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The Crystal and Molecular Structure of α-Aminomethylmethylphosphinic Acid

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The structure of α-aminomethylmethylphosphinic acid ($H_3^+N{-}CH_2{-}PCH_3O_2^-$) has been determined by single-crystal X-ray diffraction. Crystals are monoclinic, space group $P2_1/c$, with $a = 5{\cdot}867\,(1)$, $b = 6{\cdot}279\,(1)$, $c = 13{\cdot}262\,(2)$ Å, $\beta = 98{\cdot}91\,(1)°$, $Z = 4$. The structure was solved by the heavy-atom technique and refined by full-matrix least squares to $R = 0{\cdot}043$ for 533 counter reflexions for which $F > 3{\cdot}92\,\sigma(F)$. The molecule exists as $H_3^+N{-}CH_2{-}PCH_3O_2^-$. The NH_3^+ group is a donor for three hydrogen bonds of lengths 2·775, 2·778, 2·747 Å.

Introduction

Interest in aminophosphinic and aminophosphonic acids stems from the fact that they are P analogues of the amino acids. Many papers deal with aminophosphonic acids but only two report structures (Okaya, 1966; Darriet, Darriet, Cassaigne & Neuzil, 1975).

However, there are no publications dealing with structural studies on the aminophosphinic acids. These acids of general formula $R-CH_2-NH_2-P(O)(R)$-(OH) have, like most neutral amino acids, one basic and one acidic group. This fact may exert important influences on their biological properties, which have not been thoroughly studied. This paper presents the results of a study of the structure of α-aminomethylmethylphosphinic acid.

Experimental

Crystals selected for X-ray analysis were prepared by the method developed by Dr R. Tyka at the Institute of Organic and Physical Chemistry, Technical University of Wrocław. Weissenberg photographs showed the crystals to be monoclinic with systematic absences: $h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$, which fix the space group uniquely as $P2_1/c$. Unit-cell dimensions were obtained from the angular settings of 15 reflexions measured on a diffractometer. The density was measured by flotation in a $CHCl_3-CCl_4$ mixture. Crystal data are given in Table 1.

All measurements for a crystal 0·15 × 0·15 × 0·12 mm were made on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a scintillation counter and graphite monochromator. Intensities were collected with Cu $K\alpha$ radiation by the θ–2θ scan technique. 617 independent reflexions were measured up to $2\theta = 114°$. The scan rate varied from 2·0 to 20·0° min^{-1} depending on the intensity. After each group of 15 reflexions the intensity of a standard was measured and no significant change observed. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure determination

The P atom was located from a Patterson synthesis. The positions of the other non-hydrogen atoms were found from a Fourier synthesis. Full-matrix least-squares refinement with isotropic thermal parameters for all non-hydrogen atoms reduced $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ to 0·09. Full-matrix refinement with anisotropic thermal parameters yielded a final $R_1 =$ 0·076. A difference synthesis at this stage revealed the positions of all H atoms. In subsequent full-matrix refinement the coordinates of the H atoms and their isotropic thermal factor (B = 3·8 Å^2) were not refined.

Table 1. *Crystal data*

$C_2H_8NO_2P$, FW 109·07, $F(000) = 232$
Monoclinic, space group $P2_1/c$

$a = 5{\cdot}867\,(1)$ Å	$V = 483{\cdot}3$ Å^3
$b = 6{\cdot}279\,(1)$	$Z = 4$
$c = 13{\cdot}262\,(2)$	$D_m = 1{\cdot}52$ g cm^{-3}
$\beta = 98{\cdot}91\,(1)°$	$D_x = 1{\cdot}51$
λ(Cu $K\alpha$) = 1·5418 Å	μ(Cu $K\alpha$) = 39·6 cm^{-1}

Table 2. *Positional parameters* (×10^4; *for* H ×10^3) *with estimated standard deviations in parentheses*

The atomic parameters of H were not refined; B_{iso} = 3·8 Å^2.

	x	y	z
P	3364 (2)	1413 (2)	1227 (1)
O(1)	2260 (5)	2214 (5)	2119 (2)
O(2)	3314 (5)	−951 (5)	1066 (2)
C(1)	2194 (6)	2787 (5)	64 (6)
C(2)	6353 (9)	2321 (6)	1425 (8)
N	7721 (6)	1505 (6)	2283 (8)
H(1)	713	186	83
H(2)	639	394	144
H(3)	775	0	250
H(4)	725	225	295
H(5)	955	185	250
H(6)	318	273	−45
H(7)	45	273	−25
H(8)	225	439	23

