

## The Crystal and Molecular Structure of 2-Diethylphosphorylguanidine–Hemi(guanidinium chloride)

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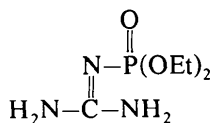
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### Abstract

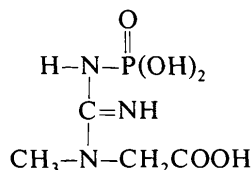
Crystals of 2-diethylphosphorylguanidine–hemi(guanidinium chloride),  $(\text{EtO})_2\text{P}(\text{O})\text{NC}(\text{NH}_2)_2 \cdot \frac{1}{2}[\text{C}(\text{NH}_2)_3^+\text{Cl}^-]$ ,  $\text{C}_5\text{H}_{14}\text{N}_3\text{O}_3\text{P} \cdot \frac{1}{2}(\text{CH}_6\text{N}_3^+\text{Cl}^-)$ , are monoclinic,  $C2/c$  with  $a = 18.326(3)$ ,  $b = 9.174(3)$ ,  $c = 15.543(7)$  Å,  $\beta = 103.22(4)^\circ$ ,  $V = 2543.9$  Å<sup>3</sup>;  $M_r = 242.9$ ,  $D_o = 1.26(2)$ ,  $D_c = 1.268$  Mg m<sup>-3</sup>,  $Z = 8$ . 2-Diethylphosphorylguanidine is not one of the high-energy phosphate compounds. Both the P–N distance of 1.595(5) Å and the phosphoryl P–O distance of 1.482(4) Å are short enough to indicate considerable double-bond character.

### Introduction

This study is part of a structural investigation of phosphate esters to determine whether there is a recognizable connection between the reactivity of the ‘high-energy’ phosphates and some geometrical features such as bond lengths, bond angles or conformational angles. Although 2-diethylphosphorylguanidine (I) is not a ‘high-energy’ compound, it is reasonable to postulate that comparisons between this compound and a ‘high-energy’ compound such as phosphorylcreatine (Herriott & Love, 1968) (II) would be fruitful.



(I)



(II)

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### Experimental

The data were collected on a Picker diffractometer with Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å). Intensities were measured in the  $\theta$ – $2\theta$  scan mode with a scan rate of  $1^\circ \text{ min}^{-1}$  and a scan width of  $\Delta 2\theta = 3.0^\circ$ . Of the 2320 independent reflections measured in the range  $5.0^\circ < 2\theta < 136.5^\circ$ , 2102 had  $I > 2\sigma(I)$  where  $\sigma^2(I) = T + k^2B + (0.02I)^2$ ,  $T$  is the total peak,  $B$  is the total background normalized to the time interval of the scan and  $k$  is the normalization factor. The single monitor reflection showed a systematic decrease of intensity of about 20% during the period of data collection. Data were scaled to allow for this decrease and corrected for polarization and geometrical factors. No correction was made for absorption [ $\mu(\text{Cu } K\alpha) = 2.32 \text{ mm}^{-1}$ ].

The structure was solved by a combination of direct methods and weighted Fourier syntheses (Wampler, Kennard, Coppola, Motherwell & Watson, 1971), and refined by full-matrix least squares. After anisotropic refinement of the heavy atoms had converged at  $R = 0.188$ , a difference Fourier synthesis revealed the positions of seven H atoms attached to N. Owing to the high thermal motion of the ethyl groups, H atoms of these groups were not located in the difference map.

The final cycles of refinement included a secondary-extinction parameter in addition to positional and anisotropic thermal parameters for the heavy atoms. Although seven H atoms were included in the model, their parameters were not refined. The refined value for the extinction parameter,  $g$ , is  $4.9(4) \times 10^{-6}$ . Final atomic coordinates are given in Table 1 with atoms numbered as shown in Fig. 1.‡

‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34710 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$  for heavy atoms,  $\times 10^3$  for H atoms)

The notation (-) indicates that the coordinate is fixed by symmetry. Parameters of H atoms were not refined.

