3.12	-2.95	83	0	8	4.22	-3.71	83	0	8	4.22	-3.71
122	1	0	0.32	0.42	67	6	1	1.31	-1.31	84	3	5	3.19	-1.43	84	0	8	6.50	-6.00	84	0	8	6.50	-6.00
124	1	0	0.79	0.11	68	6	1	1.40	-1.70	85	3	5	3.02	-1.44	85	0	8	4.40	-3.92	8				

Description and discussion of the hydrogen bonding system in the structure

The hydrogen bonding description given as a result of the X-ray analysis of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Ferraris & Chiari, 1970*a*), has been confirmed completely by the present neutron-diffraction analysis. While the differences in the bond lengths and angles involving hydrogen atoms derived from the two analyses are not formally significant, they are clearly different in the two cases; it is noticeable that, for all except two of the O–H distances, those from the X-ray analysis are shorter than the corresponding values from the neutron data (Table 4). This confirms the hypothesis (see *e.g.* Coppens & Coulson, 1967) that, at least for light atoms, the centres of gravity of the electron cloud and the nucleus are different. It is also remarkable that the coordinates obtained from the X-ray difference synthesis are almost always nearer those from the neutron data (Table 2) than are the coordinates from the X-ray data least-squares refinement.* The X-ray results do not justify any useful comparison between the two sets of temperature factors.

In sodium arsenate, as in pharmacolite (Ferraris, Jones & Yerkess, 1970), the acidic hydrogen atom, H(1), is linked to the oxygen atom, O(4), involved in the longest As–O bond. In turn this hydrogen atom is engaged in a markedly non-linear hydrogen bridge which is the shortest among those in sodium arsenate; in contrast with the diagrams correlating O–H and O...O lengths (see *e.g.* Hamilton & Ibers, 1968), the O(4)–H(1) bond is not the longest among the O–H bonds in sodium arsenate. However, since all the O...O contacts involving the water molecules are about 2.8 Å long and, further, the gradient of the curve is very shallow, the O–H length is almost insensitive to

* For pharmacolite also the hydrogen atoms of the water molecules have been 'seen' in an X-ray difference Fourier synthesis; the computed O–H distances were very near those from the neutron data instead of being too short, as are the distances usually obtained from an X-ray least-squares refinement.

O...O distance variations in this region. Examination of neutron-diffraction studies of hydrogen bridges of water molecules in the literature indicates that only exceptionally is the O...O distance shorter than 2.70 Å.

Conformation of the water molecules

In the $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ structure, all the seven groups consisting of the three atoms of a water molecule together with the two acceptor oxygen atoms are planar; their best mean-planes (Schomaker, Waser, Marsh & Bergman, 1959), in fractional coordinates and referred to the unit-cell axes, are reported in Table 3 and designated α . The only possible exception is the *W*(5) group, where the H(11)–plane distance is greater than 2σ .

While the H–O–H angles range from 104 to 110°, with a mean slightly below 108°, the values for the corresponding O...O...O angles extend from 102.4 to 143.3°. Almost all the hydrogen bridges are appreciably non-linear; evidently, when some distortion of the hydrogen bonding geometry is needed to facilitate packing, this is mainly reflected in a lack of linearity of the hydrogen bridge As in pharmacolite (Ferraris, Jones & Yerkess, 1970), however, the distortion does not affect the planarity of the donor–hydrogen–atoms–acceptors group; the vertex of the O–H...O angles is always towards the bisector of the H–O–H angle, except for $\text{H}_2\text{W}(7)$ (see the values in Table 3)

According to the classification of hydrogen-bonded water molecules with respect to their lone-pair electrons (Chidambaram, Sequeira & Sikka, 1964), five of the water molecules in the $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ structure are of type *A* and two of type *G*. Each of the lone-pair orbitals in a water oxygen atom is involved in a specific contact with a sodium atom; one sodium atom is substituted by one hydrogen atom in the contacts involving $\text{H}_2\text{W}(5)$ and $\text{H}_2\text{W}(6)$ molecules. The water molecules are, of course, only roughly tetrahedral. In fact, the angles between the two sodium (or hydrogen) contact atoms and the oxygen of the water molecules range from 82 to 106°; the plane β containing these three atoms forms an angle with the corresponding plane α

Table 4. O–H bond lengths: uncorrected (*A*) and corrected for thermal motion (*B*, *C*, *D*); lower (*B*) and upper (*C*) limits and 'riding' model (*D*)