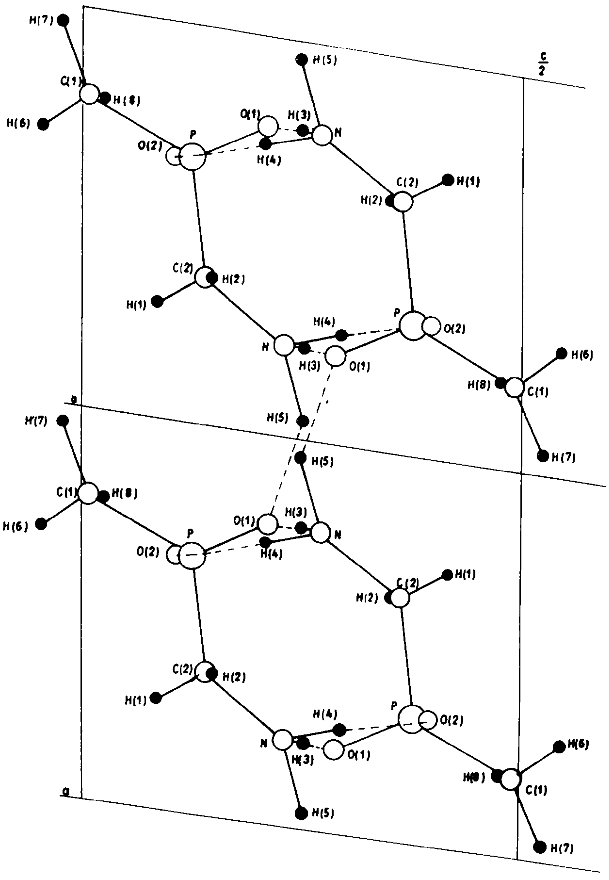

Fig. 1. Projection of the crystal structure along **b**. Hydrogen bonds are shown by broken lines.

The final R_1 is 0·043 and the final $R_2 = [\Sigma\ w(|F_o| - |F_c|)^2/\Sigma\ w|F_o|^2]^{1/2}$ is 0·049 for 533 observed structure factors. For all 617 reflexions R_1 and R_2 are both 0·05. The function minimized was $\Sigma\ w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Computations were performed by the Syntex XTL Structure Determination System which consists of a Nova 1200 computer and additional external disc memory. The programs used were those from the Syntex set of programs. Final atomic coordinates are presented in Table 2.* Fig. 1 shows a projection of the crystal structure along **b**.

Discussion

Interatomic distances and angles are given in Table 3 and are similar to those found in 2-aminoethanol phosphate (Kraut, 1961), 2-aminoethylphosphonic acid (Okaya, 1966) and aminomethylphosphonic acid (Darriet *et al.*, 1975). The P atom is situated at the centre of a tetrahedron formed by O(1), O(2), C(1) and C(2). The six angles at the P atom differ from 109·5° by a maximum of 7·8°. Although the P atom environment is tetrahedral, most of the atoms lie practically in one plane. The plane through C(2), P, C(1) and N is given by $(0{\cdot}1549)X + (0{\cdot}7919)Y + (-0{\cdot}5907)Z - (-0{\cdot}9397) = 0$. Deviations are C(2) −0·0246, P 0·0012, C(1) 0·0345, N −0·0162 Å. The distances of O(1) and O(2) from this plane are −1·3328 and 1·2885 Å respectively. The P–O lengths in the phosphonic groups of 2-aminoethylphosphonic acid (β-ciliatine) and aminoethylphosphonic acid (β-AMPh) may be divided into two categories: two short P–O bonds and one long P–OH bond (Table 3). The difference in P–O and P–OH lengths is about 0·06 Å. The two aminophosphonic acids form two types of hydrogen bonds: three N–H···O and one strong O–H···O bond (Table 4). O(1) takes part in two hydrogen bonds: N···O(1), average 2·785 Å, and a strong O(3)···O(1) hydrogen bond, average 2·550 Å. On the other hand, O(2) forms two N···O(2) hydrogen bonds, average 2·890 Å.

Table 4. *Interatomic distances* (Å) *in the phosphonic group and hydrogen-bond distances*

Bond type	β-Ciliatine	β-AMPh
P–O(1)	1·51	1·51
P–O(2)	1·50	1·49
P–HO(3)	1·56	1·57
N···O(1)	2·78	2·79
N···O(2)	2·94	3·04
N···O(2)	2·77	2·81
O(3)···O(1)	2·54	2·57

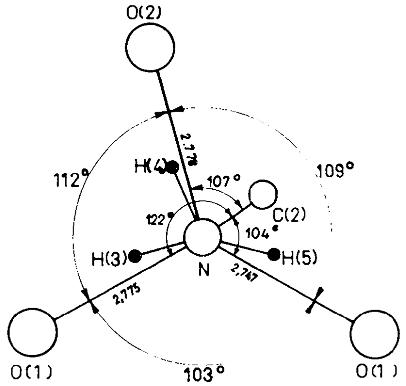

Fig. 2. Configuration of the three hydrogen bonds around the nitrogen atom.

