

MINGOS, J. M. P. (1971). *Nature, Lond.* **229**, 193.
 NORTH, A. C. T. & PHILLIPS, D. C. (1968). *Acta Cryst.* **A24**, 351.
 PAULING, L. (1930). *Phys. Rev.* **36**, 430.
 POPLE, J. A., SCHNEIDER, W. G. & BERNSTEIN, H. J. (1959). *High-resolution Nuclear Magnetic Resonance*, p. 387. New York: McGraw-Hill.

ROBSON, A. & TRUTER, M. R. (1968). *J. Chem. Soc. (A)*, p. 791.
 RÖHRSCHEID, F. (1964). Dissertation Universität München.
 SCHNEPP, O. (1958). *J. Chem. Phys.* **29**, 56.
 WHEATLEY, P. J. (1967). In *Perspectives in Structural Chemistry*, Vol. I, p. 1. Edited by J. D. DUNITZ. New York: John Wiley.

Acta Cryst. (1972). **B28**, 2060

The Crystal and Molecular Structure of Photoaldrin, $C_{12}H_8Cl_6$

BY AJAZ A. KHAN, WERNER H. BAUR AND M. A. Q. KHAN*

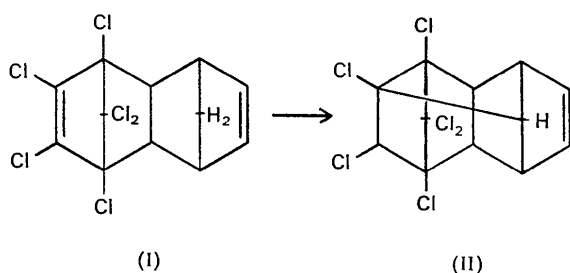
Department of Geological Sciences, University of Illinois at Chicago, Chicago, Illinois 60680, U.S.A.

(Received 5 November 1971 and in revised form 19 January 1972)

Photoaldrin $C_{12}H_8Cl_6$ is monoclinic, space group $P2_1/n$ with cell constants $a=9.344$ (4), $b=15.756$ (18), $c=8.952$ (4) Å and $\beta=91.31$ (4)°. The crystal structure has been determined and refined using counter diffractometer data to $R=0.045$ for 2787 observed reflections. The single C–C bonds exhibit a wide range of variation, from 1.51 to 1.62 Å. The longest among these bonds appears to be the longest ever reported as a C–C bonding distance.

Introduction

Investigations of the toxicity and metabolism of photoaldrin (II), a photoisomer of aldrin (I), have shown recently that it is more toxic to house flies and mosquito larvae than the parent compound (Sutherland & Rosen, 1968; Khan, Sutherland, Rosen & Carey, 1970). Because of its toxic properties, the photoisomer has potential as an insecticide.



The structure of (II) has been established from spectrographic data only (Rosen, 1967). The frameworks of the saturated hydrocarbons are flexible enough to deviate appreciably from an expected model. An X-ray diffraction study has therefore been carried out to confirm the molecular structure of photoaldrin and to determine, in detail, the stereochemical features.

Experimental

Photoaldrin was obtained from the photolysis of aldrin (Rosen, 1967). It was separated by chromatography on thick layer silica gel *G* plates, scrapped and extracted with petroleum ether and then recrystallized from hexane. Crystal symmetry and the approximate cell parameters were determined from precession photographs. A nearly spherical crystal with an average diameter of 0.4 mm was used for the collection of the intensity data on an automatic diffractometer. $Ag K\alpha$ radiation monochromated by a graphite crystal was used and θ - 2θ scans were made. Details of the technique are reported elsewhere (Baur & Kahn, 1970). Cell parameters were measured from well resolved reflections using only the α_1 component. 7250 reflections, measured in two quadrants with $\sin \theta/\lambda$ values up to 0.68 \AA^{-1} , were averaged to give 3636 reflections. Of these, 849 were considered to be of zero intensity because their magnitudes were smaller than 2σ . Lorentz-polarization corrections were applied but absorption corrections were neglected.

