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Structural Investigations of Methylenediphosphonic Acids. 2. The Molecular and Crystal Structure of Propane-1,3-diphosphonic Acid[1]

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Propane-1,3-diphosphonic acid, $(CH_2)_3(PO_3H_2)_2$, PC_3P, crystallizes in the noncentrosymmetric, monoclinic, space group Pc [C_s^2, no. 7] with unit cell constants a = 9.540(2), b = 9.964(2), c = 9.705(2) Å, β = 118.90(1)°, and Z = 4. The asymmetric unit of PC_3P consists of two crystallographically unique molecules. The structure was solved by a combination of direct methods, Fourier, and least-squares refinement techniques; the final R_F = 0.024 for 1412 independent unique reflections. The two PC_3P molecules within the asymmetric unit have quite different conformations. Hydrogen-bonded rings of differing size shape the P–C–C–C–P backbone of one PC_3P molecule into an almost planar conformation, while the backbone of the other molecule is distorted into a distinctive nonplanar conformation. Eight intermolecular hydrogen bonds of lengths varying from 2.579(8) to 2.711(5) Å are involved in four rings of 10, 12, 14, and 16 members. The hydrogen bond length appears to be correlated with the size of the hydrogen bonded ring in which it participates.

Introduction

Chemical and physical properties have been measured for the series of methylenediphosphonic acids, $(CH_2)_n(PO_3H_2)_2$, where n = 1–6.[3] The observed melting points, IR spectra, and NMR spectra show interesting changes as n increases. In a previous paper,[4] we have discussed the molecular and crystal structures of $(CH_2)(PO_3H_2)_2$, PCP, and $(CH_2)_2(PO_3H_2)_2$, PC_2P. Each of these materials contains an interwoven network of strong intermolecular hydrogen bonds formed between phosphonic acid groups. The two halves of P–C–C–P are related by a center of symmetry hence the backbone is precisely planar. The planar conformations affect both the physical and chemical properties of each material. Planarity of the backbone is not required for $(CH_2)_3(PO_3H_2)_2$, PC_3P, hence this molecule is likely to be structurally quite different than PCP or PC_2P. An x-ray structural investigation of PC_3P was undertaken in order to investigate the correlation of structure with chemical and physical properties and to better define the potential binding sites for metal ions.

Experimental Section

Collection and Reduction of X-Ray Data. Propane-1,3-diphosphonic acid, PC_3P, was prepared by the method of Moedritzer and Irani.[3] Crystals of sufficient size and quality were grown from a benzene solution by slow evaporation. A diamond shaped plate (0.038 × 0.038 × 0.025 cm) was selected for data collection. Preliminary oscillation, Weissenberg, and precession photographs showed 2/m Laue symmetry and gave the systematic absences as $h0l$ for $l = 2n + 1$, which is consistent with the two monoclinic space groups, Pc[C_s^2, no. 7] and $P2/c$ [C_{2h}^4, no 13]. Accurate unit-cell lattice constants were determined by least-squares analysis of x-ray powder diffraction

TABLE I: Experimental Details for PC_3P

Formula: $(CH_2)_3(PO_3H_2)_2$
Formula weight: 204.06 g equiv
Space group: Pc [C_s^2, no. 7]
Extinctions: $h0l$, $l = 2n + 1$
Cell constants: a = 9.540 (2), b = 9.964 (2), c = 9.705 (2) Å, β = 118.90 (1)°
Cell volume: 807.67 Å^3
Calculated density: 1.68 g cm^{-3}
Measured density: 1.66 g cm^{-3} [by flotation in $HCCl_3$ + $HCBr_3$]
Number of molecules in the asymmetric unit: 2 (Z = 4)
Radiation: (data collection) Mo Kα, λ = 0.71073, 2° take-off angle
Absorption coefficient: 5.214 cm^{-1}
Maximum 2θ: 50°
Scan width: 1.6°
Scan speed: 0.1° steps
Counting time: 4 s/step (background 16 s each side of peak)
Crystal: b axis mounted
Volume = 0.296 × 10^{-4} cm^3 (0.038 × 0.038 × 0.025 cm)
Maximum transmission factor = 0.90
Minimum transmission factor = 0.86
Number of reflections above σ = 1391
Number of independent reflections = 1412
R_F factor for all reflections = 0.024
R_F factor for all reflections above 1 σ = 0.024
wR_{F^2} = 0.057

TABLE II: Final Positional and Isotropic Thermal Parameters for PC_3P[a]

