The Crystal Structure of Guanidinium Pyrophosphate Monohydrate

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$[C(NH_2)_3]_4P_2O_7.H_2O$ is monoclinic, space group $P2_1$, with $a = 7.05$ (2), $b = 11.69$ (2), $c = 12.01$ (2) Å, $\beta = 111.7$ (1)°, $Z = 2$. The P–O–P bridge is symmetrical with P–O distances of 1.63 (1) and 1.64 (1) Å; the angle is 126.5°. The pyrophosphate group has an almost staggered conformation. The hydrogen bonding is complicated and three-dimensional with 23 of a possible 26 H atoms involved. Each O atom accepts up to four hydrogen bonds.

Introduction

This study was undertaken for two reasons. Firstly this pyrophosphate has a high ratio of H to O atoms (3.25:1) which makes it likely that there will be multiple hydrogen bonds to oxygen, continuing a previous line of investigation (Adams & Ramdas, 1976). Secondly, on recrystallization from aqueous hydrogen peroxide solutions an extremely stable adduct with H_2O_2 is formed (Adams & Ramdas, 1977).

An initial differential scanning calorimetric study (Fig. 1) gave an overall ΔH for the dehydration of the monohydrate of 51 kJ mol⁻¹. The weight loss corresponded exactly to the loss of one molecule of water per formula unit. The shape of the endotherm is unusual since it exhibits a long induction period followed by a short reaction period, these being obviously distinct. The more usual type of hydrate decomposition is typified by $BaCl_2.H_2O$ (Guarini & Spinicci, 1972) which has a smooth endothermic decomposition extending over 60 K.

Experimental

To a suspension of 18 g of guanidinium carbonate in water were added 8.9 g of $H_4P_2O_7$. After filtration of excess solid, the filtrate was evaporated slowly and long needles formed. The density was determined by

Table 1. *Crystal data*

Space group $P2_1$, $a = 7.05$ (2), $b = 11.69$ (2), $c = 12.01$ (2) Å, $\beta = 111.7$ (1)° (Cu $K\alpha$, $\lambda = 1.5418$ Å), $Z = 2$, $d_o = 1.59$, $d_c = 1.56$ g cm⁻³. Analysis: observed: C 10.9, N 38.9, P 14.3, H 6.0%; calculated: C 11.1, N 39.3, P 13.9, H 5.9%.

flotation. Photographs were used to determine the cell parameters and space group. Film packs (0–3*kl* and *h0l–h5l*) were used to collect the intensities. The films were scanned and the intensities corrected for Lorentz–polarization effects and absorption [μ(Cu $K\alpha$) = 26.6 cm⁻¹] and put on a common scale by the SRC Microdensitometer Service at the Atlas Computer Laboratory. Crystal data are in Table 1.

Structure determination

A Wilson plot of the 1467 unique reflexions gave an overall $B = 1.8$ Å². The 190 planes with $E > 1.4$ were used to solve the structure with *MULTAN* (Germain, Main & Woolfson, 1971). The set of phases with the highest figure of merit was used to compute an E map and although only the P atoms were easily recognizable, the other nonhydrogen atoms were located from difference maps calculated during the course of least-squares refinement. Refinement ceased at $R = 0.15$
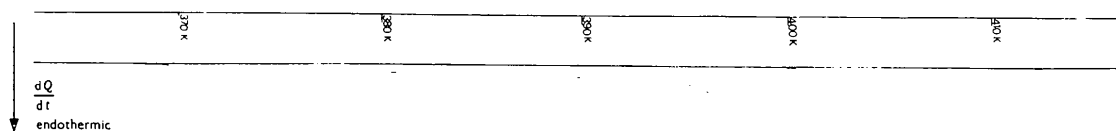

Fig. 1. Differential scanning calorimeter run on the title compound. Note the long induction period followed by the relatively sharp endothermic peak.