Crystal data

Photoaldrin, $C_{12}H_8Cl_6$, is monoclinic with $a=9.344$ (4), $b=15.756$ (18), $c=8.952$ (4) Å, $\beta=91.31$ (4)°, $V=1317.6 \text{ \AA}^3$, $Z=4$, the pycnometric $D_m=1.83$, $D_c=1.84 \text{ g.cm}^{-3}$, F.W. 365.0, $\mu(Ag K\alpha)=6.4 \text{ cm}^{-1}$, $\mu R=0.13$. Space group $P2_1/n$ was established from systematic absences ($h+l=2n+1$ for $h0l$ and $k=2n+1$ for $0k0$) and by the successful refinement of the structure.

* Department of Biological Sciences, University of Illinois at Chicago.

Structure determination

The crystal structure was solved using direct methods. A package of four programs (*FAME*, *MAGIC*, *LINK* and *SYMPL*) written by R. B. K. Dewar & Allen Stone for the application of the symbolic addition method of Karle & Hauptman (1956) was used. An *E* map prepared with 206 reflections gave the positions of the six chlorine atoms. All other atoms including the hydrogens were located from direct or difference Fourier maps. A full-matrix least-squares refinement of the structure with anisotropic temperature factors for the chlorine and carbon atoms, and isotropic temperature factors for the hydrogen atoms, resulted in a final *R* of 0.045 for the 2787 observed reflections. The value of the weighted *R* is 0.056.

The atomic scattering factors used were, for the chlorine and carbon atoms, those reported by Doyle & Turner (1968), and for the hydrogen atoms, those given in *International Tables for X-ray Crystallography* (1962). Atomic coordinates and thermal parameters of the chlorine and carbon atoms are listed in Table 1 and the atomic coordinates and the isotropic temperature factors of the hydrogen atoms are listed in Table 2. Structure factors are compared in Table 3.

The average length of the C–H bond using the observed atomic coordinates listed in Table 1 is 1.01 Å, which is slightly smaller than the accepted value of 1.09 Å (Baur, 1970). The atomic positions of the hydrogen atoms were also calculated using the computer program *CALHPO*, written by Baur (1972). These calculations were made assuming the vector C–H to be 1.09 Å long and inclined equally to the C–C and/or C–Cl bonds involved in the valence bonding with the central carbon atom. The hydrogen atom positions obtained from these purely geometrical considerations are also listed in parentheses in Table 2. Based on the calculated hydrogen positions all the

Table 2. Positional and thermal parameters for the hydrogen atoms

The calculated positions are enclosed in parentheses below the observed.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	0.842 (4) (0.848)	0.478 (2) (0.474)	0.364 (4) (0.385)	2.7 (9) Å ²
H(2)	0.777 (4) (0.779)	0.515 (3) (0.508)	0.095 (5) (0.092)	4.8 (10)
H(3)	0.917 (4) (0.925)	0.639 (2) (0.633)	0.008 (4) (0.010)	2.5 (8)
H(4)	0.621 (3) (0.606)	0.269 (2) (0.260)	0.182 (3) (0.174)	0.3 (5)
H(5)	0.047 (4) (0.054)	0.706 (2) (0.709)	0.266 (4) (0.263)	2.2 (8)
H(6)	0.959 (3) (0.972)	0.617 (2) (0.613)	0.482 (3) (0.489)	1.1 (7)
H(7)	0.207 (3) (0.218)	0.577 (2) (0.580)	0.159 (3) (0.180)	1.5 (7)
H(8)	0.083 (4) (0.095)	0.446 (2) (0.437)	0.254 (4) (0.257)	3.3 (9)

H–H approach distances, except that between H(4) and H(5), are greater than 2.43 Å. The H(4)–H(5) distance is 1.81 Å although it should be at least 2.0 Å because of the van der Waals radius of hydrogen. The experimentally determined value for this distance is 1.93 Å. The true positions of these two atoms must be slightly different from the calculated or the observed ones. The programs used here are the same as those reported in an earlier work (Khan & Baur, 1972).