Atom	x	y	z	B_0
P(1)	0.6384[b]	0.2892 (1)	0.7396[b]	
P(2)	1.2070 (2)	0.4817 (1)	1.2176 (2)	
P(3)	0.0624 (2)	−0.0124 (1)	0.2769 (2)	
P(4)	0.6341 (1)	−0.1850 (1)	0.7818 (1)	
O(1)	0.4642 (4)	0.2596 (4)	0.6992 (4)	
O(2)	0.6447 (4)	0.3809 (3)	0.6143 (4)	
O(3)	0.7199 (3)	0.1575 (3)	0.7551 (3)	
O(4)	1.2620 (4)	0.5450 (3)	1.1124 (4)	
O(5)	1.2572 (4)	0.3326 (3)	1.2550 (4)	
O(6)	1.2783 (4)	0.5631 (3)	1.3736 (4)	
O(7)	−0.0139 (4)	−0.1543 (3)	0.2421 (4)	
O(8)	0.0206 (3)	0.0673 (3)	0.3830 (4)	
O(9)	0.0052 (4)	0.0646 (4)	0.1196 (4)	
O(10)	0.6625 (4)	−0.0528 (3)	0.8748 (3)	
O(11)	0.5528 (3)	−0.2834 (3)	0.8369 (3)	
O(12)	0.7976 (4)	−0.2439 (3)	0.8119 (4)	
C(1)	0.7349 (5)	0.3860 (4)	0.9154 (5)	
C(2)	0.9137 (6)	0.4023 (5)	0.9769 (5)	
C(3)	0.9956 (6)	0.4765 (4)	1.1340 (5)	
C(4)	0.2725 (5)	−0.0433 (5)	0.3604 (5)	
C(5)	0.3503 (5)	−0.0967 (5)	0.5277 (5)	
C(6)	0.5179 (5)	−0.1507 (4)	0.5769 (5)	
H(1)	0.686 (6)	0.461 (5)	0.885 (6)	3.3 (11)
H(2)	0.716 (5)	0.349 (5)	0.984 (6)	2.9 (10)
H(3)	0.928 (6)	0.438 (5)	0.909 (7)	3.6 (11)
H(4)	0.964 (6)	0.305 (5)	0.992 (6)	3.6 (11)
H(5)	0.954 (7)	0.584 (6)	1.122 (7)	5.4 (14)
H(6)	0.983 (6)	0.428 (5)	1.214 (6)	3.4 (11)
H(7)	0.308 (5)	0.035 (5)	0.352 (5)	2.3 (9)
H(8)	0.293 (5)	−0.111 (4)	0.294 (5)	2.7 (9)
H(9)	0.358 (5)	−0.028 (4)	0.594 (5)	2.6 (9)
H(10)	0.281 (5)	−0.164 (4)	0.536 (5)	2.4 (9)
H(11)	0.516 (5)	−0.223 (5)	0.530 (5)	2.7 (9)
H(12)	0.584 (5)	−0.084 (4)	0.555 (5)	1.8 (8)
H(13)	0.429 (9)	0.308 (7)	0.684 (9)	5.6 (23)
H(14)	0.614 (6)	0.333 (5)	0.537 (6)	3.2 (11)
H(15)	1.340 (8)	0.326 (6)	1.270 (8)	4.9 (15)
H(16)	1.283 (8)	0.530 (6)	1.441 (7)	4.2 (15)
H(17)	0.008 (7)	0.022 (6)	0.075 (7)	3.0 (16)
H(18)	−0.099 (7)	−0.161 (6)	0.235 (7)	4.3 (14)
H(19)	0.681 (6)	0.003 (5)	0.847 (6)	2.5 (11)
H(20)	0.870 (6)	−0.188 (4)	0.836 (5)	2.2 (9)

[a] Estimated standard deviations are given in parentheses. [b] The x and y coordinates were fixed in the least-squares refinement because of the polar axes along x and z.

data. The crystal mounted along the crystallographic b axis was placed on a GE XRD-490 automated diffractometer for data collection. Details specific to data collection and analysis are given in Table I. Specific details on the instrumentation used in this data collection have been described previously.[5]

