Crystal Structure of Methylenebis(phosphonic dichloride)

By **William S. Sheldrick**, Gesellschaft für Molekularbiologische Forschung mbH, D-3300 Braunschweig-Stöckheim, Mascheroder Weg 1, Bundesrepublik Deutschland

Crystals of the title compound are monoclinic, space group $C2/c$, with a = 15·866(5), b = 5·845(1), c = 9·161(3) Å, β = 106·59(2)°, Z = 4. The molecules, which display a crystallographically imposed C_2 symmetry, are linked together through two C–H · · · O(P) hydrogen bonds, of length 3·23(1) Å, into infinite chains in the z direction. Rigid-body analysis reveals that pronounced rotational and translational motions are associated with the axis of minimum inertia and least cross-section. Bond lengths (corrected for libration) are: P–Cl 1·994(2) and 1·997 (2), P=O 1·463(4), P–C 1·804(4) Å; angle P–C–P 116·4(4)°. The structure was solved by direct methods and refined by full-matrix least-squares to R 0·041 for 641 diffractometer-measured unique reflections.

THERE is considerable current interest in the structural evaluation of diphosphonic acids, their salts and hydrates.[1-4] In view of their potential analogy to naturally occurring phosphoric acids, one of the major features of structural interest lies in the determination of the nature of the patterns of intermolecular hydrogen bonding taking place *via* O–H · · · O(P) interactions. It has, however, recently been postulated,[5] on the basis of ^{13}C n.m.r. concentration studies of bisphosphonates of the type $CH_2[PO(OR)_2]_2$ (R = Me, Et, or Pr^i), that the drastic variation of the coupling constant J(PP′), observed upon dilution (5—0·5 Hz), may be explained in terms of intermolecular interactions between the methylene protons and the phosphonoyl oxygen. It was also found that the ^{13}C chemical shift of the bridging carbon in bisphosphonic acid derivatives shows a marked downfield shift in comparison to other mono-substituted C–P derivatives. This phenomenon may be interpreted in terms of a widening of the P–C–P angle, which would *ipso facto* be indicative of a distortion of the sp^3 hybridisation in the direction of sp^2. Such a trend, if confirmed, should be accompanied by an increase in the acidity of the methylene protons, which might be expected to manifest itself in the formation of C–H · · · O(P) intermolecular hydrogen bonds.

A structural investigation of $CH_2[PO(OH)_2]_2$ [1] confirmed that widening of the P–C–P angle does take place [117·2(1)°] but the presence of hydroxy-groups leads to the formation of the, presumably, stronger O–H · · · O(P)

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[4] A. J. Collins, G. W. Fraser, P. G. Perkins, and D. R. Russell, *J.C.S. Dalton*, 1974, 960.
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hydrogen bonds. The crystal structure of $CH_2(POCl_2)_2$ (I), which displays an anomalously high melting point (98—100 °C),[6] was, therefore, undertaken in order to investigate whether C–H · · · O(P) intermolecular interactions occur in a methylenebisphosphonic acid derivative which does not have hydroxy-groups available for hydrogen bonding.

EXPERIMENTAL

A sample of (I) was prepared by the method of Maier.[6] Intensity data, from a tabular crystal sealed into a Lindemann glass-capillary tube and with dimensions *ca.* 0·18 × 0·05 × 0·20 mm, were collected on a Syntex $P2_1$ four-circle diffractometer by use of graphite-monochromated Mo-K_α radiation. Measurements were carried out in the θ—2θ mode (2θ ⩽ 50°) at scan speeds varying linearly between 2·93° min^{-1} (150 c/s and below) and 19·53° min^{-1} (3500 c/s and above). Scan and total background times were equal. Three standard reflections, monitored at regular intervals, showed no significant variations due to crystal deterioration during data collection. A standard deviation $\sigma(I) = t(N_s + N_b)^{1/2}$ was assigned to each net intensity I, with t being the scan rate, N_s the gross count, and N_b the total background count. 674 (78·6%) Of the 858 unique reflections having $I \geqslant 1{\cdot}96\sigma(I)$ were considered to be observed. Lorentz and polarisation, but no absorption corrections were applied to the raw intensity data. Accurate unit-cell dimensions were obtained from measurements of 15 high-angle 2θ values by use of Mo-$K_{\alpha1}$ (λ = 0·70926 Å) radiation.