	x	y	z
Cl(1)	0000 (-)	3849 (3)	-2500 (-)
P	1474 (1)	0148 (2)	0822 (1)
O(1)	0727 (2)	0343 (6)	1021 (3)
O(2)	2131 (2)	0212 (6)	1655 (3)
O(3)	1575 (4)	-1439 (6)	0498 (4)
N(1)	1746 (2)	1293 (5)	0189 (3)
N(2)	1612 (2)	2949 (6)	-0937 (3)
N(3)	0563 (3)	1815 (6)	-0748 (4)
C(1)	1310 (3)	1984 (6)	-0479 (4)
C(2)	1283 (7)	-2096 (14)	-0274 (8)
C(3)	1291 (8)	-3578 (13)	-0243 (10)
C(4)	2128 (6)	-0728 (12)	2434 (5)
C(5)	2815 (6)	-0516 (14)	3052 (8)
C(6)	0000 (-)	2117 (14)	2500 (-)
N(4)	0323 (3)	2857 (8)	1954 (4)
N(5)	0000 (-)	0688 (11)	2500 (-)
H(1)	217	313	-078
H(2)	130	349	-145
H(3)	028	114	-043
H(4)	027	241	-126
H(5)	034	395	193
H(6)	059	231	152
H(7)	025	014	209

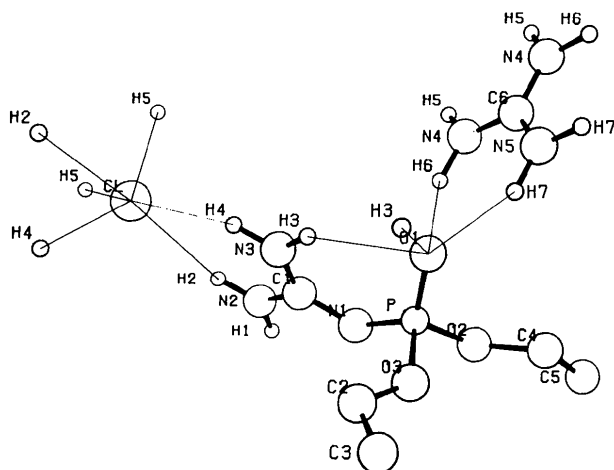


Fig. 1. A perspective drawing of the complex showing the numbering scheme used in the text and the geometry of the hydrogen bonding at the acceptor sites O(1) and Cl<sup>-</sup>.

The refinement converged with  $R = 0.105$  and  $R_w = (\sum w\Delta^2 / \sum wF^2)^{1/2} = 0.092$ . Reflections with  $I \leq 2\sigma(I)$  were given a weight of zero in the refinement. Scattering factors for C and H were taken from *International Tables for X-ray Crystallography* (1962), while those for P, O, N and Cl are from Cromer & Mann (1968). The quantity minimized in the refinement was  $\sum w\Delta^2$ . A final difference Fourier map showed no significant features.

## Crystal structure and hydrogen bonding

The crystal structure (Fig. 2) is a hydrogen-bonded complex between 2-diethylphosphorylguanidine molecules, guanidinium ions and chloride ions. The ratio of 2-diethylphosphorylguanidine to guanidinium chloride is 2 : 1. The molecules sit in general positions in the unit cell, while the guanidinium ions and chloride ions occupy special positions on the twofold axes. The structure is linked in three dimensions by hydrogen bonds involving the H atoms attached to N and the acceptor sites N(1), O(1) and Cl<sup>-</sup>. Dimensions of the hydrogen bonds are listed in Table 2.

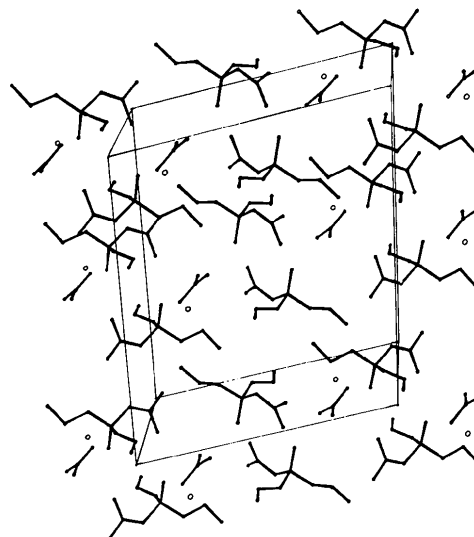


Fig. 2. Packing diagram. H atoms have been omitted for clarity. Chloride ions are indicated by small circles. The origin is in the upper left corner with  $a$  down the page,  $b$  into the page and  $c$  across.