Solution and Refinement of the Structure. The structure was solved by the application of direct methods using the program MULTAN-74.[6] Phillips, Howells, and Rogers statistics,[7] and $|E^2 - 1|$ and $|E|$ values supplied by MULTAN indicated that the noncentrosymmetric space group Pc is preferred, and thus two unique PC_3P molecules per asymmetric unit are indicated. MULTAN supplied the coordinates of 26 peaks for a solution whose combined figure of merit was 2.513. Analysis of the interpeak distances and angles permitted assignment of all 22 non-hydrogen atoms. Subsequent Fourier and isotropic full-matrix least-squares refinements converged at R_F = 0.12. The positions of all hydrogen atoms were located from difference Fourier maps. Several cycles of anisotropic full-matrix least-squares refinement of all non-hydrogen atoms and positional refinement of the hydrogen atoms with fixed isotropic thermal parameters (B = 5.0 Å^2) converged at R_F = 0.028. Further refinement varying the isotropic thermal parameters of the hydrogen atoms gave a final R_F = 0.024, R_{F^2} = 0.043, R_{wF^2} = 0.057, and Σ_2 = 2.20 for 1412 unique reflections, where

$$R_F = \Sigma \left||F_o| - |F_c|\right| / \Sigma |F_o|$$

$$R_{wF^2} = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w F_o^2]^{1/2}$$

$$\Sigma_2 = [\Sigma w (F_o^2 - F_c^2)^2 / (N_o - N_R)]^{1/2}$$

N_o is the number of independent observations and N_R is the number of parameters varied. A final difference Fourier map revealed no peaks above 0.33 e/Å^3. No parameter varied by more than Δ/σ = 0.28 in the last cycle of the refinement. The very satisfactory measures of agreement which were achieved are attributed to the extensive hydrogen bonding which knits the molecules tightly and restricts thermal disorder.

TABLE III: Final Anisotropic Thermal Parameters[a] (× 10[4]) for PC_3P[b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P(1)	56 (1)	41 (1)	62 (1)	0 (1)	28 (1)	−1 (1)
P(2)	61 (2)	53 (1)	57 (1)	−7 (1)	30 (1)	−7 (1)
P(3)	57 (2)	61 (1)	58 (1)	4 (1)	30 (1)	6 (1)
P(4)	55 (1)	47 (1)	59 (1)	3 (1)	24 (1)	−5 (1)
O(1)	63 (4)	65 (4)	112 (5)	−1 (4)	38 (4)	3 (3)
O(2)	122 (5)	59 (3)	72 (4)	−19 (3)	47 (4)	−5 (3)
O(3)	76 (4)	52 (3)	114 (4)	4 (3)	52 (3)	−1 (3)
O(4)	88 (4)	92 (3)	66 (4)	−19 (3)	43 (3)	−8 (3)
O(5)	75 (5)	59 (3)	146 (6)	4 (3)	45 (4)	−4 (3)
O(6)	105 (5)	78 (3)	58 (4)	−22 (3)	36 (4)	−12 (3)
O(7)	94 (5)	69 (3)	133 (5)	−2 (3)	71 (4)	−2 (3)
O(8)	77 (4)	73 (3)	89 (4)	10 (3)	44 (4)	−4 (3)
O(9)	104 (6)	78 (4)	71 (5)	7 (3)	34 (4)	8 (4)
O(10)	111 (5)	55 (3)	83 (4)	12 (3)	52 (4)	2 (3)
O(11)	73 (4)	71 (3)	78 (4)	15 (3)	28 (3)	−16 (3)
O(12)	64 (4)	62 (3)	129 (5)	7 (3)	32 (4)	8 (3)
C(1)	67 (6)	72 (5)	72 (5)	−4 (4)	42 (5)	−7 (4)
C(2)	79 (7)	84 (5)	58 (6)	−11 (4)	36 (5)	−16 (4)
C(3)	70 (7)	73 (5)	75 (6)	−1 (4)	43 (5)	−11 (4)
C(4)	71 (7)	75 (5)	70 (6)	11 (4)	35 (5)	14 (4)
C(5)	64 (6)	92 (5)	66 (5)	13 (4)	40 (5)	15 (4)
C(6)	72 (6)	73 (5)	60 (5)	−8 (4)	32 (5)	2 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Estimated standard deviations are given in parentheses.

A comparison of the observed and calculated structure factor amplitudes is available as supplementary material (see paragraph at end of text regarding supplementary material).

Scattering factors for neutral atoms were taken from the compilation of Cromer and Waber.[8] The phosphorus, oxygen, and carbon atoms were corrected for anomalous dispersion using the values of Cromer.[9] Computational programs used for these structural determinations were RTMON,[10] data collection and reduction; DATALIB,[11] absorption, Lorentz, and polarization corrections; DATASORT,[12] data sorting; S5XFLS,[13] least-squares refinement; S5FOUR,[13] Fourier synthesis; ORFFE3,[13] distance and angles calculation; and OR-TEPII,[14] molecular drawing. All calculations were carried out on the Xerox Sigma V computer of the Chemistry Division, ANL, and the IBM 370/195 of the Applied Mathematics Division, ANL.

