Crystal and Molecular Structure of Tetramethylformamidiniumphosphonate, $[Me_2N]_2CPO_3H$

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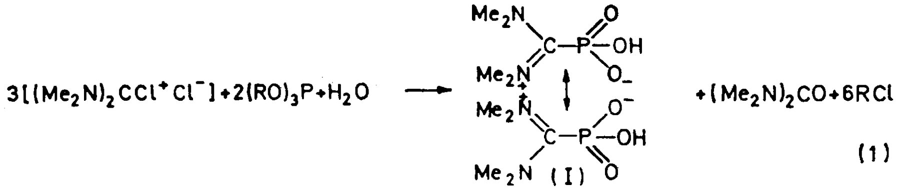
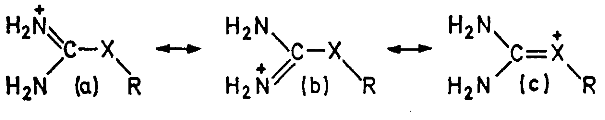
Crystals of the title compound, an inner salt $[Me_2N]_2CPO_3H$, are monoclinic, space-group $P2_1/c$ with a = 8·415 b = 7·719, c = 12·719 Å, β = 91·5°, Z = 4. The structure was solved by direct methods from diffractometer data for 1414 planes, and refined by least squares to a final R of 0·047. The $(PO_3H)^-$ group is linked to the central carbon atom of the $(Me_2N\dot{\cdot}C\cdot NMe_2)^+$ group by a P–C bond of 1·890(2) Å. The central carbon atom and the two nitrogen atoms of the formamidinium group all adopt planar configurations.

BIRUM[1] has shown that tetramethylformamidiniumphosphonate (I) may be synthesised according to equation (1). This novel compound is related to the uronium (II) and thioronium (III) ions but it is an inner salt and has no lone pair of electrons available on the phosphorus atom to give a form analogous to (IIc) or (IIIc). The structure of (I) has been determined to find the effect of the environment on the P–C bond length and to extend the knowledge of formamidinium and phosphonate derivatives.



(1)



(II) X=O (III) X=S

EXPERIMENTAL

Crystal Data.—$C_5H_{13}N_2O_3P$, M = 180·1, Monoclinic, a = 8·415(5), b = 7·719(5), c = 12·719(8) Å, β = 91·5(2)°, U = 825·9 Å^3, D_m = 1445, Z = 4, D_c = 1449. Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 2·94 cm^{-1}. Space-group $P2_1/c$.

Cell dimensions were obtained by a least-square process from precession photographs and standard deviations derived from this process have been doubled to allow for

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[1] G. H. Birum, personal communication, 1970.

systematic errors. Throughout this paper the standard deviations are given in parentheses as units in the last place of decimals.

The intensities were collected round *a* on a Hilger and Watts linear diffractometer [2] equipped with strontium carbonate–zirconium oxide balanced filters. The crystal used was 0·6 × 0·4 × 0·2 mm and the 1414 strongest reflections were used for the analysis.

Structure Determination and Refinement.—The positions of all atoms except hydrogen were found from the *E* map [3] after an application of direct methods [4,5] and this trial structure was then refined, first with isotropic and then with anisotropic temperature factors. When *R* had fallen to 0·083 a difference map was calculated which gave the positions of the hydrogen atoms. After further refinement (*R* 0·064) it was found that the scale-factors used for the layers 4—9*kl* were the squares of the correct values. This error was put right and refinement was continued until convergence at *R* 0·044 and *R′* 0·0045 ($R' = \Sigma\omega\Delta^2/\Sigma\omega F_o^2$).

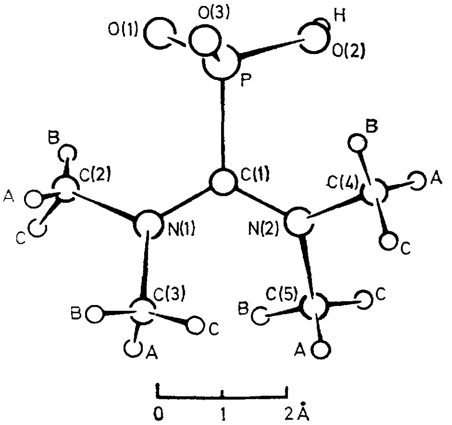

FIGURE 1 The molecule projected on the least-squares plane through P, C(1), N(1), and N(2)

Since the anisotropic temperature factors of the hydrogen atoms were unrealistic, they were replaced by isotropic ones 0·01 units of *U* higher than the atoms to which they are bonded and the final structure-factors so calculated gave *R* 0·047. A least-squares block-diagonal (3 × 3 for positional and 1 × 1 or 6 × 6 for thermal parameters) process was used with $w^{-1} = 3{\cdot}0 + |F_o| + 0{\cdot}03\,F_o^2$.