Results and discussion

The results confirm the molecular structure of photoaldrin proposed by Rosen (1967). Fig. 1 shows the molecular and crystal structure projected on a plane perpendicular to the *c* axis. Following the suggestion of Dr Loening (private communication) the compound has been given the systematic name 3,4,5,6,6,7-hexa-

Table 1. Positional parameters in fractions of the cell edges ($\times 10^4$) and thermal parameters ($\times 10^4$)

The form of the anisotropic thermal ellipsoid is $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	9544 (1)	279 (1)	1862 (1)	110 (2)	38 (1)	125 (2)	27 (1)	4 (1)	–6 (1)
Cl(2)	7874 (1)	7955 (1)	127 (1)	110 (2)	38 (1)	111 (2)	3 (1)	12 (1)	31 (1)
Cl(3)	3143 (1)	3487 (1)	4459 (1)	100 (1)	42 (1)	67 (1)	1 (1)	14 (1)	2 (1)
Cl(4)	8288 (1)	3246 (1)	1352 (1)	120 (2)	28 (1)	130 (2)	–15 (1)	7 (1)	8 (1)
Cl(5)	324 (1)	2149 (1)	3313 (1)	67 (1)	48 (1)	116 (2)	–8 (1)	–3 (1)	–6 (1)
Cl(6)	1022 (1)	8856 (1)	4505 (1)	124 (2)	51 (1)	77 (1)	–1 (1)	–32 (1)	9 (1)
C(1)	8982 (5)	5214 (3)	3135 (5)	106 (6)	27 (2)	87 (5)	10 (2)	–10 (4)	1 (2)
C(2)	9168 (4)	6108 (3)	3807 (4)	80 (5)	26 (2)	76 (5)	4 (2)	–4 (4)	4 (2)
C(3)	7358 (4)	1510 (2)	1228 (4)	77 (5)	26 (2)	59 (4)	3 (2)	2 (3)	0 (2)
C(4)	7163 (4)	2409 (3)	1943 (4)	83 (5)	21 (2)	0 (5)	–5 (2)	4 (4)	–3 (2)
C(5)	7693 (4)	7123 (2)	1419 (4)	75 (5)	27 (2)	73 (5)	0 (2)	2 (4)	12 (2)
C(6)	6281 (4)	6620 (3)	1319 (4)	75 (5)	33 (2)	63 (4)	3 (2)	–8 (4)	–3 (2)
C(7)	8214 (4)	969 (3)	2496 (4)	88 (5)	23 (2)	70 (5)	10 (2)	0 (4)	0 (2)
C(8)	8047 (5)	5546 (3)	1784 (4)	89 (5)	28 (2)	87 (5)	4 (2)	–5 (4)	2 (2)
C(9)	8847 (4)	6385 (3)	1233 (4)	75 (5)	26 (2)	87 (5)	3 (2)	2 (4)	4 (2)
C(10)	69 (4)	6459 (3)	2470 (4)	72 (5)	37 (2)	78 (5)	6 (2)	–2 (4)	6 (3)
C(11)	1104 (5)	5740 (3)	2221 (5)	89 (6)	50 (3)	106 (6)	22 (3)	–12 (5)	8 (3)
C(12)	471 (5)	5000 (3)	2614 (5)	118 (6)	44 (2)	92 (6)	25 (3)	–6 (5)	0 (3)

Table 3 (cont.)

Table with multiple columns of numerical data, likely representing crystallographic parameters or atomic coordinates. The table is organized into several groups of columns, each with a header (e.g., 'L', 'FC', 'SIG', 'L', 'FC', 'SIG', etc.). The data values are small integers and decimals, representing various crystallographic measurements.