Table II is a listing of the final positional parameters of all atoms and the isotropic thermal parameters for hydrogen atoms in PC_3P. Final anisotropic thermal parameters for all non-hydrogen atoms are given in Table III.

The Molecular and Crystal Structure. Interatomic distances for PC_3P are given in Table IV, while interatomic angles are given in Table V. Torsion angles are shown

TABLE IV: Interatomic Distances for PC_3P[a]

Bond	Distance, Å	Bond	Distance, Å
(a) Intramolecular Distances			
P(1)-O(3)	1.495 (3)	P(3)-O(8)	1.499 (4)
P(1)-O(1)	1.540 (5)	P(3)-O(7)	1.551 (4)
P(1)-O(2)	1.545 (3)	P(3)-O(9)	1.553 (6)
P(2)-O(4)	1.495 (5)	P(4)-O(11)	1.500 (4)
P(2)-O(5)	1.549 (4)	P(4)-O(10)	1.545 (3)
P(2)-O(6)	1.554 (7)	P(4)-O(12)	1.556 (4)
P(1)-C(1)	1.780 (10)	P(3)-C(4)	1.789 (10)
P(2)-C(3)	1.774 (10)	P(4)-C(6)	1.781 (13)
C(2)-C(1)	1.519 (9)	C(5)-C(4)	1.518 (10)
C(2)-C(3)	1.526 (10)	C(5)-C(6)	1.528 (8)
C(1)-H(1)	0.85 (5)	C(4)-H(7)	0.88 (5)
C(1)-H(2)	0.86 (5)	C(4)-H(8)	1.02 (5)
C(2)-H(3)	0.82 (6)	C(5)-H(9)	0.92 (5)
C(2)-H(4)	1.06 (5)	C(5)-H(10)	0.97 (5)
C(3)-H(5)	1.13 (6)	C(6)-H(11)	0.85 (5)
C(3)-H(6)	0.97 (5)	C(6)-H(12)	1.01 (4)
(b) Non-Hydrogen Bonding Interactions			
O(1)-O(3)	2.449 (7)	O(7)-O(9)	2.533 (5)
O(1)-O(2)	2.544 (7)	O(7)-O(8)	2.534 (5)
O(2)-O(3)	2.527 (5)	O(8)-O(9)	2.488 (5)
O(4)-O(6)	2.470 (5)	O(10)-O(11)	2.478 (4)
O(4)-O(5)	2.541 (4)	O(10)-O(12)	2.534 (5)
O(5)-O(6)	2.533 (5)	O(11)-O(12)	2.493 (5)
P(1)-P(2)	5.505 (2)	P(3)-P(4)	5.558 (2)
P(1)-P(2)′	4.620 (2)	P(2)-P(4)′	4.824 (6)
P(1)-P(3)′	4.763 (3)	P(2)-P(2)′	4.866 (1)
P(1)-P(4)′	4.543 (2)	P(3)-P(4)′	4.556 (2)
P(1)-P(4)′	4.745 (2)	P(3)-P(3)′	4.859 (1)
		P(3)-P(4)′	4.874 (4)

[a] Estimated standard deviations are given in parentheses.

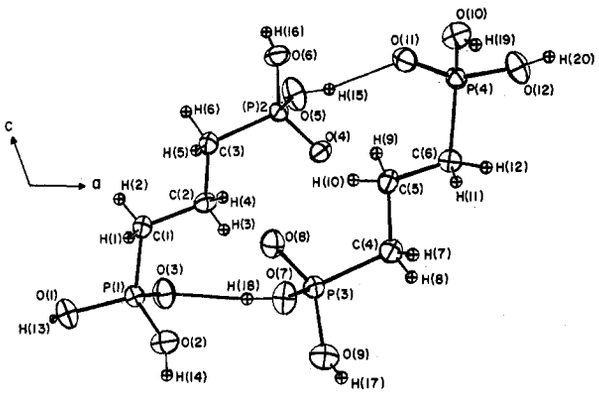

Figure 1. Sixteen-membered ring formed by PC_3P asymmetric unit.