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
O(4)–H(1)	0.972 Å	0.976 Å	1.138 Å	0.997 Å
<i>W</i> (1)–H(2)	0.943	0.943	1.075	0.940
<i>W</i> (1)–H(3)	0.933	0.936	1.123	0.957
<i>W</i> (2)–H(4)	0.922	0.928	1.149	0.958
<i>W</i> (2)–H(5)	0.986	0.988	1.158	1.003
<i>W</i> (3)–H(6)	0.942	0.954	1.186	0.997
<i>W</i> (3)–H(7)	0.997	0.998	1.153	1.008
<i>W</i> (4)–H(8)	0.934	0.937	1.113	0.959
<i>W</i> (4)–H(9)	0.953	0.954	1.105	0.965
<i>W</i> (5)–H(10)	0.925	0.925	1.085	0.932
<i>W</i> (5)–H(11)	0.986	0.987	1.137	0.999
<i>W</i> (6)–H(12)	0.937	0.937	1.067	0.941
<i>W</i> (6)–H(13)	0.985	0.986	1.125	0.999
<i>W</i> (7)–H(14)	0.940	0.945	1.108	0.969
<i>W</i> (7)–H(15)	0.941	0.946	1.117	0.970

(Table 3) ranging from 73 to 88°. Finally, the line of intersection between the α and β planes does not coincide with the H–O–H bisector (see angles in Table 3).

The structure of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ is generally in accord with the electrostatic balance scheme proposed by Baur & Khan (1970). The balance would be even better with the hypothesis that O(1), O(2) and O(3) receive a charge 1.33 (instead of 1.25) and O(4) a charge 1.00 (instead of 1.25) from the arsenic atom, an assumption corresponding to a roughly inverse dependence of the distribution of electrostatic charges on the atomic distance (Baur, 1962).

Thermal motion and accuracy of the structure

The O–H bond lengths have been corrected for thermal motion according to Busing & Levy (1964). Table 4 presents the lower and upper limits for the corrected length, together with the uncorrected length, and the length on the assumption of the 'riding' model for the O–H bond. The difference between the last value and the uncorrected one is always smaller than the σ value for the O–H lengths.

With regard to the relatively high apparent coordinate e.s.d.'s of 0.03–0.04 Å for the hydrogen atoms, similar considerations to those which were discussed for pharmacolite (Ferraris, Jones & Yerkess, 1970) apply to $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$. Table 5 gives details of the thermal vibration ellipsoids.

Table 5. Parameters characterizing the principal directions 1, 2, 3 of thermal vibration for the hydrogen atoms: root-mean-square displacement (Å) and the angles the principal directions make with the a (B), b (C) and c (D) axes

		A	B	C	D
H(1)	1	0.18 Å	113°	28°	103°
	2	0.33	26	73	114
	3	0.11	78	69	27
H(2)	1	0.20	87	49	42
	2	0.25	123	50	119
	3	0.08	33	68	118
H(3)	1	0.20	82	48	44
	2	0.31	106	133	46
	3	0.12	18	107	90
H(4)	1	0.20	43	130	109
	2	0.33	85	106	20
	3	0.17	47	44	85
H(5)	1	0.20	63	28	102
	2	0.26	27	115	85
	3	0.13	95	77	13
H(6)	1	0.21	127	77	35
	2	0.40	43	104	55
	3	0.13	71	19	93
H(7)	1	0.19	44	114	129
	2	0.23	52	41	79
	3	0.19	71	121	41

Table 5 (cont.)

		A	B	C	D
H(8)	1	0.20	69	43	128
	2	0.28	36	124	106
	3	0.09	62	67	43
H(9)	1	0.22	27	79	120
	2	0.27	63	111	40
	3	0.111	91	24	66
H(10)	1	0.18	64	125	50
	2	0.28	94	42	49
	3	0.09	27	70	112
H(11)	1	0.14	113	82	19
	2	0.28	43	124	71
	3	0.10	56	35	86
H(12)	1	0.15	60	31	88
	2	0.28	32	118	109
	3	0.09	80	101	19
H(13)	1	0.20	81	80	18
	2	0.24	20	74	107
	3	0.11	108	19	95
H(14)	1	0.22	33	70	121
	2	0.26	108	20	80
	3	0.18	63	89	33
H(15)	1	0.22	97	61	29
	2	0.28	50	46	111
	3	0.17	41	122	71

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