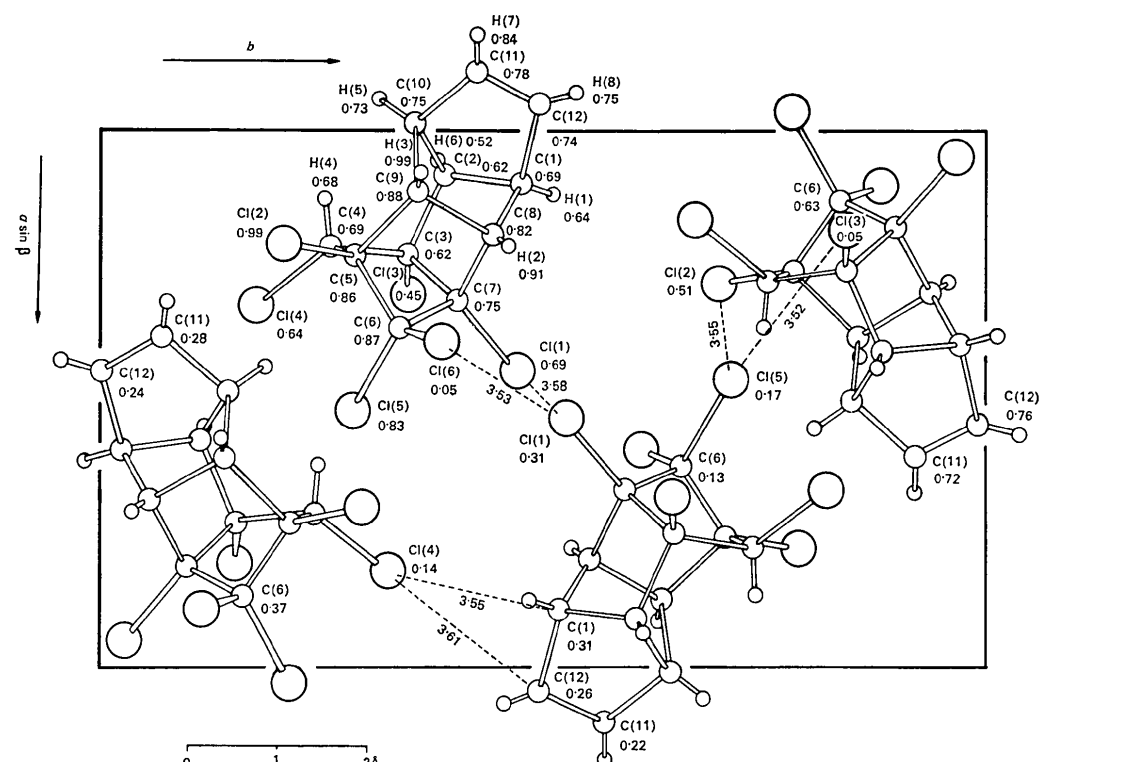


Fig. 1. Photoaldrin, $C_{12}H_8Cl_6$, view parallel to [001]. The heights of selected atoms are indicated in fractional coordinates. The broken lines represent some short intermolecular distances (Å).