TABLE V: Interatomic Angles for PC_3P[a]

Angle	Deg	Angle	Deg
(a) Interatomic Angles			
O(1)-P(1)-O(2)	111.1 (6)	O(7)-P(3)-O(9)	109.4 (5)
O(1)-P(1)-O(3)	107.6 (2)	O(7)-P(3)-O(8)	112.4 (3)
O(2)-P(1)-O(3)	112.4 (3)	O(8)-P(3)-O(9)	109.3 (2)
O(4)-P(2)-O(5)	113.2 (2)	O(10)-P(4)-O(12)	109.6 (5)
O(4)-P(2)-O(6)	108.2 (2)	O(10)-P(4)-O(11)	108.9 (2)
O(5)-P(2)-O(6)	109.4 (4)	O(11)-P(4)-O(12)	109.3 (2)
C(1)-P(1)-O(1)	110.0 (6)	C(4)-P(3)-O(7)	104.3 (3)
C(1)-P(1)-O(2)	103.6 (2)	C(4)-P(3)-O(8)	113.1 (5)
C(1)-P(1)-O(3)	112.1 (5)	C(4)-P(3)-O(9)	108.3 (6)
C(3)-P(2)-O(4)	113.4 (5)	C(6)-P(4)-O(10)	109.1 (3)
C(3)-P(2)-O(5)	103.5 (3)	C(6)-P(4)-O(11)	111.9 (4)
C(3)-P(2)-O(6)	109.0 (6)	C(6)-P(4)-O(12)	108.0 (6)
P(1)-C(1)-C(2)	113.4 (6)	P(3)-C(4)-C(5)	114.0 (7)
P(2)-C(3)-C(2)	113.0 (7)	P(4)-C(6)-C(5)	114.2 (7)
C(1)-C(2)-C(3)	112.3 (7)	C(4)-C(5)-C(6)	110.7 (7)
H(1)-C(1)-H(2)	111 (5)	H(7)-C(4)-H(8)	109 (4)
H(3)-C(2)-H(4)	106 (5)	H(9)-C(5)-H(10)	107 (4)
H(5)-C(3)-H(6)	112 (4)	H(11)-C(6)-H(12)	107 (4)

[a] Estimated standard deviations are given in parentheses.

TABLE VI: Torsion Angles for PC_3P[a]

Angle	Deg
P(1)-C(1)-C(3)-P(2)	−2.7 (8)
P(3)-C(4)-C(6)-P(4)	−42.6 (8)
P(1)-C(1)-C(2)-C(3)	−175.7 (3)
P(2)-C(3)-C(2)-C(1)	174.0 (3)
P(3)-C(4)-C(5)-C(6)	166.9 (3)
P(4)-C(6)-C(5)-C(4)	168.3 (3)

[a] Estimated standard deviations are given in parentheses.

in Table VI. Table VII lists the hydrogen bonded distances and angles. Atom labels and bond distances are shown in Figure 1 while molecular packing and hydrogen bonding are shown in Figure 2.

The crystal structure of PC_3P consists of two crystallographically unrelated and unique molecules of $(CH_2)_3(PO_3H_2)_2$. The atoms in each molecule are oriented to form P–C–C–C–P chains which are linked by hydrogen bonded bridges, O(3)–H(18)–O(7) = 2.603(4) Å and O(11)–H(15)–O(5) = 2.580(10) Å, forming the asymmetric unit of the unit cell (see Figure 1). Analysis of the torsion angles (Table VI) of the two independent PC_3P molecules clearly shows that they adopt differing conformations. The torsion angles P(1)–C(1)–C(3)–P(2) = −2.7°, P(1)–

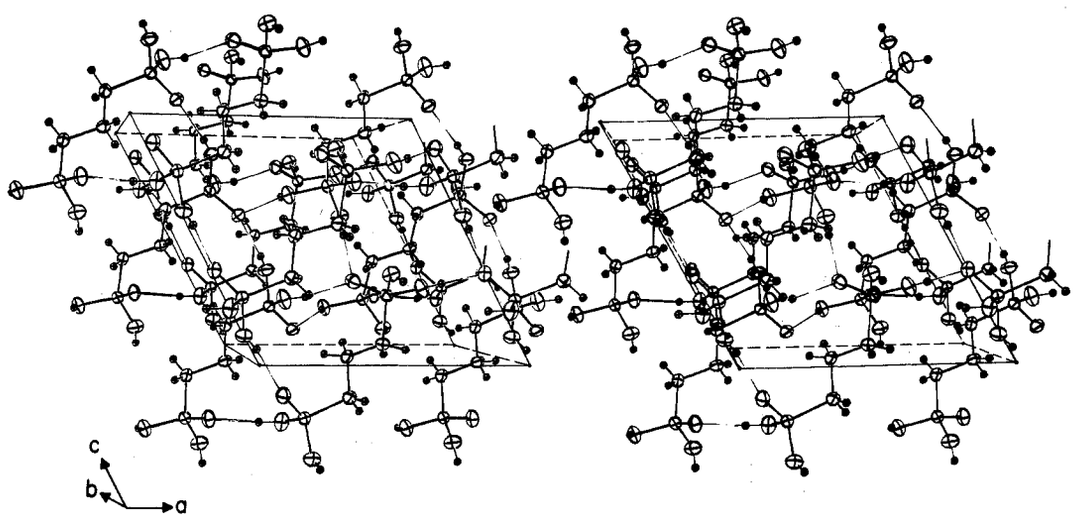

Figure 2. Stereoview of the packing of PC_3P molecules within the unit cell. The hydrogen bonding is clearly shown.