RESULTS AND DISCUSSION

The final observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20344 (10 pp., 1 microfiche).* Table 1 summarises these data as a function of *h* and of the magnitude of $|F_o|$; it shows the usual trend found with our diffractometer, that *R* increases as the magnitude of $|F_o|$ decreases and so the weaker high layers exhibit less good agreement than the stronger lower layers. Tables 2—4 give the final parameters and the bond lengths and angles. Table 5 lists some important planes in the molecule. Figure 1 shows the molecule projected on the weighted (*w* = atomic number) plane through P, C(1), N(1), and N(2), and the labelling of the atoms. Figure 2 illustrates the packing and the hydrogen bonding.

TABLE 1

R as a function of the layer index, *h*, and of the magnitude of $|F_o|$

h	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	No. planes	*R*
0	1707·75	1712·38	67·95	114	0·040
1	3085·93	3120·49	147·06	219	0·048
2	2522·01	2500·54	97·87	200	0·039
3	1943·99	1921·24	93·11	196	0·048
4	1920·89	1882·98	87·55	182	0·046
5	1705·21	1667·94	90·25	165	0·053
6	1309·21	1293·09	62·32	142	0·048
7	779·71	802·31	41·96	98	0·054
8	372·34	367·78	24·66	63	0·066
9	198·15	197·75	17·18	35	0·087
$\|F_o\|$ range					
0—2	29·55	26·69	8·68	17	0·294
2—4	812·83	780·01	114·40	260	0·141
4—6	1248·17	1239·09	89·64	252	0·072
6—8	1390·38	1390·26	74·70	200	0·054
8—10	1294·74	1285·42	58·58	144	0·045
10—12	1181·19	1180·58	45·65	108	0·039
12—14	1050·43	1045·12	40·97	81	0·039
14—16	1151·49	1141·18	43·75	77	0·038
16—18	885·37	885·21	31·12	52	0·035
18—64	6501·04	6492·94	222·42	223	0·034
All planes	15545·19	15466·50	729·91	1414	0·047

TABLE 2

Final co-ordinates *X*, *Y*, *Z* with standard deviations (Å)

	X	*Y*	*Z*
P	1·5597(7)	0·8931(7)	1·2615(6)
O(1)	0·0802(20)	1·0959(23)	1·3261(20)
O(2)	1·8450(20)	0·0401(24)	−0·0066(17)
O(3)	2·4802(26)	2·0422(24)	1·3906(24)
N(1)	1·6917(22)	0·0256(23)	3·9303(20)
N(2)	2·9013(21)	−1·2585(21)	2·4894(21)
C(1)	2·0863(24)	−0·2265(23)	2·7038(23)
C(2)	0·5521(38)	0·8901(44)	4·2243(32)
C(3)	2·4211(31)	−0·4350(33)	5·1460(25)
C(4)	3·9297(28)	−1·2474(31)	1·4865(28)
C(5)	2·9101(32)	−2·5085(29)	3·2638(32)
H	1·115(41)	−0·408(45)	−0·400(40)
H(2A)	0·972(46)	1·602(53)	4·798(47)
H(2B)	0·028(47)	1·067(51)	3·569(47)
H(2C)	0·006(43)	0·396(53)	4·899(45)
H(3A)	1·971(43)	−1·110(43)	5·570(46)
H(3B)	2·410(40)	0·324(45)	5·766(42)
H(3C)	3·227(43)	−0·647(49)	4·913(41)
H(4A)	3·671(43)	−1·922(45)	0·852(41)
H(4B)	3·914(41)	−0·398(45)	1·043(40)
H(4C)	4·822(42)	−1·479(45)	2·011(42)
H(5A)	3·726(46)	−2·560(47)	3·854(43)
H(5B)	2·010(44)	−2·547(46)	3·746(46)
H(5C)	2·912(43)	−3·224(48)	2·620(44)

The compound (I) forms centrosymmetric hydrogen bonded dimers (O · · · O 2·57 Å) using the hydrogen atom of the phosphonate group. Two phosphonic acids, which both also contain a P–C bond and a PO_3H^-

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[2] U. W. Arndt and D. C. Phillips, *Acta Cryst.*, 1961, **14**, 807.