Table 3. *Interatomic distances* (Å) *and bond angles* (°)

P–O(1)	1·521 (4)	P–O(2)	1·500 (4)	P–C(1)	1·807 (6)
P–C(2)	1·825 (6)	O(1)–O(2)	2·561 (5)	O(1)–C(1)	2·744 (6)
O(2)–C(1)	2·725 (6)	C(2)–N	1·486 (6)	N–H(3)	0·96
N–H(4)	0·97	N–H(5)	1·07	C(1)–H(6)	1·01
C(1)–H(7)	1·09	C(1)–H(8)	1·03	C(2)–H(1)	1·01
C(2)–H(2)	1·02	H(3)···O(1)	1·82	H(4)···O(2)	1·79
H(5)···O(1)	1·77	N···O(1)	2·775 (3)	N···O(2)	2·778 (6)
N···O(1)	2·747 (6)				
				C(1)–P–O(2)	110·5 (2)
N–C(2)–P	109·2 (5)	O(1)–P–O(2)	115·9 (2)	C(1)–P–C(2)	101·7 (2)
O(1)–P–C(1)	110·6 (2)	O(2)–P–C(2)	109·1 (2)	O(1)–P–C(2)	107·5 (3)
P–C(1)–H(6)	104·0	P–C(1)–H(7)	116·8	P–C(1)–H(8)	106·7
H(6)–C(1)–H(7)	104·4	H(7)–C(1)–H(8)	111·4	H(6)–C(1)–H(8)	116·3
P–C(2)–H(1)	109·6	P–C(2)–H(2)	109·4	H(1)–C(2)–H(2)	111·1
C(2)–N–H(3)	113·2	C(2)–N–H(4)	108·6	C(2)–N–H(5)	116·4
H(3)–N–H(4)	110·6	H(4)–N–H(5)	100·9	H(3)–N–H(5)	108·4
N–H(3)···O(1)	172·1	N–H(4)···O(2)	169·2	N–H(5)···O(1)	155·0

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* A list of structure factors and thermal parameters has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32284 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Although both O(1) and O(2) take part in two hydrogen bonds, only O(1) forms a strong hydrogen bond. There is only one type of hydrogen bond NH···O in $H_3^+N{-}CH_2{-}P{-}CH_3O_2^-$. The NH_3^+ group is a donor for three hydrogen bonds with lengths: N···O(1) $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$ 2·775, N···O(2) $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$ 2·778, N···O(1) $(1+x, y, z)$ 2·747 Å. The geometry of the hydrogen-bond system is given in Fig. 2. N–H(3)···O(1), 172·1, and N–H(4)···O(2), 169·2°, are almost linear; N–H(5)···O(1), 155·0°, is less so. O(1) takes part in two hydrogen bonds while O(2) participates in only one, which leads to a difference in the P–O(1), P–O(2) lengths, P–O(1) being larger.

The α-aminophosphinic and α-aminophosphonic acids are generally considered to be analogues of the amino acids. It should, therefore, be possible to demonstrate that the differences in the P–O lengths, similar to those observed in the C–O(1) and C–O(2) lengths in the carboxyl group of the zwitterionic amino acids, result from different numbers and strengths of the hydrogen bonds. In DL-alanine (Donohue, 1950), L-alanine (Simpson & Marsh, 1966), L-alanine (Lehmann, Koetzle & Hamilton, 1972), L-valine (Torii & Iitaka, 1970), L- and DL-serine (Frey, Lehmann, Koetzle & Hamilton, 1973; Kistenmacher, Rand & Marsh, 1974) where O(1) takes part in only one hydrogen bond, the difference in the C–O lengths ranges from 0·1 to 0·02 Å. The fact that O(2) forms two hydrogen bonds of the NH···O(2) type probably results in lengthening of the C–O(2) bond in the carboxyl group. A difference in the carboxyl C–O(1) and C–O(2) distances might also be expected if both O atoms are linked to the same number of H atoms, but the H contacts to O(1) and O(2) are non-equivalent. On the other hand, in glycine (Marsh, 1958), DL-histidine (Edington & Harding, 1974), L-(+)-histidine (Madden, McGandy & Seeman, 1972) where both the carboxyl O atoms form equal numbers of equivalent hydrogen bonds, the C–O(1), C–O(2) lengths are equal. It may be interesting to study the hydrogen-bond systems in similar crystals and establish the relation between hydrogen-bond strength and the related configuration around the hydrogen-bond acceptor.

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