Crystal Data.—$CH_2Cl_4PO_2$, M = 249·8, Monoclinic, a = 15·866(5), b = 5·845(1), c = 9·161(3) Å, β = 106·59(2)°, U = 814·1(4) Å^3, Z = 4, D_c = 2·04. Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 17·7 cm^{-1}. Space group Cc or $C2/c$ from systematic absences: hkl for $h + k$ odd and $h0l$ for l odd. The distribution of normalised structure factors (E values) was typical of a centrosymmetric space group, thereby indicating $C2/c$ as the probable space group, in which the carbon atoms must lie on, and the other atoms be related by, diad axes at (0,y,0·25) and (0·5,y,0·25). $C2/c$ Was confirmed by the subsequent successful structure refinement.

Structure Solution and Refinement.—The structure was solved by multisolution application of the tangent formula. The resultant chlorine, phosphorus, oxygen, and carbon positional parameters, together with their associated anisotropic temperature-factor components, were refined by full-matrix least-squares. At this stage of the refinement, the generalised index $R_G\{= [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}, \Delta = F_o - F_c\}$ had converged to 0·053 with a corresponding weighted index $R'[= \Sigma w^{1/2}\Delta/\Sigma w^{1/2}F_o]$ of 0·044. A difference-Fourier synthesis then revealed the hydrogen atom position clearly, but an attempt to refine its positional parameters led to an unreasonable H–C–H angle. These were, therefore, introduced as fixed parameters (0·011,0·131,0·334) in the final cycles of least-squares refinement, together with an isotropic temperature factor which subsequently refined to 0·021(19) Å^2. Complex neutral-atom scattering factors [7,8] were employed for all atoms. The terminal value of R_G was 0·051 with R' 0·042 and the corresponding unweighted index, R 0·041. A final difference-Fourier synthesis displayed no peaks of density >0·45 eÅ^{-3}. The results from the final least-squares cycle (Table 1) were used, together with the full co-variance matrix, to calculate bond lengths and angles, and their estimated standard deviations (Table 2). The shortest non-bonded distances are summarised in Table 3.

TABLE 1

Atom co-ordinates and anisotropic vibrational amplitudes (Å^2 × 10^3),* with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	0·0948(1)	−0·1126(3)	0·2424(1)	32(1)	28(1)	26(1)	0(1)	8(1)	4(1)
Cl(1)	0·1942(1)	0·1051(3)	0·3138(2)	34(1)	47(1)	61(1)	−5(1)	14(1)	−7(1)
Cl(2)	0·1154(1)	−0·3401(3)	0·4098(2)	62(1)	37(1)	45(1)	15(1)	12(1)	15(1)
O	0·0904(3)	−0·2141(8)	0·0955(4)	57(3)	48(3)	34(2)	−8(2)	15(2)	10(2)
C	0	0·0494(13)	0·25	29(4)	24(4)	24(3)	0	6(3)	0

* The anistropic temperature factor takes the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

Figures 1 and 2 depict the unit-cell contents shown perpendicular to a and c^* respectively. Figure 3 shows a diagram of the molecule together with the atom numbering scheme used in the analysis. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21261 (5 pp., 1 microfiche).*

TABLE 2

Molecular geometry

(*a*) Interatomic distances (Å), and, in square brackets, librationally corrected values

P–Cl(1)	1·985(2)	[1·994]
P–Cl(2)	1·986(2)	[1·997]
P–O	1·455(4)	[1·463]
P–C	1·795(4)	[1·804]
C–H	0·88	

(*b*) Angles (°)

P–C–P′	116·4(4)	C–P–O	115·6(2)
C–P–Cl(1)	104·2(2)	C–P–Cl(2)	106·1(2)
Cl(1)–P–Cl(2)	103·6(1)	O–P–Cl(1)	113·0(2)
O–P–Cl(2)	113·3(2)	H–C–P	111
H–C–H′	114		

TABLE 3

Non-bonded distances (Å) <4·0 Å

P · · · O^{II}	3·77	P · · · $Cl(1^{IV})$	3·90
Cl(1) · · · O^{II}	3·49	Cl(1) · · · $Cl(2^{II})$	3·81
Cl(1) · · · $Cl(1^{III})$	3·77	Cl(1) · · · $Cl(2^{III})$	3·68
Cl(1) · · · O^{IV}	3·45	Cl(1) · · · $Cl(1^{IV})$	3·77
Cl(2) · · · O^{II}	3·20	O · · · O^{I}	3·83
O · · · C^{II}	3·23	O · · · H^{II}	2·42

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x,y,z:

I $-x, -y, -z$ III $\frac{1}{2} - x, \frac{1}{2} - y, -z$
II $x, -y, \frac{1}{2} + z$ IV $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[6] L. Maier, *Helv. Chim. Acta*, 1965, **48**, 133.
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The rigid-body hypothesis has been satisfactorily applied to describe the thermal motion observed in the structurally analogous $[S_2O_7]^{2-}$, $[CH_2(SO_3)_2]^{2-}$, and $[NH(SO_3)_2]^{2-}$ anions,

