

Dicyclohexylammonium Arsonomethylphosphonate

BY LARRY FALVELLO, PETER G. JONES,* OLGA KENNARD† AND GEORGE M. SHEDRICK

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(Received 17 May 1977; accepted 4 June 1977)

Abstract. $2(\text{C}_6\text{H}_{14}\text{N}^+).\text{CH}_4\text{AsO}_6\text{P}^{2-}$, $M_r = 418.31$, orthorhombic, $Pca2_1$, $a = 8.118$ (8), $b = 6.827$ (9), $c = 33.81$ (3) Å, $U = 1874$ Å³, $Z = 4$, $D_x = 1.483$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 18.5$ cm⁻¹. The anions are disordered, with P and As atoms interchanged in the two orientations. The structure was refined to an R of 0.086 for 792 unique reflexions.

Introduction. The structure determination was undertaken as part of a study of compounds containing the $\text{O}-M-C-M'-\text{O}$ linkage, where M and M' are Group V elements. Crystals were grown as thin colourless

plates from methanol/diethyl ether. Intensities were determined with an automated Stoe two-circle diffractometer, Mo $K\alpha$ radiation, and two crystals mounted respectively about **a** ($0.2 \times 0.3 \times 0.03$ mm, layers 0–3, 402 reflexions) and **b** ($0.4 \times 0.3 \times 0.02$ mm, layers 0–8, 1154 reflexions). Lp corrections were applied but no correction was made for absorption; interlayer scale factors were derived by least-squares analysis of equivalent reflexions from different layers. Averaging equivalent reflexions gave 792 unique reflexions with $F > 4\sigma(F)$. Cell dimensions were obtained by a least-squares analysis of 63 $0kl$ and 130 $h0l$ diffractometer ω -angle measurements.

Patterson and difference syntheses located two

* Author to whom correspondence should be addressed.

† External Staff, Medical Research Council.

Table 1. Final atomic coordinates ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
	Anion position A			Anion position B		
As	1551 (8)	2049 (10)	0	3464 (17)	1984 (24)	735 (6)
P	3854 (30)	2135 (28)	750 (7)	1175 (41)	1947 (45)	-71 (14)
O(1)	2370 (40)	3460 (37)	-361 (8)	3837 (80)	3510 (70)	1120 (13)
O(2)	-495 (23)	2616 (34)	-47 (10)	4914 (50)	2356 (69)	382 (12)
O(3)	1990 (34)	-355 (27)	-21 (12)	3241 (62)	-303 (42)	919 (16)
O(4)	3969 (43)	3224 (44)	1149 (9)	2376 (66)	2940 (74)	-359 (17)
O(5)	5207 (32)	2875 (40)	466 (8)	-577 (46)	2295 (67)	-234 (15)
O(6)	3841 (38)	-82 (33)	800 (10)	1487 (64)	-274 (51)	-68 (20)
C(7)	1906 (47)	3015 (56)	535 (13)	1414 (69)	2803 (81)	442 (17)
H(12)	1997	4585	503	2734	2956	416
H(13)	815	2658	703	1126	1387	567
	Cation 1			Cation 2		
N(1)	-608 (34)	3159 (35)	4494 (8)	2411 (31)	6786 (34)	1265 (8)
C(1)	-944 (37)	2806 (42)	4059 (8)	2682 (41)	7287 (39)	1671 (9)
H(1)	-2226	2639	3982	3972	7651	1699
C(2)	-328 (40)	4505 (41)	3834 (9)	2175 (42)	5501 (40)	1936 (9)
H(2)	-964	5827	3921	2960	4281	1859
H(3)	977	4678	3886	908	5127	1874
C(3)	-635 (40)	4082 (41)	3383 (9)	2377 (41)	5935 (41)	2379 (9)
H(4)	-1937	3845	3339	3667	6056	2453
H(5)	-237	5312	3207	1842	4724	2540
C(4)	355 (38)	2246 (41)	3259 (9)	1510 (41)	7818 (40)	2502 (9)
H(6)	1662	2516	3282	200	7596	2468
H(7)	47	1898	2956	1789	8103	2809
C(5)	-180 (41)	485 (44)	3532 (9)	1960 (39)	9642 (45)	2265 (9)
H(8)	606	-741	2459	1185	10865	2346
H(9)	-1447	101	3473	3233	10010	2322
C(6)	61 (40)	884 (41)	3968 (10)	1742 (38)	9134 (39)	1803 (9)
H(10)	-432	-316	4140	2159	10369	1630
H(11)	1344	1092	4042	445	8896	1750

heavy-atom positions. Least-squares refinement followed by difference syntheses located the cations and possible sites for anion O and C atoms; however, this model would not refine. A disordered structure was therefore suspected. Further refinement was with a disordered model involving two anions with P and As atoms interchanged. All atoms of both anions were allowed to refine from positions initially common to both, with the following sets of distances constrained equal within an e.s.d. of 0.01 Å (by the addition of extra observational equations to the least-squares matrix): As–O, P–O, O···O and C···O (atoms on As), O···O and C···O (atoms on P). The site occupation factors of the two anions refined with their sum constrained to 1.