with isotropic thermal parameters; anisotropic parameters only reduced R to 0·138. Six reflexions which suffered from extinction were omitted, and refinement converged at $R = 0·108$. It did not prove possible to locate the H atoms from difference syntheses. Unit weights were used.
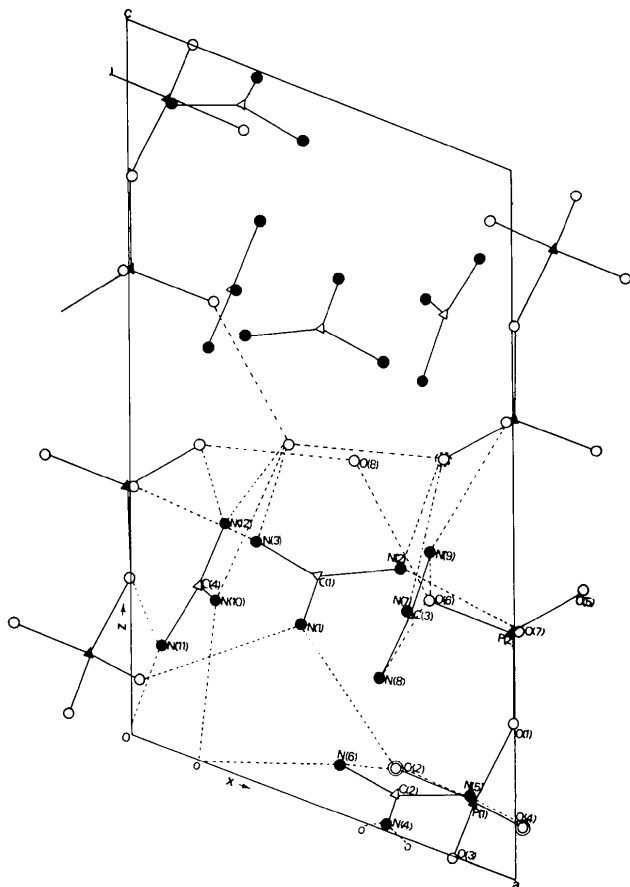

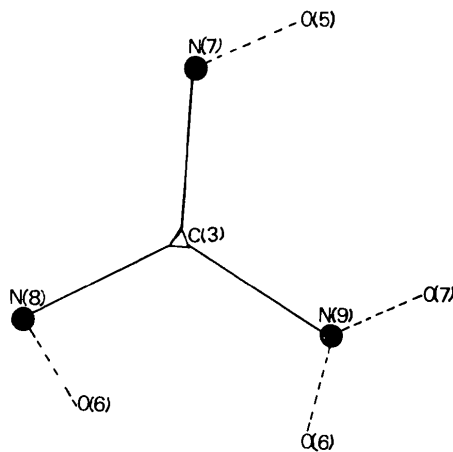Fig. 2. Projection of the structure down **b**. A large broken circle represents an atom one **b** translation below the cell.

Fig. 3. Projection of the C(3), N(7), N(8), N(9) group on to (100).

Table 2. *Fractional atomic coordinates and their standard deviations*

	x	y	z
P(1)	0·8893 (5)	0·2307 (5)	0·0916 (3)
P(2)	0·9933 (5)	0·2562 (5)	0·3499 (3)
O(1)	0·9979 (15)	0·2966 (15)	0·2210 (8)
O(2)	0·7045 (15)	0·1654 (15)	0·0931 (10)
O(3)	0·8362 (16)	0·3269 (16)	−0·0002 (9)
O(4)	1·0531 (16)	0·1529 (14)	0·0811 (9)
O(5)	1·1742 (15)	0·3185 (15)	0·4391 (9)
O(6)	0·7886 (16)	0·3001 (17)	0·3509 (11)
O(7)	1·0146 (16)	0·1273 (16)	0·3562 (9)
O(8)	0·5860 (16)	0·2694 (16)	0·5082 (7)
C(1)	0·4981 (22)	0·0358 (14)	0·3245 (11)
N(1)	0·4542 (19)	0·1256 (13)	0·2516 (11)
N(2)	0·6894 (19)	0·0004 (13)	0·3781 (11)
N(3)	0·3422 (20)	−0·0208 (13)	0·3434 (12)
C(2)	0·6972 (22)	0·8747 (16)	0·0577 (12)
N(4)	0·6687 (21)	0·7681 (14)	0·0142 (14)
N(5)	0·8843 (20)	0·9220 (14)	0·0957 (13)
N(6)	0·5429 (24)	0·9329 (15)	0·0732 (14)
C(3)	0·7271 (29)	0·5947 (22)	0·3182 (18)
N(7)	0·7347 (30)	0·7079 (21)	0·3253 (17)
N(8)	0·6524 (30)	0·5379 (20)	0·2110 (14)
N(9)	0·7900 (23)	0·5304 (15)	0·4171 (13)
C(4)	0·1758 (27)	0·5997 (15)	0·2395 (13)
N(10)	0·2188 (24)	0·7040 (14)	0·2298 (12)
N(11)	0·0790 (25)	0·5344 (13)	0·1425 (11)
N(12)	0·2346 (23)	0·5515 (16)	0·3487 (11)