Table 2. Details of hydrogen bonds

The symmetry operation indicated in the last column is applied to the coordinates of the donor atom as listed in Table 1 to give the bond as illustrated in Fig. 1. Parameters of H atoms have not been refined. N—H distances range from 1.00 to 1.04 Å.

N...X	H...X	$\angle$ N—H...X	S*
N(2)'...N(1)	H(1)'...N(1)	2.06	166 4
N(2)...Cl	H(2)...Cl	2.58	148 1,3'
N(3)...O(1)	H(3)...O(1)	2.33	124 1
O(1)'	O(1)	2.31	128 2
N(3)...Cl	H(4)...Cl	2.30	161 1,3'
N(4)...Cl	H(5)...Cl	2.35	146 2',4'
N(4)...O(1)	H(6)...O(1)	2.00	143 1
N(5)...O(1)	H(7)...O(1)	2.06	144 1,3

\* Symmetry code

(1)	$x, y, z$	(2')	$-x, 1-y, -z$
(2)	$-x, -y, -z$	(3')	$-x, y, -\frac{1}{2}-z$
(3)	$-x, y, \frac{1}{2}-z$	(4')	$x, 1-y, -\frac{1}{2}+z$
(4)	$\frac{1}{2}-x, \frac{1}{2}-y, -z$		

Fig. 1 shows the numbering scheme used in this discussion and illustrates the geometry of the acceptor sites. The chloride ion is acceptor for three symmetry-related pairs of hydrogen bonds. There are two pairs of strong hydrogen bonds involving H(4) and H(5) with H...Cl distances of 2.30 Å and 2.35 Å respectively. The H(4)–Cl–H(4') angle is 109.8°. Since the two symmetry-related H(5) atoms are attached to the same N atom, the H(5)–Cl–H(5') angle is only 61.2°. The H(2)...Cl distances of 2.58 Å are longer than the other contacts to Cl but they are significantly shorter than the sum of the van der Waals radii, 2.76 Å. The H(2)–Cl–H(2') angle is 165.4°.

The coordination at the phosphoryl O is somewhat unusual in that the O atom is acceptor for four hydrogen bonds rather than the more usual two or three bonds. The geometry at O can be described as a distorted trigonal bipyramid with P, H(3') and H(6) in the equatorial plane. Although H(3) lies near the perpendicular to that plane, H(7) lies some distance away. The angle H(3)–O(1)–H(7) is 134°.

N(1) accepts one hydrogen bond from H(1') at  $\frac{1}{2} - x, \frac{1}{2} - y, -z$ . The H atom lies out of the P, N(1), C(1) plane by about 0.47 Å with angles C(1)–N(1)–H(1') and P–N(1)–H(1') of 126 and 107° respectively.

### Molecular structure

An examination of bond angles in Table 3 shows that angles at O(3), N(1) and C(1) have been expanded significantly above 120°. In the case of O(3) the contact between O(1) and C(2) has been relieved to some extent by increasing the torsion angle about the P–O(3) bond to 74° (Table 4), thus bringing C(2) into contact with N(1). The angles at C(1) and N(1) result from a combination of repulsive van der Waals forces and attractive electrostatic potentials. Short contacts involving N(3) and C(1) are listed in Table 5. The hydrogen bonds H(4)...Cl and H(2)...Cl would tend