TABLE VII: Intermolecular Hydrogen-Bonded Distances and Angles[a]

Bond	Distance, Å	Angle, deg	Ring system (no. of members)
O(1)-H(13)-O(4)	2.579 (8)	168 (10)	12
O(1)-H(13)	0.57 (7)		
O(4)-H(13)	2.02 (7)		
O(2)-H(14)-O(11)	2.584 (10)	159 (5)	12, 14
O(2)-H(14)	0.81 (5)		
O(11)-H(14)	1.81 (5)		
O(5)-H(15)-O(11)	2.580 (10)	169 (7)	12, 16
O(5)-H(15)	0.73 (7)		
O(11)-H(15)	1.86 (7)		
O(6)-H(16)-O(4)	2.628 (5)	171 (7)	12
O(6)-H(16)	0.72 (6)		
O(4)-H(16)	1.92 (6)		
O(9)-H(17)-O(8)	2.711 (5)	161 (8)	14
O(9)-H(17)	0.62 (5)		
O(8)-H(17)	2.12 (5)		
O(7)-H(18)-O(3)	2.603 (4)	168 (6)	10, 14, 16
O(7)-H(18)	0.78 (6)		
O(3)-H(18)	1.83 (6)		
O(10)-H(19)-O(3)	2.580 (5)	176 (5)	10
O(10)-H(19)	0.68 (5)		
O(3)-H(19)	1.90 (5)		
O(12)-H(20)-O(8)	2.585 (7)	178 (5)	10, 14
O(12)-H(20)	0.83 (5)		
O(8)-H(20)	1.75 (5)		

[a] Estimated standard deviations are given in parentheses.

C(1)–C(2)–C(3) = –175.7(3)°, and P(2)–C(3)–C(2)–C(1) = 174.0(3)° for unit 1 [P(1)–C(1)–C(2)–C(3)–P(2)] indicate a nearly planar molecular backbone. However, the torsion angles P(3)–C(4)–C(6)–P(4) = –42.6°, P(3)–C(4)–C(5)–C(6) = 166.9(3)°, and P(4)–C(6)–C(5)–C(4) = 168.3(3)° for unit 2 [P(3)–C(4)–C(5)–C(6)–P(4)] show a distinct nonplanar conformation attributed to rotations about the C(4)–C(5) and C(5)–C(6) bonds. This result may be contrasted with the related $(CH_2)_2(PO_3H_2)_2$, PC_2P, molecule[4] where the P–C–C–P chain unit is planar.

The coordination around the P atoms is essentially tetrahedral as indicated by the interatomic angles given in Table V. Each P is bound to three oxygen atoms and one carbon atom. Two P–O bond distances represent P–O single bonds while the third shows considerable double bond character (see Table IV). Average P=O, P–O(H), and P–C distances are 1.497(3), 1.549(9), and 1.781(8) Å, respectively. The C–P–O angles show small deviations from a tetrahedral value depending upon the environment of the oxygen atom. The C–P=O angles have an average value of 112.6(8)° whereas C–P–O angles, where the oxygen is hydrogen bonded to phosphonyl oxygens O(11) or O(3), average to 105.1(10)° and those C–P–O angles where the oxygen is hydrogen bonded to O(4) or O(8) average to 108.9(13). The latter differences seem to indicate a greater amount of strain present for hydrogen bonding involving O(11) and O(3). The O(3) and O(11) atoms are involved in eight hydrogen bonded ring networks while the O(4) and O(8) atoms are involved in only five ring networks.

The average C–C distance, 1.523(5) Å, in PC_3P is appreciably shorter than the C–C distance, 1.544(4) Å, observed for PC_2P. This difference may be attributed to a shielding of the carbon atoms from the electron-withdrawing phosphonic acid groups. In PC_2P, both carbon atoms are adjacent to phosphonic acid groups, while in PC_3P the central carbon is shielded by the additional methylene groups. Average P–C–C and C–C–C angles in PC_3P are 113.7(7) and 111.5(8)°, respectively.