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations apart from the structure solution were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Fractional atomic coordinates are in Table 2.* Fig. 2 is a projection of the structure down **b**, and Fig. 3 is a projection of the C(3), N(7), N(8), N(9) group on to (100).

Description and discussion of the structure

The geometry of the ions (Table 3) is normal with all C—N bonds close to 1·33 Å. The P—O—P bridge is symmetrical with an angle of 126·5° and the terminal P—O bonds are all reasonably equal at 1·52 Å. The conformation of the pyrophosphate is almost staggered (Fig. 4), a feature that is very sensitive to environment. In $Na_4P_2O_7$ the pyrophosphate is eclipsed (Leung & Calvo, 1972) whereas in $Na_4P_2O_7.10H_2O$ it is staggered (Calvo, 1965).

Translationally equivalent $P_2O_7^{4-}$ ions are joined by hydrogen bonds from a bridging water molecule along the **a** direction. The guanidinium groups join the pyrophosphate anions and water molecules together in a three-dimensional network. All the H atoms on three of

Table 3. *Bond lengths* (Å) *and bond angles* (°)

|			
P(1)—O(1)	1·64 (1)	O(1)—P(1)—O(3)	104·0 (7)
P(1)—O(2)	1·51 (1)	O(1)—P(1)—O(4)	104·8 (6)
P(1)—O(3)	1·52 (1)	O(2)—P(1)—O(3)	113·4 (6)
P(1)—O(4)	1·51 (1)	O(2)—P(1)—O(4)	112·6 (8)
P(2)—O(1)	1·63 (1)	O(3)—P(1)—O(4)	112·0 (7)
P(2)—O(5)	1·51 (1)	O(1)—P(2)—O(5)	103·0 (6)
P(2)—O(6)	1·53 (1)	O(1)—P(2)—O(6)	105·0 (7)
P(2)—O(7)	1·51 (1)	O(1)—P(2)—O(7)	107·4 (7)
C(1)—N(1)	1·33 (2)	O(5)—P(2)—O(6)	112·4 (7)
C(1)—N(2)	1·33 (2)	O(5)—P(2)—O(7)	113·6 (6)
C(1)—N(3)	1·37 (2)	O(6)—P(2) O(7)	114·1 (7)
C(2)—N(4)	1·33 (2)	N(1)—C(1)—N(2)	120·8 (15)
C(2)—N(5)	1·34 (2)	N(1)—C(1)—N(3)	118·9 (13)
C(2)—N(6)	1·35 (2)	N(2)—C(1)—N(3)	120·1 (14)
C(3)—N(7)	1·32 (3)	N(4)—C(2)—N(5)	120·1 (16)
C(3)—N(8)	1·36 (2)	N(4)—C(2)—N(6)	120·6 (15)
C(3)—N(9)	1·33 (2)	N(5)—C(2)—N(6)	118·9 (17)
C(4)—N(10)	1·27 (2)	N(7)—C(3)—N(8)	122·4 (20)
C(4)—N(11)	1·34 (2)	N(7)—C(3)—N(9)	120·8 (19)
C(4)—N(12)	1·34 (2)	N(8)—C(3)—N(9)	116·7 (22)
		N(10)—C(4)—N(11)	121·6 (15)
P(1)—O(1)—P(2)	126·5 (8)	N(10)—C(4)—N(12)	119·5 (14)
O(1)—P(1)—O(2)	108·9 (7)	N(11)—C(4)—N(12)	118·7 (16)
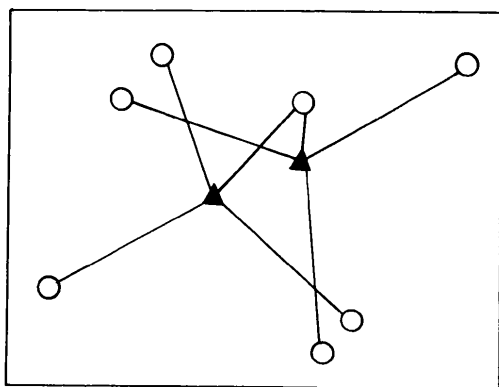
Fig. 4. Projection of the pyrophosphate group on to (001).