Common temperature factors were allocated to the following sets of atoms: all As and P (anisotropic), C and H of the anion CH₂ groups, all anion O, and all cation C and N. Initial refinement employed damped blocked full-matrix least squares (with the anions and cations as separate blocks). In the final stages H atoms with a common overall temperature factor were introduced riding on cation C atoms (with H–C = 1.08 Å and H–C–H 109.5°); the e.s.d.'s on constrained non-bonded distances were relaxed to 0.05 Å and no damping or blocking was used. The remaining acidic H atoms of the anion were not located. Refinement converged (maximum shift/e.s.d. 0.015) at $R = 0.0859$, $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.0872$; the weighting scheme was $w = 1/[\sigma^2(F) + 0.001F^2]$. Final constrained parameters were: site-occupation factors, 0.66 and 0.34(1) for anions A and B respectively; bond lengths (Å), As–O 1.695 (17), P–O 1.539 (18); non-bonded distances (Å), O···O (atoms on As) 2.77 (3), O···O (atoms on P) 2.51 (3), O···C (atoms on As)

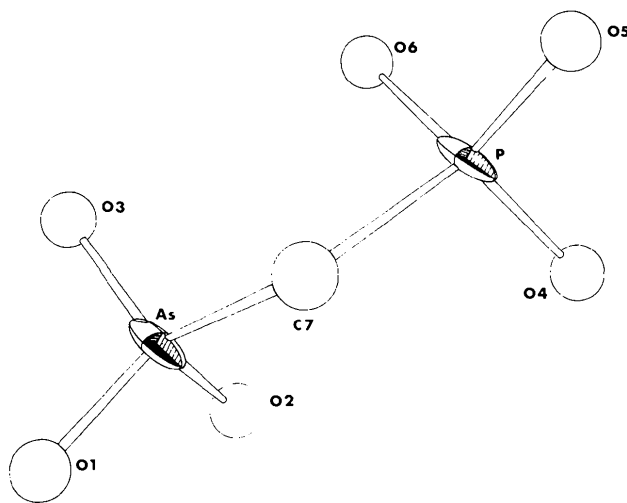


Fig. 1. An ORTEP plot of the anion in position B (H atoms omitted).

2.97 (5), O···C (atoms on P) 2.75 (5); anisotropic temperature factors for As and P ($\text{Å}^2 \times 10^3$), U_{11} 25 (4), U_{22} 14 (2), U_{33} 38 (3), U_{23} 2 (4), U_{13} –23 (3), U_{12} –9 (3) [where the temperature exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^*)$]; isotropic temperature factors ($\text{Å}^2 \times 10^3$), anion CH₂ groups 35 (11), anion O atoms 29(3), cation C and N atoms 32 (2), cation H atoms, 38 (15).

Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2. In view of the constrained bond lengths and non-bonded distances, some e.s.d.'s are omitted in Table 2 for the anions. A diagram of anion B is given (Fig. 1).†

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32763 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths (Å) and angles (°)

	Anion position A	Anion position B
As–O(1)	1.691	1.693
As–O(2)	1.713	1.697
As–O(3)	1.681	1.689
As–C(7)	1.95 (4)	2.02 (5)
P–O(4)	1.539	1.536
P–O(5)	1.540	1.543
P–O(6)	1.535	1.537
P–C(7)	1.84 (5)	1.84 (6)
O(1)–As–O(2)	101	109
O(1)–As–O(3)	116	108
O(2)–As–O(3)	115	118
O(1)–As–C(7)	115	111
O(2)–As–C(7)	99	101
O(3)–As–C(7)	110	110
O(4)–P–O(5)	111	107
O(4)–P–O(6)	112	110
O(5)–P–O(6)	113	108
O(4)–P–C(7)	104	113
O(5)–P–C(7)	105	113
O(6)–P–C(7)	111	107
As–C(7)–P	113	118
	Cation 1	Cation 2
N(1)–C(1)	1.51 (4)	1.43 (4)
C(1)–C(2)	1.47 (4)	1.57 (4)
C(2)–C(3)	1.57 (4)	1.54 (4)
C(3)–C(4)	1.55 (4)	1.52 (4)
C(4)–C(5)	1.58 (4)	1.52 (4)
C(5)–C(6)	1.51 (4)	1.61 (4)
C(6)–C(1)	1.58 (5)	1.54 (4)
N(1)–C(1)–C(2)	108 (2)	109 (2)
N(1)–C(1)–C(6)	103 (2)	113 (3)
C(2)–C(1)–C(6)	112 (2)	110 (2)
C(1)–C(2)–C(3)	108 (2)	112 (2)
C(2)–C(3)–C(4)	109 (3)	112 (3)
C(3)–C(4)–C(5)	109 (2)	116 (2)
C(4)–C(5)–C(6)	113 (2)	108 (2)
C(5)–C(6)–C(1)	106 (3)	114 (2)