Table IV shows the P---P interactions within the unit cell. The average P---P interaction distance within a molecule of PC_3P, 5.53(3) Å, is larger than the close intermolecular P---P interactions of average distance, 4.72(3) Å. This compound represents a crossover point within the series $(CH_2)_n(PO_3H_2)_2$ where members with $n \geq 3$ will show closer intermolecular P---P contacts than intramolecular contacts.

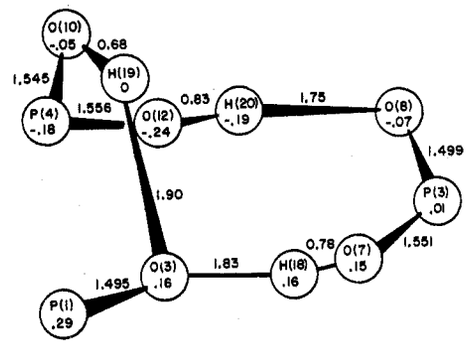

Figure 3. Fourteen-membered ring formed by hydrogen bonding involving three of the four phosphorus atoms. The *y* coordinate for each atom is given in the circle.

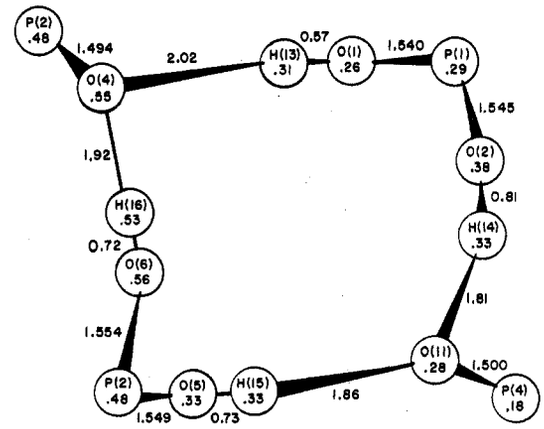

Figure 4. Twelve-membered ring formed by hydrogen bonding. The *y* coordinate for each atom is given in the circle.

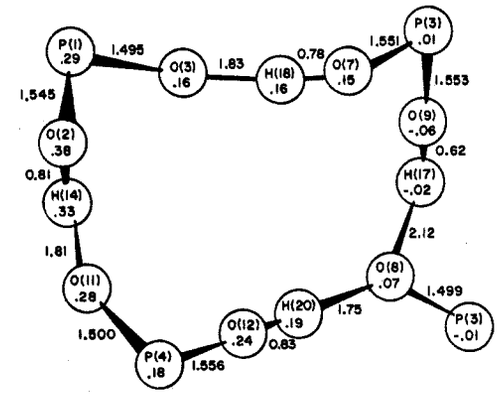

Figure 5. Ten-membered ring formed by hydrogen bonding involving only two of the four phosphorus atoms. The *y* coordinate for each atom is given in the circle.

The hydrogen bonding observed in the crystal structure of PC_3P is quite similar to that previously observed for PCP and PC_2P. Each P=O oxygen participates in two hydrogen bonds, while each P–O(H) group is active in a single hydrogen bond (Table VII). Of the eight hydrogen bonds which are formed, two participate in linking two PC_3P molecules into a 16-membered ring (Figure 1). However, these hydrogen bonds also participate in smaller H-bonded rings (see Figure 3–5). Figures 3–5 show hydrogen-bonded rings of 14-, 12-, and 10-members, respectively, which are formed by the eight hydrogen bonds.

TABLE VIII: Physical and Chemical Data of Methylenediphosphonic Acids $(CH_2)_n(PO_3H_2)_2$[c]

n	Mp, °C	^{31}P NMR[a]	P=O stretching,[b] cm^{-1}	P-OH stretching,[b] cm^{-1}
1	200	−16.7	1215	2695, 2273
2	220-223	−27.4	1220	2690, 2272
3	178	−28.2	1208	2660, 2336
4	217-220	−31.6	1205	2690, 2326
5	155	−31.9	1212	2625, 2326
6	206-208	−30.6	1170	2675, 2309

[a] ^{31}P NMR chemical shifts in ppm relative to 85% H_3PO_4. [b] KBr pellets. [c] Reference 3.

Several hydrogen bonds are unique to only one of the ring systems. Seven of the eight hydrogen bonds are quite short and lie within the range of 2.579(8) to 2.628(5) Å; the eighth bond shows a distance of 2.711(5) Å. This latter distance, which is significantly longer and therefore weaker than the other hydrogen bonds, is found only in the 14-membered ring, the largest of the rings which contain unique hydrogen bonds.