Table 4. Intramolecular bond lengths and bond angles

(a) Lengths			
C(3)—Cl(3)	1.764 (4) Å	C(5)—C(6)	1.543 (6) Å
C(4)—Cl(4)	1.779 (4)	C(6)—C(7)	1.546 (6)
C(5)—Cl(2)	1.764 (4)	C(7)—C(8)	1.514 (6)
C(6)—Cl(5)	1.756 (4)	C(8)—C(9)	1.607 (6)
C(6)—Cl(6)	1.805 (4)	C(9)—C(10)	1.580 (6)
C(7)—Cl(1)	1.760 (4)	C(10)—C(11)	1.513 (7)
Mean C—Cl	1.771	C(11)—C(12)	1.361 (7)
		C(12)—C(1)	1.518 (6)
C(1)—C(2)	1.543 (6)	C(1)—C(8)	1.569 (6)
C(2)—C(3)	1.563 (6)	C(2)—C(10)	1.583 (6)
C(3)—C(4)	1.572 (6)	C(3)—C(7)	1.620 (5)
C(4)—C(5)	1.541 (5)	C(5)—C(9)	1.601 (6)
(b) Angles			
C(12)—C(1)—C(2)	103.2 (4)°	C(7)—C(6)—Cl(5)	115.9 (3)°
C(12)—C(1)—C(8)	109.7 (3)	C(7)—C(6)—Cl(6)	112.0 (3)
C(2)—C(1)—C(8)	93.0 (3)	C(5)—C(6)—Cl(5)	118.7 (3)
C(1)—C(2)—C(10)	94.7 (3)	C(5)—C(6)—Cl(6)	111.4 (3)
C(1)—C(2)—C(3)	105.6 (3)	Cl(5)—C(6)—Cl(6)	105.7 (2)
C(10)—C(2)—C(3)	110.2 (3)	C(8)—C(7)—C(6)	103.3 (3)
C(4)—C(3)—C(2)	105.2 (3)	C(8)—C(7)—C(3)	98.9 (3)
C(4)—C(3)—C(7)	104.5 (3)	C(8)—C(7)—Cl(1)	115.3 (3)
C(4)—C(3)—Cl(3)	114.8 (3)	C(6)—C(7)—C(3)	105.7 (3)
C(2)—C(3)—C(7)	103.7 (3)	C(6)—C(7)—Cl(1)	115.3 (3)
C(2)—C(3)—Cl(3)	112.5 (3)	C(3)—C(7)—Cl(1)	116.3 (3)
C(7)—C(3)—Cl(3)	115.1 (3)	C(7)—C(8)—Cl(1)	104.2 (3)
C(5)—C(4)—C(3)	96.6 (3)	C(7)—C(8)—C(9)	98.1 (3)
C(5)—C(4)—Cl(4)	117.6 (3)	C(1)—C(8)—C(9)	104.9 (3)
C(3)—C(4)—Cl(4)	118.4 (3)	C(10)—C(9)—C(8)	100.4 (3)
C(4)—C(5)—C(6)	105.2 (3)	C(10)—C(9)—C(5)	110.6 (3)
C(4)—C(5)—C(9)	105.6 (3)	C(8)—C(9)—C(5)	104.4 (3)
C(4)—C(5)—Cl(2)	113.6 (3)	C(11)—C(10)—C(9)	107.2 (3)
C(6)—C(5)—C(9)	101.5 (3)	C(11)—C(10)—C(2)	101.6 (3)
C(6)—C(5)—Cl(2)	116.2 (3)	C(9)—C(10)—C(2)	96.7 (3)
C(9)—C(5)—Cl(2)	113.5 (3)	C(12)—C(11)—C(10)	108.9 (4)
C(7)—C(6)—C(5)	93.1 (3)	C(11)—C(12)—C(1)	107.2 (4)

The molecule is composed of two fused bicycloheptane rings also bridged by one C—C bond. This results in the cage structure of the molecule, consisting of six and five membered rings.

The average C—Cl bond length is 1.771 (8) Å. It is interesting to note that the three close values, 1.760, 1.764 and 1.764 Å with an average of 1.763 Å, involve C₃—C—Cl type bonding. The C=C bond length in the norbornene nucleus is 1.361 (7) Å which compares well, within the limits of the errors, with 1.34 (3) Å found by Macdonald & Trotter (1965) in *anti*-7-norbornenyl *p*-bromobenzoate. The two bonds C(10)—C(11) and C(1)—C(12) have the usual lengths of an *sp*³—*sp*² C—C bond with an average value of 1.515 Å.

The 13 single C—C bonds exhibit a wide range of variation, from 1.51 to 1.62 Å. The average length of the 13 bonds is 1.568 Å and the longest among these appears to be the longest ever reported for a C—C bonding distance. The bond lengthening appears to be a common phenomenon in cage molecules (Ammon & Jensen, 1967; Shimanouchi & Sasada, 1970). In a comparable cage molecule, 3,6-dichloro-11,12-benzotetracyclo[5,3,2,0^{2,6},0^{3,8}]dodecan-9-one, investigated by Shimanouchi & Sasada (1970), the average value of the single C—C bond lengths is 1.552 Å.

