Crystal and Molecular Structure of Tetramethylformamidinium Phosphonic Anhydride, $[(Me_2N)_2CPO_2]_2O$

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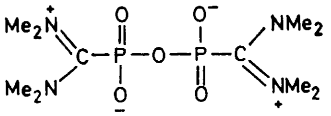
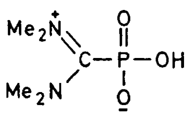
Crystals of the title compound are monoclinic, space group *C*2/*c* with a = 11·170, b = 10·613, c = 14·077 Å, β = 103° 24′, Z = 4. Diffractometer data for 2092 planes were used to solve the structure by direct methods and were refined by least-squares to a final R of 0·065 (for 2092 planes). The molecule possesses a two-fold crystallographic symmetry axis passing through the central oxygen atom. Important bond lengths are P–O(terminal) 1·469(2), P–O(bridge) 1·619(2), P–C 1·880(2), N–C(sp^2) 1·331(3), N–C(sp^3) 1·463(4) Å; P–O–P is 125·9(1)°

TETRAMETHYLFORMAMIDINIUM phosphonic anhydride (I) may be synthesised from tetramethylformamidinium chloride and triethyl phosphite.[1] It has several features of structural interest; for example it contains a P–C bond which links two groups of opposite formal charge, it is a double inner salt, and it is an organophosphorus compound with a P–O–P linkage of the type found in pyrophosphates. Structural analyses of the parent acid (II)[2] and the related phosphonoformate ion (III)[3] have already been published. Formulae equivalent to (I) may also be written so that one would expect bond lengths to fall into groups, N–C(sp^2), N–C(sp^3), P–O(terminal), P–O(bridge), and P–C.



(I)



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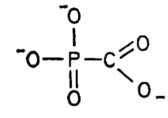

(III)

EXPERIMENTAL

Crystal Data.—$C_{10}H_{24}N_4O_5P_2$, M = 342·3, Monoclinic, a = 11·170(9), b = 10·613(8), c = 14·077(13) Å, β = 103° 24(10)′, U = 1623·4 Å^3, Z = 4, D_c = 1400. Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 298 m^{-1}, space group, from extinctions and successful analysis, *C*2/*c*.

Cell dimensions were obtained from precession photographs by a least-squares process. Intensities were collected round the b axis of a triclinic unit cell which is related to the monoclinic cell by the matrix $(a_t,b_t,c_t) = (-\frac{1}{2},-\frac{1}{2},0|\frac{1}{2},-\frac{1}{2},0|0,0,1)\ (a_m,b_m,c_m)$. These intensities were reduced to a set of $|F_o|$, indexed in the monoclinic system, and averaged to give 2092 independent measurements.

Structure Determination and Refinement.—The positions of the heavy atoms were found from an E-map after an application of direct methods.[4] The signs of the E values were obtained by hand from a computer listing of the triple product relations. This trial structure was refined by least squares, first with isotropic, then with anisotropic temperature factors. When R was 0·10 a difference-Fourier map was calculated which showed the positions of the hydrogen atoms and refinement was continued with all atoms until R, for 2092 planes, was 0·065 and R' (= $\Sigma w\Delta^2/\Sigma wF_o^2$), for 2018 planes, was 0·008. Planes with $3|F_c| \leqslant |F_o|$ were omitted from the least-squares totals and from R'. The weights[5] were given by $w^{-1} = 3{\cdot}91 + |F_o| + 0{\cdot}016\,F_o^2$, a block-diagonal process was used with 3 × 3 matrices for positional parameters and 1 × 1 or 6 × 6 matrices for the thermal parameters.

RESULTS AND DISCUSSION

The final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20465 (14 pp., 1 microfiche).† Table 1 shows an analysis of

TABLE 1

Average values of $\Sigma\omega\Delta^2$ as a function of the magnitude of $|F_o|$ and of $(2 \sin \theta/\lambda)^2$

Range of $\lvert F_o \rvert$	$\Sigma\omega\Delta^2/n$	n *
0—1·0	0·03	3
1·0—2·0	0·01	14
2·0—4·0	0·02	334
4·0—8·0	0·01	511
8·0—16·0	0·01	568
16·0—32·0	0·01	355
32·0—64·0	0·01	185
64·0—128·0	0·02	43
128·0—256·0	0·01	7
$(2 \sin \theta/\lambda)^2$ Interval		
0—0·128	0·01	36
0·128—0·256	0·01	70
0·256—0·384	0·01	96
0·384—0·512	0·02	109
0·512—0·640	0·01	118
0·640—0·768	0·01	134
0·768—0·896	0·01	141
0·896—1·024	0·01	144
1·024—1·152	0·01	150
1·152—1·280	0·01	161
1·408—1·536	0·01	165
1·536—1·664	0·01	155
1·664—1·792	0·01	162
1·792—1·920	0·01	124
1·920—2·048	0·03	101
2·048—2·176	0·03	71
2·176—2·304	0·04	50
2·304—2·432	0·03	27
2·432—2·560	0·04	4

* n = No. of planes.