Discussion

Two different conformations of the same molecule existing together in the same crystal is structurally unusual. The conformational differences result from group rotations about C–C single bonds in the nonplanar conformer which are undoubtedly in response to hydrogen bond and packing forces. The phosphonic acid moieties of the nonplanar PC_3P backbone contain atoms P(3) and P(4), which are part of the 10- and 14-membered ring (Figures 5 and 3). The 10-membered ring is highly nonplanar and shows considerable strain in the puckering of the P(4)–O(10)–H(19)–O(3) part of the ring. The phosphonic ring group involving P(4) rotates about the C(5)–C(6) bond to form the strong 2.580(5)-Å, O(10)–H(19)–O(3), hydrogen bond. The phosphonic acid group containing P(3) must be rotated also in order to form the strong remaining 2.585-Å, O(12)–H(20–O(8), and 2.603-Å, O(7)–H(18)–O(3), hydrogen bonds of the 10-membered ring. Thus, the rotations of the phosphonic acid groups to achieve strong hydrogen bonds lead to the −42.6° dihedral angle between P(3) and P(4) as viewed down the C(4)–C(6) vector.

In this study of PC_3P and in the previous study of PCP and PC_2P, the longest hydrogen bonds are part of the largest hydrogen-bonded rings. As the ring size decreases so does the length of the longest hydrogen bonds observed in the ring until very short (~2.50 Å) hydrogen bonds are observed for the eight-membered rings and spiral hydrogen-bonded units.[15] In PCP, the 16-membered rings contain 2.604(3)- and 2.677(3)-Å hydrogen bonds, while the eight-membered ring and spirals show 2.542(3)- and 2.565(3)-Å hydrogen bonds, respectively. In PC_2P, spiral bonds of 2.527(2) and 2.543(2) Å were observed. In PC_3P, as was discussed above, similar trends hold. Therefore, the trend that the smaller the ring size the stronger the hydrogen bonding seems to hold in these unsubstituted polymethylenediphosphonic acids.

Moedritzer and Irani[3] have measured the melting points, the ^{31}P NMR chemical shifts, and the IR spectra for $(CH_2)_n(PO_3H_2)_2$ molecules of n = 1, 6 (see Table VIII). The structural parameters which we have deduced by x-ray diffraction for n = 1–3 show correlations with this chemical and physical data. The strongest hydrogen bonding occurs in PC_2P corresponding to the highest melting point, 223 °C, the weakest in PC_3P corresponding to a low melting point of 178 °C, while PCP shows an intermediate hydrogen bond strength and a melting point of 200 °C. It is quite clear that for n = 4, 6, since the melting point has again increased, the molecules may have a center of symmetry and strong spiral hydrogen bonds may be formed. For n = 5, the melting point drops to 155 °C indicating a very loose hydrogen-bonded system.

The ^{31}P NMR data indicate that for $n > 3$ the influence of one phosphonic acid group on the other is completely shielded by the methylene carbons. For n = 3, the phosphorus atoms are 5.5 Å apart and are not completely shielded by the methylene carbons. It might be speculated that, if a similar hydrogen bonded network is established in solution, the intermolecular phosphorus atoms which have an average distance of 4.72 Å are actually influencing the chemical shifts.

The IR P=O stretching frequency shows a constant value for n = 1–3 confirming what has been observed structurally that all P=O bond distances in each of the three materials fall within a very small range of 1.493(2)–1.502(2) Å. The P–O–H frequency remains constant at n = 1, 2 but increases 60 cm^{-1} for one vibration and decreases 30 cm^{-1} for the other vibration for n = 3. Structurally, all P–O–(H) distances are similar for all three molecules where a range of 1.540(5)–1.556(4) Å is observed; however, the minimum and maximum distances listed are observed in PC_3P and the P–O(H) frequency changes may be indicative of this deviation.

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Supplementary Material Available: A listing of calculated and observed structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(11) An IBM 370/195 program written by H. A. Levy.
(12) An IBM 370/195 program written by H. A. Levy.
(13) S5XFLS and S5FOUR are Sigma 5 versions of the programs: ORXFLS3 written by W. R. Busing and H. A. Levy and FOURIER by R. J. Dellaca and W. T. Robinson. OPFFE3 written by W. R. Busing and H. A. Levy.
(14) OR-TEPII written by C. Johnson.
(15) A spiral hydrogen bonded unit has a similar eight-membered repeat as if an eight-membered ring were broken and then linked to another opened ring.