The influence of nonbonded interactions on bond

distances has been emphasized by Bartell (1959, 1962). In accordance with this idea, an approximate correlation has been observed between the closest approach of the nonbonded atoms and the bond lengths. Fig. 2 shows the X—X distances between some nonbonded atoms; all the carbon—carbon contacts less than 2.32 Å are shown. A close approach of this type is likely to lengthen the C—C bond in an arrangement like X—C—C—X, as a result of repulsive interaction. Of the seven C—C bonds longer than or equal to 1.57 Å, five involve an approach smaller or equal to 2.32 Å between the nonbonded carbon atoms. For five out of the remaining six shorter C—C bonds there is no such close approach below 2.34 Å. The longest C—C bond, C(3)—C(7), has, in addition to a C—C contact of 2.26 Å, the closest contact (3.17 Å) between the nonbonded Cl atoms.

The tetrahedral angles listed in Table 4 also show a wide range of variation. It is rather unusual that all the C—C—Cl angles (average value 115.1°) are larger than the tetrahedral value. Similarly the average value of the C—C—H angles is 115.0°. On the other hand, the C—C—C angles in general are smaller with an average value of 102.6°. The likely explanation seems to be that the constraint imposed by the polycyclic nature of the cage molecule results in smaller values of the C—C—C angles. The tetrahedral angles containing the substituent atoms chlorine and hydrogen are automatically large because of the geometry of the arrangement.

Fig. 1 shows some close intermolecular approaches. The shortest intermolecular contacts are: Cl—Cl (3.52 Å), C—Cl (3.55 Å) and C—C (3.67 Å). The packing appears to be efficient.

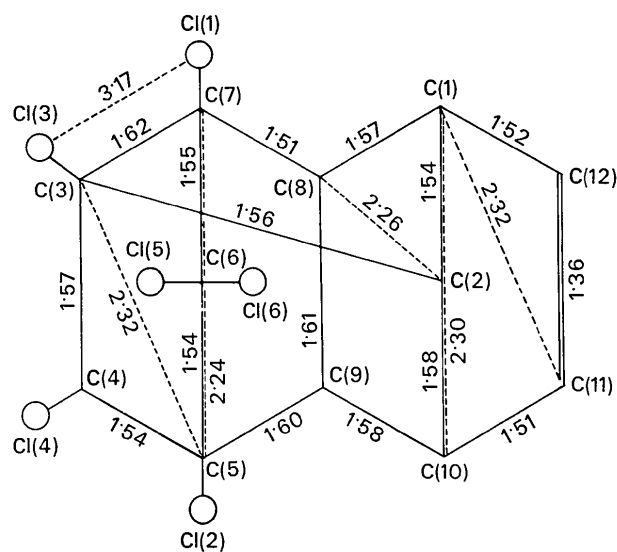


Fig. 2. Schematic diagram of the molecule showing the C—C bonds and some nonbonded intramolecular distances (Å).

We would like to thank Dr K. L. Loening for suggesting the von Baeyer name of photoaldrin and the Computer Center of the University of Illinois at Chicago for the computing facilities.

References

- AMMON, H. L. & JENSEN, L. H. (1967). *Acta Cryst.* **23**, 805.
 BARTELL, L. S. (1959). *J. Amer. Chem. Soc.* **81**, 3496.
 BARTELL, L. S. (1962). *Tetrahedron*, **17**, 177.
 BAUR, W. H. (1970). In *Handbook of Geochemistry, Hydrogen, 1-A-(1-5)*. Berlin: Springer.
 BAUR, W. H. (1972). *Acta Cryst.* **B28**, 1456.
 BAUR, W. H. & KHAN, A. A. (1970). *Acta Cryst.* **B26**, 1584.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 KARLE, J. & HAUPTMAN, M. (1956). *Acta Cryst.* **9**, 635.
 KHAN, A. A. & BAUR, W. H. (1972). *Acta Cryst.* **B28**, 683.
 KHAN, M. A. Q., SUTHERLAND, D. J., ROSEN, J. D. & CAREY, W. F. (1970). *J. Econ. Entomol.* **63**, No. 2, 470.
 MACDONALD, A. C. & TROTTER, J. (1965). *Acta Cryst.* **19**, 456.
 ROSEN, J. D. (1967). *Chem. Commun.* p. 189.
 SHIMANOUCI, H. & SASADA, Y. (1970). *Acta Cryst.* **B26**, 563.
 SUTHERLAND, D. J. & ROSEN, J. D. (1968). *Mosq. News.* **28**, 155.