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

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[5] D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. R. Truter, 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961, p. 32.

these data as a function of the monoclinic k index and of the magnitude of $|F_o|$. Tables 2—4 give the co-ordinates, the thermal parameters, and the bond lengths and angles. Standard deviations are given in parentheses as units in the last significant figure. The Figure shows the molecule projected down b and the labelling of the atoms.

TABLE 2

Final atomic co-ordinates, X, Y, and Z (Å)

	X	Y	Z
P(1)	0·1341(5)	1·8466(5)	4·9859(5)
O(2)	0·2623(19)	2·8957(19)	6·0390(18)
O(3)	−0·9046(18)	0·7873(19)	4·8419(20)
N(1)	2·1605(20)	−0·1104(18)	5·8357(20)
N(2)	2·9387(20)	1·8236(18)	5·0433(21)
C(1)	1·9033(21)	1·0991(20)	5·2761(21)
C(2)	1·1577(30)	−1·2069(25)	5·6231(32)
C(3)	3·4303(31)	−0·4526(28)	6·8313(28)
C(4)	2·8949(29)	3·2762(25)	4·8567(32)
C(5)	4·1876(28)	1·2227(32)	4·7903(35)
O(1)	0·0000(0)	2·5831(20)	3·5193(0)
H(2A)	1·63(4)	−1·99(3)	5·44(4)
H(2B)	0·41(4)	−1·00(3)	4·92(4)
H(2C)	0·86(4)	−1·47(4)	6·42(3)
H(3A)	3·99(3)	0·36(3)	7·12(3)
H(3B)	3·96(4)	−1·09(3)	6·41(4)
H(3C)	3·07(3)	−0·87(3)	7·61(3)
H(4A)	2·06(3)	3·63(2)	5·12(3)
H(4B)	3·61(4)	3·59(3)	5·46(4)
H(4C)	2·89(5)	3·51(3)	3·99(5)
H(5A)	4·03(3)	0·25(3)	4·52(3)
H(5B)	4·35(4)	1·56(3)	4·01(5)
H(5C)	5·07(3)	1·28(4)	5·65(5)

TABLE 3

(*a*) Anisotropic temperature factors *

	10^4U_{11}	10^4U_{22}	10^4U_{33}	2 × 10^4U_{12}	2 × 10^4U_{23}	2 × 10^4U_{13}
P(1)	391(2)	452(3)	381(3)	−000(4)	−010(4)	272(4)
O(2)	595(10)	687(10)	463(9)	144(17)	−271(15)	388(15)
O(3)	464(8)	647(10)	620(10)	−220(15)	201(16)	280(15)
N(1)	505(9)	404(8)	453(9)	068(15)	048(13)	260(14)
N(2)	422(8)	467(9)	471(10)	−068(14)	−056(13)	257(14)
C(1)	429(9)	408(8)	371(9)	−056(15)	−086(13)	243(14)
C(2)	691(16)	453(11)	695(16)	−130(22)	130(21)	449(26)
C(3)	687(16)	574(13)	534(14)	358(24)	103(20)	077(22)
C(4)	557(13)	471(11)	711(16)	−191(20)	005(20)	397(24)
C(5)	520(13)	712(16)	831(20)	−028(25)	−206(28)	696(27)
O(1)	466(10)	409(9)	390(10)	000(0)	000(0)	201(16)

* In the form $\exp - 2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})$.

(*b*) Isotropic temperature factors for hydrogen atoms

	10^4U_{iso}		10^4U_{iso}
H(2A)	613	H(4A)	580
H(2B)	613	H(4B)	580
H(2C)	613	H(4C)	580
H(3A)	598	H(5A)	688
H(3B)	598	H(5B)	688
H(3C)	598	H(5C)	688

The analysis shows that the $[(Me_2N)_2CPO_2]_2O$ molecule (I) has a crystallographic two-fold symmetry axis which passes through the bridging oxygen atom. The asymmetric unit of (I) is structurally very similar to the parent acid (II) [2] as may be seen from a comparison of the molecular parameters; e.g. some mean bond lengths are (values for the anhydride given first) P–O(terminal) **1·469, 1·486**; **P–O(–X) 1·619, 1·561**; N–C(sp^2) **1·331, 1·330**; N–C(sp^3) **1·463, 1·467**; and **P–C 1·880, 1·890 Å**. A long bond between a four-co-ordinate phosphorus atom and an sp^2 hybridised carbon atom (1·827 Å) has also been found in the $(PO_3CO_2)^{3-}$ ion.[3] The usual observed value,[3] a mean of 118 measurements, is 1·804 Å. The P–O(bridge) bond length (1·619 Å) is considerably