Table 3. Bond distances (Å) and bond angles (°) for the heavy atoms

P–O(1)	1.482 (4)	O(1)–P–O(2)	113.5 (3)
P–O(2)	1.554 (5)	O(1)–P–O(3)	111.2 (4)
P–O(3)	1.565 (6)	O(1)–P–N(1)	118.9 (3)
P–N(1)	1.595 (5)	O(2)–P–O(3)	100.2 (4)
		O(2)–P–N(1)	101.4 (3)
O(2)–C(4)	1.488 (8)	O(3)–P–N(1)	109.7 (3)
C(4)–C(5)	1.412 (12)	P–O(2)–C(4)	120.6 (5)
O(3)–C(2)	1.340 (10)	O(2)–C(4)–C(5)	107.8 (7)
C(2)–C(3)	1.360 (14)	P–O(3)–C(2)	130.8 (8)
N(1)–C(1)	1.319 (7)	O(3)–C(2)–C(3)	114.8 (1.2)
C(1)–N(2)	1.333 (7)	P–N(1)–C(1)	125.7 (4)
C(1)–N(3)	1.346 (7)	N(1)–C(1)–N(2)	119.3 (5)
		N(1)–C(1)–N(3)	125.4 (6)
C(6)–N(4)	1.328 (8)	N(2)–C(1)–N(3)	115.3 (6)
C(6)–N(5)	1.311 (12)	N(4)–C(6)–N(5)	120.7 (6)
		N(4)–C(6)–N(4)	118.5 (7)

Table 4. Torsional angles in 2-diethylphosphoryl-guanidine compared with corresponding angles in phosphorylcreatine (°)

	2-Diethylphosphoryl-guanidine	Phosphoryl-creatine
P–N(1)–C(1)–N(2)	177.9 (5)	171.1 (4)
P–N(1)–C(1)–N(3)	–1.4 (5)	–9.1 (3)
O(1)–P–N(1)–C(1)	–32.7 (4)	–35.6 (2)
O(2)–P–N(1)–C(1)	–157.8 (4)	–158.1 (3)
O(3)–P–N(1)–C(1)	96.9 (4)	81.2 (3)
P–O(2)–C(4)–C(5)	175.5 (6)	
P–O(3)–C(2)–C(3)	–160.0 (10)	
O(1)–P–O(2)–C(4)	52.7 (5)	
O(1)–P–O(3)–C(2)	74.0 (8)	
O(2)–P–O(3)–C(2)	–165.8 (8)	
O(3)–P–O(2)–C(4)	–66.0 (5)	
N(1)–P–O(2)–C(4)	–178.7 (5)	
N(1)–P–O(3)–C(2)	–59.7 (8)	

Table 5. Selected non-bonded contacts (Å)

N(1)...H(1)	2.50 (*)	N(1)...C(2)	3.260 (14)
N(1)...O(1)	2.650 (7)	O(1)...C(2)	3.322 (14)
O(2)	2.437 (7)	O(1)...C(1)	3.160 (8)
O(3)	2.584 (8)	O(3)...C(1)	3.474 (8)
O(1)...O(2)	2.539 (5)		
O(3)	2.515 (8)	N(3)...O(1)	3.016 (8)
O(2)...O(3)	2.393 (7)	N(3)...P(1)	3.036 (6)

\* Parameters of H atoms not refined.

to expand both angles but the hydrogen bond between H(3) and O(1) would oppose that tendency.

Bond angles at P follow the trends usual for phosphate compounds. The extreme values are: 100.2 (4)° for the angle subtended at P by the ester oxygens, and 118.9 (3)° for the angle between the phosphoryl P–O bond and the P–N bond. In general, angles between bonds of low bond valence (see Table 6) are smaller than tetrahedral, while those between bonds of high bond valence are larger.

Bond lengths in the guanidino residue and the guanidinium ion are similar to those in guanidinium chloride (Haas, Harris & Mills, 1965). It may be significant that the sum of the bond distances in the guanidino group, 3.998 Å, is 0.03 Å longer than in either of the guanidinium ions.

It is instructive to compare bond lengths (Table 6) in 2-diethylphosphorylguanidine with those in phenyl phosphorodiamidate (Bullen & Dann, 1973). The phosphoryl P–O bonds are essentially the same. Both P–O(ester) distances in the guanidine derivative are shorter than the P–O(ester) distance in the diamidate. The difference in length between P–O(2) and P–O(3) is consistent with the difference in conformation about the two bonds. The P–N distances in these compounds are similar to those observed in cyclic phosphazanes such as N<sub>4</sub>P<sub>4</sub>Me<sub>8</sub> (Dougill, 1961).