[3] H. Hauptman and J. Karle, ' Solution of the Phase Problem. I. The Centrosymmetric Crystal,' A.C.A. Monograph, No. 3, 1953.

[4] W. H. Zachariasen, *Acta Cryst.*, 1952, **5**, 68.

[5] D. Sayre, *Acta Cryst.*, 1952, **5**, 60.

TABLE 3

Anisotropic temperature factors * and standard deviations for the heavy atoms

	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^42U_{12}	10^42U_{23}	10^42U_{13}	10^4U_{iso}/Å^2
P	420(4)	351(3)	282(3)	97(5)	63(5)	−135(5)	355
O(1)	473(12)	625(13)	399(10)	456(20)	266(18)	−181(17)	508
O(2)	440(11)	746(15)	265(8)	201(21)	−108(18)	−27(15)	523
O(3)	811(16)	469(12)	584(13)	−291(24)	346(21)	−374(23)	637
N(1)	422(12)	400(11)	251(9)	11(19)	−12(16)	3(16)	365
N(2)	386(11)	299(10)	346(10)	64(17)	35(17)	−61(17)	346
C(1)	331(12)	277(11)	281(10)	0(18)	−5(17)	−97(17)	297
C(2)	673(22)	917(28)	381(16)	701(39)	−156(32)	89(29)	693
C(3)	593(18)	485(15)	279(12)	−218(27)	−134(22)	−164(22)	471
C(4)	410(14)	463(14)	406(13)	121(24)	−139(24)	47(22)	427
C(5)	564(18)	319(13)	567(17)	56(25)	149(25)	−123(27)	497

* In the form: $\exp -2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})$. Isotropic temperature factors, U_{iso}, are defined by $[(U_{11}^2 + U_{22}^2 + U_{33}^2)/3]^{\frac{1}{2}}$.

group, $H_3N^+\text{-}CH_2{\cdot}CH_2{\cdot}PO_3H^-$ [6] and $HN^+(CH_2{\cdot}PO_3H_2)_2\text{-}(CH_2{\cdot}PO_3H)^-$ [7] have a more complex hydrogen-bonding system which involves NH···O hydrogen bonds.

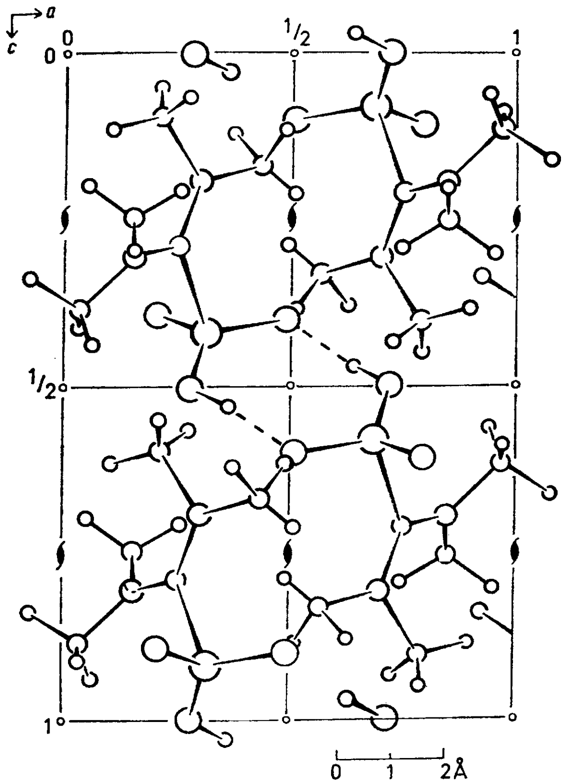

FIGURE 2 The packing arrangement in the (010) projection. Hydrogen bonds are shown as dashed lines

The three phosphinic acids Me_2PO_2H,[8] Ph_2PO_2H,[9] and $C_{13}H_{11}O_2P$ (IV) [10] form infinite chains through hydrogen bonding.