the guanidinium groups are involved in hydrogen-bonding; in the C(3), N(7), N(8), N(9) group, N(7) is involved in only one hydrogen bond and N(8) in none [the only close contact of N(8) is 3·21 Å to O(6); the C—N···O angle is very small at 89·5°]. N(5) has three short contacts: O(4^{vi}) at 2·97, O(3^{iv}) at 2·84 and O(2^{vi}) at 3·10 Å. The C—N···O angles are 135·6, 95·4 and 91·6°. The evidence, therefore, favours bonds to O(4^{vi}) and O(3^{iv}) rather than O(2^{vi}).

The O atoms accept varying numbers of hydrogen bonds: O(1) has one, O(7) two, and the rest have three, except for O(4) and O(5) which have four; this appears to be the maximum value both in these simple salts (Adams & Ramdas, 1976) and urea (Sklar, Senko &

Post, 1961). Details of the hydrogen bonding are in Table 4. Table 5 gives the deviations of atoms from some least-squares planes.

Table 4. *Hydrogen-bonding geometry*

(a) Bond lengths (Å)

N(1)···O(2)	3·08 (2)	N(7)···O(5^{vii})	2·95 (2)
N(1)···O(4^i)	2·82 (1)	|N(8)···O(6)	3·21 (2)|
N(2)···O(7)	2·82 (2)	N(9)···O(6)	2·81 (2)
N(2)···O(5^{ii})	2·95 (1)	N(9)···O(7^{vii})	2·79 (1)
N(3)···O(7^i)	2·93 (2)	N(10)···O(8^{viii})	3·03 (1)
N(3)···O(8^{iii})	2·96 (2)	N(10)···O(3^v)	3·00 (2)
N(4)···O(4^{iv})	2·94 (2)	N(11)···O(1^i)	3·05 (2)
N(4)···O(2^v)	2·74 (1)	N(11)···O(4^v)	2·85 (1)
N(5)···O(4^{vi})	2·97 (2)	N(12)···O(5^i)	3·02 (2)
|N(5)···O(2^{vi})	3·10 (2)|	N(12)···O(8^{viii})	3·06 (2)
N(5)···O(3^{iv})	2·84 (2)	O(8)···O(6)	2·78 (2)
N(6)···O(2^{vi})	2·92 (2)	O(8)···O(5^i)	2·76 (1)
N(6)···O(3^v)	2·78 (2)		

(b) Bond angles (°)

C(1)—N(1)···O(2)	119	C(2)—N(6)···O(3^v)	118
C(1)—N(1)···O(4^i)	120	C(3)—N(7)···O(5^{vii})	120
C(1)—N(2)···O(7)	120	|C(3)—N(8)···O(6)	90|
C(1)—N(2)···O(5^{ii})	125	C(3)—N(9)···O(6)	109
C(1)—N(3)···O(7^i)	115	C(3)—N(9)···O(7^{vii})	121
C(1)—N(3)···O(8^{iii})	122	C(4)—N(10)···O(8^{viii})	100
C(2)—N(4)···O(2^v)	125	C(4)—N(10)···O(3^v)	126
C(2)—N(4)···O(4^{iv})	110	C(4)—N(11)···O(1^i)	110
C(2)—N(5)···O(4^{vi})	136	C(4)—N(11)···O(4^v)	115
|C(2)—N(5)···O(2^{vi})	92|	C(4)—N(12)···O(5^i)	134
C(2)—N(5)···O(3^{iv})	95	C(4)—N(12)···O(8^{viii})	97
C(2)—N(6)···O(2^{vi})	100		