Table 6. *A comparison of bond length (Å) and bond orders*

	2-Diethylphosphorylguanidine		Phenylphosphorodiamidate		Bond length	Bond valence
	Bond length	Bond valence	Bond length	Bond valence		
P=O	1.481 (4)	1.40	1.482 (4)	1.40	1.507 (3)	1.32
P—O	1.555 (5)	1.19	1.593 (2)	1.10	1.504 (3)	1.33
	1.565 (5)	1.19			1.517 (3)	1.29
P—N	1.595 (5)	1.41	1.604 (3)	1.38	1.735 (3)	1.07
			1.628 (2)	1.32		

Bond valence can be estimated using the formula  $s = (R_o/R)^n$  (Brown & Shannon, 1973) where  $R_o$  is the single-bond length,  $R$  is the observed bond length and the exponent is chosen so that the sum of the bond valences corresponds to the valence of the central atom. Bond valences in Table 6 have been calculated using the P—O distance of 1.64 Å observed in  $P_4O_{10}$  (Cruickshank, 1964*b*) and the P—N length of 1.77 Å from Cruickshank's (1964*a*) refinement of sodium phosphoramidate (Hobbs, Corbridge & Raistrick, 1953). The value of the exponent was taken as 3.30. It is obvious from an examination of either the bond lengths or the bond valences that the P—N bonds are similar in 2-diethylphosphorylguanidine and phenyl phosphorodiamidate and that these bonds are quite distinct from the 'high-energy' bond in phosphorylcreatine. The reason for the difference is not immediately clear.

Torsional angles in the phosphorylcreatine ion and the 2-diethylphosphorylguanidine molecule are compared in Table 4. Despite the differences in bond order, the torsional angles about the P—N bond are nearly identical in the two compounds.

One of the most obvious differences between the two molecules is that the N of the 'high-energy' P—N bond carries a H atom which is not present in 2-diethylphosphorylguanidine. Since the bond angle at N is close to 120° in both cases, the hybridization at N would be approximately  $sp^2$  with the  $p_z$  orbital directed perpendicular to the plane defined by C(1)—N(1)—P. The orientation of this plane allows efficient overlap between the  $\pi$  system of the guanidino moiety and the  $d$  orbitals of the P atom. However, in phosphorylcreatine the third  $sp^2$  orbital on N forms a  $\sigma$  bond to H while in 2-diethylphosphorylguanidine the third  $sp^2$  orbital contains the lone pair.

It would appear that the major cause of the difference in the P—N bonds has little to do with the N atom but has to do with the electronegativity of the other substituents on P. A similar variation in bond order can be observed in a comparison of the triamidate  $PO(NH_2)_3$  (Bullen, Stephens & Wade, 1969) with the zwitterion  $H_3N^+.PO_3^-$  found in sodium phosphoramidate (Cruickshank, 1964*a*). The average

length of the P—N bond in  $PO(NH_2)_3$  is 1.656 Å, corresponding to a bond valence of 1.25. The P—N length in the zwitterion is 1.77 Å, the single-bond length. A similar change in bond order can be observed in comparing the triester  $(PhO)_3PO$  (Svetich & Caughlan, 1965) with the mono-ester mono-anion,  $PhO(OH)PO_2^-$  (Kennard, Watson, Fawcett, Kerr & Coppola, 1967). In the triester, the phosphoryl bond length is 1.432 Å (bond valence, 1.56) and the average length of the three P—O(ester) bonds is 1.567 Å corresponding to a bond valence of 1.16. In the mono-ester mono-anion salt, the bond P—O(H) is 1.556 Å (bond valence, 1.19); the two P—O bonds are 1.488 Å (bond valence, 1.38) and 1.491 Å (bond valence, 1.37) and the length of the P—O(ester) bond has increased to 1.601 Å. This corresponds to a bond valence of 1.08.

### Conclusion

The various comparisons made in this paper suggest that there are two central features that must be considered in predicting the relative bond orders of the P—N bond in different compounds. If the three other substituents have comparable electronegativities in the two compounds, then conformational effects will be important. If the conformations are similar, the difference in electronegativities will be important. In intermediate cases, the interplay between electronic and steric effects can be very subtle.

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