The O(3) oxygen atom, which is not involved in hydrogen bonding, undergoes more thermal motion (U_{iso} 0·064 Å^2) than the other two [U_{iso} 0·051 for O(1) and 0·052 for O(2)] and if the P–O bond lengths are corrected for riding thermal motion [11] with these values for U_{iso}, their values become: P–O(1) 1·506, P–O(2) 1·571, and P–O(3) 1·495 Å. Although the validity of

TABLE 4

Bond lengths (Å) and angles (°) with standard deviations

(*a*) Distances			
P–O			
P–O(1)	1·496(2)	P–O(3)	1·476(3)
P–O(2)	1·561(2)		
P–C			
P–C(1)	1·890(2)		
N–C(sp^2)			
C(1)–N(1)	1·323(3)	C(1)–N(2)	1·336(3)
Mean	1·330		
N–C(sp^3)			
N(1)–C(2)	1·466(4)	N(2)–C(4)	1·455(4)
N(1)–C(3)	1·475(4)	N(2)–C(5)	1·470(4)
Mean	1·467		
O–H			
O(2)–H	0·93(4)		
C–H			
C(2)–H(2A)	1·00(5)	C(4)–H(4A)	0·96(4)
C(2)–H(2B)	0·85(5)	C(4)–H(4B)	0·96(4)
C(2)–H(2C)	1·01(5)	C(4)–H(4C)	1·05(4)
C(3)–H(3A)	0·92(4)	C(5)–H(5A)	0·96(5)
C(3)–H(3B)	0·98(4)	C(5)–H(5B)	1·03(5)
C(3)–H(3C)	0·87(4)	C(5)–H(5C)	0·96(5)
Mean	0·96		
(*b*) Angles			
H–O–P			
H–O(2)–P	117(3)		
O–P–O			
O(1)–P–O(2)	108·13(12)	O(2)–P–O(3)	111·70(13)
O(1)–P–O(3)	120·38(13)		
O–P–C			
O(1)–P–C(1)	107·66(11)	O(3)–P–C(1)	103·52(12)
O(2)–P–C(1)	104·07(11)		
Mean angle at P	109·24		
Angles at C(1)			
P–C(1)–N(1)	120·73(18)	N(1)–C(1)–N(2)	119·62(22)
P–C(1)–N(2)	119·62(17)		
Mean	119·99		
Angles at N(1)			
C(1)–N(1)–C(2)	123·41(24)	C(2)–N(1)–C(3)	112·89(24)
C(1)–N(1)–C(3)	123·49(22)		
Mean	119·93		
Angles at N(2)			
C(1)–N(2)–C(4)	123·36(22)	C(4)–N(2)–C(5)	112·02(22)
C(1)–N(2)–C(5)	124·58(22)		
Mean	119·99		

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[6] Y. Okaya, *Acta Cryst.*, 1966, **20**, 712.

[7] J. J. Daly and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1967, 212.

[8] F. Giordano and A. Ripamonti, *Acta Cryst.*, 1967, **22**, 678.

[9] Tung-Tsai Liang and Kuo-Cheng Chiao, *Hua Hsueh Hsueh Pao*, 1965, **31**, 155 (*Chem. Abs.*, 1967, **66**, 6293).

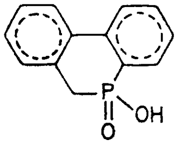
[10] P. J. Wheatley, *J. Chem. Soc.*, 1962, 3733.