Symmetry code

(i)	$-1 + x, y, z$	(v)	$1 - x, \frac{1}{2} + y, -z$
(ii)	$2 - x, -\frac{1}{2} + y, 1 - z$	(vi)	$x, 1 + y, z$
(iii)	$1 - x, -\frac{1}{2} + y, 1 - z$	(vii)	$2 - x, \frac{1}{2} + y, 1 - z$
(iv)	$2 - x, \frac{1}{2} + y, -z$	(viii)	$1 - x, \frac{1}{2} + y, 1 - z$

Table 5. *Deviations* (Å) *of atoms from least-squares planes* (*guanidinium ions*)

(a) Plane through C(1), N(1), N(2), N(3)
$$-1·3792x + 7·0207y + 9·5196z = 2·6521$$

C(1)	0·001	N(2)	−0·0005
N(1)	−0·0005	N(3)	−0·0005

(b) Plane through C(2), N(4), N(5), N(6)
$$-0·8528x - 4·4982y + 10·7492z = -3·8817$$

C(2)	−0·020	N(5)	0·009
N(4)	0·009	N(6)	0·009

(c) Plane through C(3), N(7), N(8), N(9)
$$7·0473x - 0·2431y - 4·7162z = 3·4733$$

C(3)	0·005	N(8)	−0·002
N(7)	−0·002	N(9)	−0·002

(d) Plane through C(4), N(10), N(11), N(12)
$$6·7900x - 3·0884y - 4·8690z = -1·8122$$

C(4)	−0·012	N(11)	0·004
N(10)	0·004	N(12)	0·004

We thank Professor J. M. Thomas for his encouragement.

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Electron Density Distribution in Cumulenes:
An X-ray Study of Tetraphenylbutatriene at 20°C and −160°C

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The structure of tetraphenylbutatriene (TPBT), $C_{28}H_{20}$, was investigated by X-ray ($\lambda = 0.709$ Å) diffraction at 20°C and −160°C. The space group is $P\bar{1}$ with $Z = 2$ and $a = 10.035$ (3), $b = 10.458$ (4), $c = 9.978$ (3) Å, $\alpha = 105.04$ (4), $\beta = 105.27$ (3), $\gamma = 92.17$ (3)°, at −160°C. The molecule is not planar, the rings being twisted by 27.9, 27.4, 41.8, 38.5° out of the butatriene plane. The molecular symmetry approximates to 222. The central =C=C= bond is short (1.260 Å), in contrast to the outer $>$C=C bonds, of length 1.348 Å. The molecular electron density distribution was determined from the low-temperature data by a least-squares procedure. The observed deformation densities in the butatriene skeleton show that the π lobes in adjacent C=C bonds are mutually perpendicular. The aromatic C=C bond shows π character, whereas the exocyclic C–C bond appears to be purely σ.

Introduction

The role of the crystal structures of substituted ethylenes in determining the stereochemistry of the cyclobutane photodimers obtained therefrom has been demonstrated (Schmidt, 1971). A separation of 4.0 ± 0.2 Å between potentially reactive C=C double bonds is necessary for photodimerization. It has been observed (Schmidt, 1971; Lahav & Schmidt, 1967; Frank & Paul, 1973) that neighbouring C=C bonds, which fulfil the above requirement, but which are far offset, implying insufficient overlap of their π electrons, do not dimerize. A system which allows systematic analysis of the importance of the alignment of the π electrons is provided by the cumulenes in which the π lobes of adjacent C=C bonds lie in mutually perpendicular planes. This study of TPBT was primarily motivated towards the determination of the electron density distribution in the butatriene system so as to provide information on the orientation of the π lobes of adjacent C=C bonds. Photochemical studies were also undertaken (Berkovitch-Yellin, Lahav & Leiserowitz, 1974)

to correlate the electron density distribution with topochemical behaviour in the cumulenic system.

Experimental

Yellow crystals of TPBT (1) were obtained by evaporation from ethyl acetate. The structure was determined at room temperature and at −160°C. There

(1)