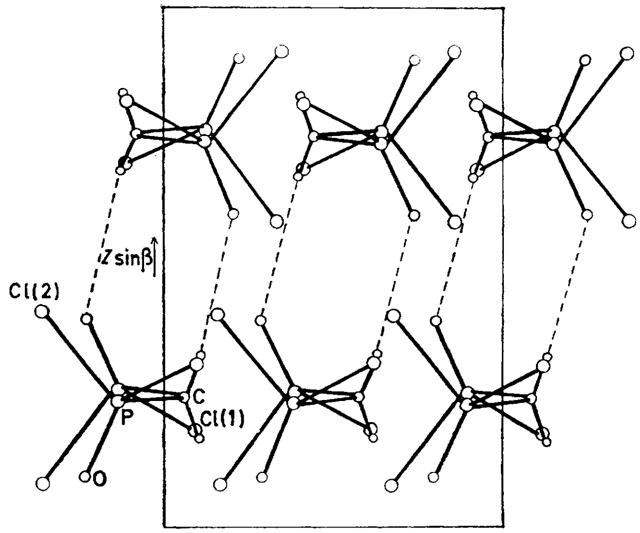

FIGURE 1 Projection of the unit-cell contents perpendicular to *a*

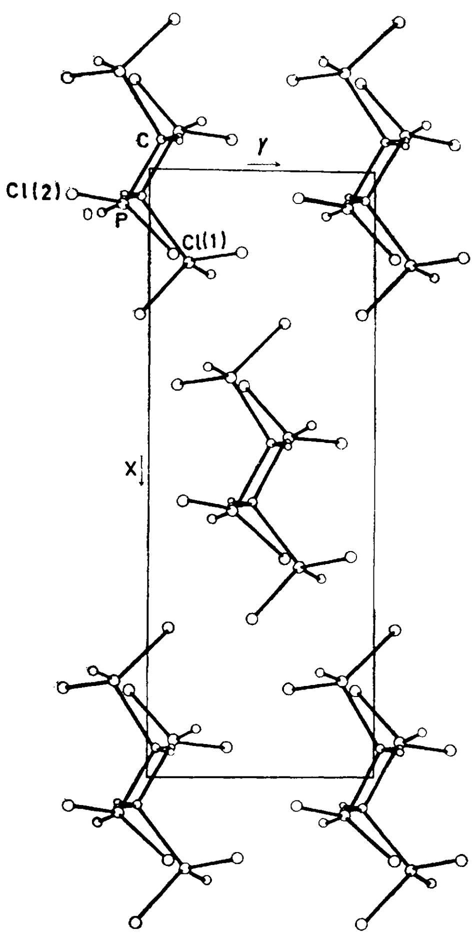

FIGURE 2 Projection of the unit-cell contents perpendicular to *c**

present as their potassium salts,[9-11] which also crystallise in space group *C*2/*c* and in which the bridging oxygen,

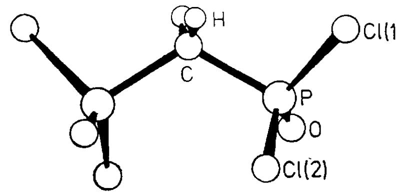

FIGURE 3 The molecule and the atom numbering system used in the analysis

carbon, and nitrogen atoms lie on diad axes. In view of this, and because of the considerable anisotropy of thermal motion displayed by (I), an analysis was performed by the method of Schomaker and Trueblood.[12] Satisfactory agreement was achieved between observed and calculated temperature factors with a value of 0·087 (unit weights) for generalised index, $R_G\{= [\Sigma w(U_c - U_0)^2/\Sigma w U_0^2]^{1/2}\}$, and 0·0031 Å^2 for the root-mean-square discrepancy. The results of the Schomaker and Trueblood analysis are displayed in Table 4, where the tensors are defined as in ref. 12, and have been used to apply the librational corrections to the bond lengths listed in Table 2. The largest root-mean-square amplitudes of translation and angular oscillation (0·170 Å and 0·092 rad) are associated with the axis of minimum inertia and least cross-section, which lies close to the *a* direction. The nature of the motion is very similar to that observed in the three analogous anions.

TABLE 4

Rigid-body librational analysis

Centre of mass (orthogonal co-ordinates*): 0, −0·1059, 0·25.