TABLE 4

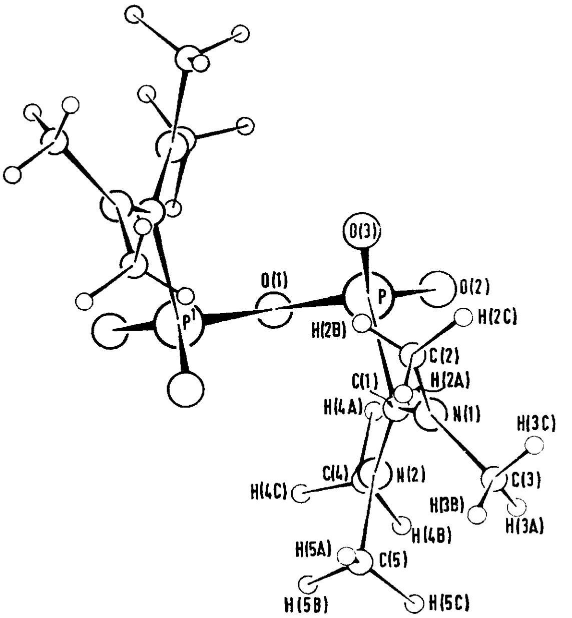
Bond lengths (Å) and angles (°)

(*a*) Distances

P–O(1)	1·619(1)
P–O(2)	1·471(2)
P–O(3)	1·467(2)
P–C(1)	1·880(2)
N–C(sp^2)	
C(1)–N(1)	1·333(3)
C(1)–N(2)	1·328(3)
Mean	1·331
N–C(sp^3)	
N(1)–C(2)	1·468(4)
N(1)–C(3)	1·461(4)
N(2)–C(4)	1·463(4)
N(2)–C(5)	1·460(4)
Mean	1·463
C–H (mean)	0·97

(*b*) Angles

P′–O(1)–P	125·87(8)
Angles at P	
O–P–O	
O(1)–O–O(2)	107·49(9)
O(1)–P–O(3)	109·35(9)
O(2)–P–O(3)	121·84(11)
O–P–C	
O(1)–P–C(1)	101·43(8)
O(2)–P–C(1)	104·49(10)
O(3)–P–C(1)	110·34(10)
Mean angle at P	109·16
Angles at C(1)	
P–C(1)–N(1)	120·59(16)
P–C(1)–N(2)	120·01(16)
N(1)–C(1)–N(2)	119·11(19)
Mean angle at C(1)	119·90
Angles at N(1)	
C(1)–N(1)–C(2)	123·94(20)
C(1)–N(1)–C(3)	123·47(20)
C(2)–N(1)–C(3)	112·36(20)
Mean angle at N(1)	119·92
Angles at N(2)	
C(1)–N(2)–C(4)	124·09(20)
C(1)–N(2)–C(5)	122·61(21)
C(4)–N(2)–C(5)	112·98(21)
Mean angle at N(2)	119·89
Mean H–C–N	110
Mean H–C–H	109



The molecule as viewed down the b axis and the labelling of the atoms longer, as expected,[6] than the P–O(terminal) bonds (1·469 Å); the latter are quite short being comparable with the P–O bond (1·46 Å) in Ph_3PO.[7] The P–O–P angle is 125·9° and is less than the angles found in the bent pyrophosphate ion in $Na_4P_2O_7,10H_2O$ (130°),[8] α-$Mg_2P_2O_7$ (144°),[9] and α-$Cu_2P_2O_7$ (157°);[10] similar P–O–P angles are found in the adamantane-type molecules P_4O_{10} (123·5°)[11] and in $P_4O_6S_4$ (124·5°).[12]

TABLE 5

Some least-squares planes in the molecule referred to orthogonal co-ordinates

Plane	*l*	*m*	*n*	*p*	Atoms	Max dev.	
(*A*)	−0·0127	0·3757	0·9267	5·1974	P(1), C(1), N(1), N(2)	C(1)	−0·037
(*B*)	−0·5677	0·3156	0·7603	3·8505	C(1)—(3), N(1)	N(1)	−0·028
(*C*)	0·1896	0·0860	0·9781	5·2583	C(1), N(2), C(4), C(5)	N(2)	0·033

Within the $PC(NMe_2)_2$ group three planes, each containing four atoms (maximum deviation 0·04 Å), may be distinguished and their equations are given in Table 5. These are the planes of the sp^2 hybridised C(1), N(1), and N(2) atoms and they might be expected to be coplanar giving optimum π-overlap between C(1) and the two nitrogen atoms. Examples of planarity of this type are to be found in urea[13] and, at least to less than 0·1 Å, in thiourea.[14] However this planar conformation of the heavy atoms in the $PC(NMe_2)_2$ group would give, with the observed bond lengths and angles, a C · · · C contact of 2·5 Å and so non-bonded repulsions between methyl groups force the NMe_2 groups to rotate about the C(1)–N bonds until the angles between planes (*B*) and (*C*) reaches 48°. This angle is still insufficient to give a normal contact (3·4 Å) between C(3) and C(5) which are only 2·87 Å apart. Further rotation of the $N(1)Me_2$ group about C(1)–N(1) would also increase the short observed contact of 2·85 Å between C(2) and O(3). These short contacts suggest that there are forces favouring planarity which are not quite overcome by non-bonded intramolecular repulsions.

The van der Waals' contacts exhibit no unusual features.

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[2/935 *Received 27th April*, 1972]

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