[11] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

TABLE 4 (*Continued*)

H–C–H			
H(2A)–C(2)–H(2B)	122(4)	H(4A)–C(4)–H(4B)	109(4)
H(2A)–C(2)–H(2C)	101(4)	H(4A)–C(4)–H(4C)	113(4)
H(2B)–C(2)–H(2C)	107(4)	H(4B)–C(4)–H(4C)	115(3)
H(3A)–C(3)–H(3B)	105(4)	H(5A)–C(5)–H(5B)	116(4)
H(3A)–C(3)–H(3C)	114(4)	H(5A)–C(5)–H(5C)	110(4)
H(3B)–C(3)–H(3C)	113(4)	H(5B)–C(5)–H(5C)	108(4)
Average	111		
N–C–H			
N(1)–C(2)–H(2A)	103(3)	N(2)–C(4)–H(4A)	106(3)
N(1)–C(2)–H(2B)	116(3)	N(2)–C(4)–H(4B)	109(3)
N(1)–C(2)–H(2C)	106(3)	N(2)–C(4)–H(4C)	105(2)
N(1)–C(3)–H(3A)	112(3)	N(2)–C(5)–H(5A)	110(3)
N(1)–C(3)–H(3B)	105(3)	N(2)–C(5)–H(5B)	107(3)
N(1)–C(3)–H(3C)	107(3)	N(2)–C(5)–H(5C)	106(3)
Average	108		

such a simplified procedure is doubtful, it makes one cautious of saying that the P–O(1) and P–O(3) bond lengths are quite different. It does, however, seem reasonable to say that the P–OH [P–O(2)] bond length is longer than the other two P–O bond lengths; a similar difference has been observed[6,7] in phosphonic acids. The angles at the phosphorus atom vary from 103·5° [O(3)–P–C(1)] to 120·4° [O(1)–P–O(3)] and the HO–P–C angle (104·1°) lies well below the tetrahedral value as it does in β-ciliatine[6] and in nitrilomethylene triphosphonic acid.[7]


(IV)

The phosphorus–carbon bond length is slightly longer than those found in two[6,7] phosphonic acids (1·820 and 1·807 Å) and than the sum of the single-bond radii (1·83 Å). The corresponding C–X bond length in uronium (II)[12-17] and thiouronium (III)[18-20] compounds is considerably less than the normal C–X length but in these compounds the lone-pair electrons may contribute to the bonding in forms such as $(H_2N)_2$-C:$X^{+}\cdot$R. In thiourea dioxide, $(H_2N)_2CSO_2$ also called Manofast, where the sulphur lone-pairs are no longer available for carbon–sulphur bonding, the C–S bond length is 1·85 Å; the standard[21] value is 1·82 Å.

The tetramethyl formamidinium group exhibits the main features of simple formamidinium compounds.[12-20,22,23] The valences at the central carbon atom are very nearly coplanar and the C(1)–N bond lengths (mean 1·330 Å) are close to the conjugated heterocyclic value[21] (1·339 Å). The equation of the least-squares plane through P, C(1), N(1), and N(2) is given in Table 5. The distance of the other heavy atoms from this plane are: O(1) −1·05, O(2) −0·46, O(3) 1·42, C(2) −0·36, C(3) 0·50, C(4) 0·68, C(5) −0·60 Å. The planes of both NMe_2 groups pass very close to C(1) [see planes (B) and (C) in Table 6] and are rotated in opposite senses about their N–C(1) bonds relieving non-bonded intramolecular strains. The angle between planes (A) and (B) (Table 5) is 21° and that between planes (A) and (C) is 32°. Despite these rotations the C(5) and C(3) atoms are quite close to one another (2·85 Å); associated contacts are H(3C) ··· H(5A) 2·25, and H(3A) ··· H(5B) 2·32 Å.

TABLE 5

The equations of some weighted (w = atomic number) least-squares planes in the molecule, in the form $lX' + mY' + nZ' + p = 0$ *

Plane	Atoms	l	m	n	p	Max. Deviation (Å)
A	P, N(1), N(2), C(1)	0·79580	0·58083	0·17131	1·9482	C(1), −0·013
B	C(1), N(1), C(2), C(3)	0·58204	0·81315	0·00389	0·9875	N(1), −0·027
C	C(1), N(2), C(4), C(5)	0·64074	0·38986	0·66141	2·9851	N(2), −0·013

* X', Y', and $Z'$are orthogonal co-ordinates in Å related to X, Y, and Z by $X' = X + Z \cos \beta$, $Z' = Z \sin \beta$.

The van der Waals' contacts are mostly of the O ··· H, C ··· H, or H ··· H types and the shortest in these categories are 2·5, 2·8, and 2·2 Å.

I thank Dr. G. Birum who suggested the problem and prepared the crystals.

[1/2290 *Received, 2nd December*, 1971]

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