(*a*) Tensors with respect to orthogonal axes and origin at the centre of mass, with estimated standard deviations in parentheses

T/Å × 10^{-4}	370(11)	0	35(11)
		168(17)	0
			215(16)
L/rad × 10^{-4}	83(7)	0	8(3)
		31(3)	0
			38(3)
S/Å rad × 10^{-4}	−8(5)	0	−3(6)
	0	−1(4)	0
	38(4)	0	9(4)

Origin (orthogonal co-ordinates) which gives symmetric S: 0, −0·1642, 0·25

(*b*) Principal root-mean-square amplitudes and direction cosines

T/Å †			
0·170	0·9990	0	0·0457
0·130	0	1·0	0
0·144	−0·0457	0	0·9990
L/rad			
0·092	0·9849	0	0·1733
0·055	0	1·0	0
0·061	−0·1733	0	0·9849

* Referred to *a*sinβ, *b*, *c*. † Reduced to keep U invariant.

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DISCUSSION

The molecules of (I) possess a crystallographically imposed C_2 symmetry, with the bridging carbon atoms lying on space-group diad axes. When viewed along the P···P′ vector, the P–O bond makes the following torsion angles: P′–O′ 130·1, P′–Cl(1)′ −86·6, and P′–Cl(2)′ 17·3°. The molecules are themselves linked into infinite chains in the *z* direction *via* C–H···O(P) hydrogen bonds of length 3·23(1) Å, as depicted in Figure 1. This is the first confirmed example of such interactions in a phosphorus derivative. The uncertainty involved in the determination of the hydrogen-atom position prevents a definite conclusion that this interaction is linear (C–H 0·88, H···O 2·42, C···O 3·23 Å), but allows the inference that any actual deviation must be small. Each molecule is involved in four such bonds, there being one C–H···O(P) and one (P)O···H–C interaction with each neighbour in the infinite chain. The strength of these interactions, which provides confirmation of the acidic nature of the methylene protons, and the efficient packing of the resultant infinite chains (Figure 2), are reflected in the anomalously high m.p. and density of (I).

Considerable deviation from the ideal tetrahedral value is observed for the C–P–O angle [115·6(2)°], caused presumably by the involvement of the oxygen in intermolecular hydrogen bonding. The librationally corrected P–Cl bond lengths [1·994(2) and 1·997(2) Å] are similar to that [1·993(3) Å] observed in an electron diffraction study of $POCl_3$.[13] The P=O bond length [1·463(4) Å] however, although within the range expected for such bonds,[14] is significantly shorter than those observed in (II)—(IV) (see Table 5), which lie between 1·494 and 1·507 Å, and which are all involved in O–H···O(P) hydrogen bonds. These latter values are similar to the mean P=O distance (1·50—1·51 Å) found in ionised phosphonates. This shortness of the P–O bond in (I) may be explained in terms of the relative weakness of the C–H···O(P) in comparison to the O–H···O(P) hydrogen bond, as witnessed by the C···O distance of 3·23(1) Å [*e.g.* O···O distances in (II) lie between 2·577(3) and 2·675(3) Å]. In the latter case, the P=O bond will be lengthened owing to an increased negative charge-density on the phosphonoyl oxygens due to attraction of the phosphonic acid protons to their hydrogen-bond acceptor.

TABLE 5

P–C bond lengths (Å) and P–C–P bond angles (°) in bis-phosphonic acid derivatives

Compound	No.	P–C	P–C–P
$CH_2\cdot(PO_3H_2)_2$	(II) [a]	1·790(3) 1·794(3)	117·2(1)
$CH_2\cdot(POCl_2)_2$	(I) [b]	1·804(4)	116·4(4)
$C(Me)(OH)\cdot(PO_3H_2)_2,H_2O$	(III) [c]	1·832(4) 1·840(4)	115·1(2)
$Ca[C(Me)(OH)\cdot(PO_3H)_2],2H_2O$	(IV) [d]	1·815(6) 1·857(4)	113·7(3)
$[NH_4]_4[C_4H_8O_{12}P_4],2H_2O$	(V) [e]	1·841(13) 1·821(13)	113·6(7)

[a] Ref. 1. [b] This work. [c] Ref. 2. [d] Ref. 3. [e] Ref. 4.

Table 5 shows that a correlation exists between the P–C bond length and P–C–P bond angle in the bis-phosphonic acid derivatives (I)—(V), widening of the angle being accompanied by a shortening of the distance, as would be expected for a distortion of sp^3 hybridisation at the bridging carbon in the direction of sp^2. In (I), the P–C–P angle [116·4(4)°] and the librationally corrected P–C bond length [1·804(4) Å] correlate nicely with the observed acidic nature of the methylene protons, exemplified by their participation in intermolecular hydrogen bonding. Structural work is planned on related derivatives in order to provide further information about the nature of the intermolecular bonding.

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