Discussion. The disorder is due to the chemical equivalence of the P and As atoms. Weissenberg photographs of some further crystals showed extra weak reflexions corresponding to a doubling of c ; these reflexions can be attributed to a supercell containing two ordered anions in opposite orientations.

There is evidence for hydrogen bonding between the N atoms of the cation and O atoms of the anion; several short O...N contacts from 2.55 to 2.8 Å are observed.

We thank the MRC for financial support, the SRC for provision of the diffractometer and the Winston Churchill Foundation for a maintenance grant (to LF). Dr H. B. F. Dixon kindly provided the compound (Dixon, Sparkes & Webster, 1977).

Reference

DIXON, H. B. F., SPARKES, M. J. & WEBSTER, D. (1977). *Biochem. Soc. Trans.* **5**, 209–210.

Acta Cryst. (1977). **B33**, 3209–3210

N-Iododimethylamine

BY R. HAGEDORN, H. PRITZKOW AND J. JANDER

Anorganisch-Chemisches Institut, Universität Heidelberg, D-6900 Heidelberg, Federal Republic of Germany

(Received 18 May 1977; accepted 4 June 1977)

Abstract. $(\text{CH}_3)_2\text{NI}$, $M_r = 170.98$, orthorhombic, *Pnma*, $a = 10.50$ (2), $b = 7.59$ (2), $c = 5.76$ (1) Å, $V = 459.04$ Å³, $Z = 4$. The structure is polymeric, with –N–I–N–I– chains, very similar to the framework found in $\text{NI}_3 \cdot \text{NH}_3$.

Introduction. The compound was prepared by the reaction of $\text{NI}_3 \cdot \text{NH}_3$ with $(\text{CH}_3)_2\text{NH}$ and recrystallized from $(\text{CH}_3)_2\text{NH}$. The yellow needles decompose slowly at temperatures higher than -30°C . For the X-ray measurements the crystals were cooled to -100°C with a Nonius low-temperature device. The cell parameters were determined from precession photographs calibrated with $\text{Pb}(\text{NO}_3)_2$. The systematic extinctions ($0kl$ for $k + l = 2n + 1$ and $hk0$ for $h = 2n + 1$) are consistent with either *Pnma* or *Pn2₁a*. The intensities of the layers $h0l$ to $h10l$ were measured with a Stoe two-circle diffractometer (Mo $K\alpha$ radiation, graphite monochromator, ω scan) up to $\theta = 30^\circ$. 800 measured hkl and $hk\bar{l}$ reflexions were averaged yielding 468 unique reflexions, of which 178 were considered unobserved with $\sigma_I > I$ [$\sigma_I = (S + 0.0009I^2)^{1/2}$, where

S is the sum of the scan and background counts, and I the net intensity]. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by Patterson and Fourier syntheses and refined by least-squares methods minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma_F^{-2}$ and $\sigma_F = 0.5\sigma_I F_o/I$.

Anisotropic temperature factors for I and isotropic for C and N were used. In the last cycle five individual scale factors (one for each two layers) were refined. The atoms lie on or near planes perpendicular to \mathbf{b} at $y = 0.0$ or 0.25 . In *Pnma*, where the atoms must lie in these special positions, $R = 0.040$ and $R_w = 0.045$ (20 parameters) were obtained. Refinement in *Pn2₁a*, where the y coordinates are not fixed, did not yield better results ($R = 0.040$ and $R_w = 0.045$, 25 parameters). The refinement of the y coordinates did not converge, the e.s.d.'s were comparatively large, and the values oscillated by nearly this amount. Therefore *Pnma* seems to be more probable. Scattering factors were taken from Cromer & Mann (1968); the anomalous dispersion correction for I was included (Cromer &

Table 1. *Positional and thermal parameters*

The anisotropic temperature factor is given by: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	0	0	0	1.38 (2)	0.86 (1)	0.96 (2)	0.02 (8)	-0.04 (8)	0.13 (8)
N	0.1033 (13)	0.25	0.1195 (25)	0.75 (17)					
C(1)	0.2343 (13)	0.25	0.0363 (26)	0.72 (17)					
C(2)	0.1105 (20)	0.25	0.3808 (37)	1.79 (26)					