Acta Cryst. (1972). **B28**, 2065

The Crystal Structure of Diammonium Hydrogen Phosphate, $(\text{NH}_4)_2\text{HPO}_4$

BY AIJAZ A. KHAN

Department of Geological Sciences, University of Illinois at Chicago, Chicago, Illinois 60680, U.S.A.

AND J. P. ROUX AND WILLIAM J. JAMES

Department of Chemistry and the Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri 65401, U.S.A.

(Received 30 December 1971)

$(\text{NH}_4)_2\text{HPO}_4$ crystallizes in the space group $P2_1/c$ with cell constants $a=11.043$ (6), $b=6.700$ (3), $c=8.031$ (4) Å, $\beta=113.42$ (3)° and $Z=4$, and is isomorphous with $(\text{NH}_4)_2\text{HAsO}_4$. The structure is refined using three-dimensional data collected on a four-circle automatic diffractometer. The final R value is 0.015 for 649 observed reflections. The positions of the hydrogen atoms indicate that only four among five $\text{N}\cdots\text{O}$ contact distances (less than 3.2 Å from each NH_4^+ ion) represent the actual $\text{N}-\text{H}\cdots\text{O}$ bonds. The length of the $\text{O}-\text{H}\cdots\text{O}$ bond is 2.615 (1) Å and differs significantly from 2.669 (13) Å found in the isomorphous arsenate. It is suggested that this is a consequence of the size difference between the P^{5+} and As^{5+} ions.

Introduction

In an earlier paper (Khan, Straumanis & James, 1970) the crystal structure of $(\text{NH}_4)_2\text{HAsO}_4$ is reported. However, it was not possible to determine the positions of the hydrogen atoms during that study and the hydrogen bonding suggested was based only on the contacts between the heavier atoms. Since each NH_4^+ ion in the structure is coordinated by five oxygen atoms, there is a certain amount of ambiguity regarding the $\text{N}-\text{H}\cdots\text{O}$ bonding. The cell dimension data and the space group reported for $(\text{NH}_4)_2\text{HPO}_4$ by Smith, Lehr & Brown (1957) indicated that this phosphate is isomorphous with the corresponding arsenate. A crystal structure study of $(\text{NH}_4)_2\text{HPO}_4$ was therefore undertaken to find the actual hydrogen bonding from the NH_4^+ ions by determining the positions of the hydrogen atoms. Further it was deemed desirable to make a comparative study of the two isomorphous structures. Such a comparison might reveal any pos-

sible influence on the structure of a replacement of a P^{5+} ion with an As^{5+} ion.

Experimental

From a commercially supplied crystalline sample of $(\text{NH}_4)_2\text{HPO}_4$, an almost spherical crystal of diameter 0.40 mm was selected for the X-ray work. The intensity data were collected on a four-circle automatic diffractometer using $\text{Ag K}\alpha$ radiation. The details of the experimental procedures are the same as described in some earlier publications (Khan, Baur & Forbes, 1972; Baur & Khan, 1970). Lattice parameters were determined from 12 carefully centered reflections. The intensities were collected in two of the four equivalent quadrants up to $\sin \theta/\lambda=0.54$ Å⁻¹. These were averaged after applying the Lorentz-polarization corrections and were converted to F_o values. Absorption corrections were neglected. 1440 non-unique reflections were averaged to 773; of these 124 were considered