

Figure 4. Packing of molecules as viewed along the  $c$  axis.

method used in our computation is very crude and is more apt to afford qualitative rather than quantitative interpretations. Nevertheless, we are confident that it may be concluded that the internal strain in this series of molecules imposes the aromatic or olefinic behavior through the influence of torsion angles.

(The geometry of the examined compounds 1–6 is considerably different from that of some related compounds, like [14]annulene, 2,7-diacetoxy-*trans*-15,16-

dimethyl-15,16-dihydropyrene, and *trans*-15,16-diethyl-dihydropyrene, which have been the object of recent crystallographic research.<sup>32–34</sup> In all these cases the configuration of the molecular perimeter is not too far from that of pyrene,<sup>35</sup> and misalignment angles  $\varphi_{ij}$  between adjacent  $2p_z$  orbitals do not exceed  $18^\circ$  for [14]-annulene<sup>32</sup> and  $9^\circ$  for the other two compounds.<sup>33,34</sup> This is in agreement with the absence of systematic alternation of shorter and longer bonds as found in these compounds on the basis of X-ray diffraction evidence.)

Carbon–hydrogen bond distances are in the range 0.94–1.00 Å ( $\sigma$  0.03 Å). The nonbonded distances C(1) . . . C(6) and C(8) . . . C(13) are 2.48 and 2.42 Å (libration corrected values, 2.49 and 2.43 Å), respectively. The range of intermolecular distances is normal. There are only four contacts appreciably shorter than the sum of van der Waals radii (C 1.7, CH<sub>2</sub> 2.0, CH<sub>3</sub> 2.0, O 1.4, H 1.2 Å).<sup>36</sup>

Atom in $x, y, z$	With atom	In position	Distance, Å
C(9)	C(18)	$-x, -y, 2 - z$	3.54
C(18)	C(18)	$-x, -y, 2 - z$	3.81
C(15)	H(14)	$-x, -y, 1 - z$	3.05
O(1)	H(16)	$x, -1/2 - y, -1/2 - z$	2.47

A plotter output of the packing of molecules in the crystal is shown in Figure 4.

(32) C. C. Chiang and I. C. Paul, *J. Amer. Chem. Soc.*, **94**, 4741 (1972).

(33) A. W. Hanson, *Acta Crystallogr.*, **18**, 599 (1965).

(34) A. W. Hanson, *ibid.*, **23**, 476 (1967).

(35) A. Camerman and J. Trotter, *Acta Crystallogr.*, **18**, 636 (1965).

(36) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

## Triethylammonium Tris(*o*-phenylenedioxy)phosphate. Crystal and Molecular Structure<sup>1</sup>

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**Abstract:** Triethylammonium tris(*o*-phenylenedioxy)phosphate (III) was isolated from the reaction of tris(*o*-phenylenedioxy)cyclotriphosphazene (I) with catechol and triethylamine. Crystals of III are trigonal, space group  $P\bar{3}$ , with lattice constants of  $a = 12.046$  (13) Å,  $c = 8.744$  (12) Å, and with  $Z = 2$ . The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to an  $R$  value of 0.043 for 529 unique reflections. The phosphorus atom within each spirophosphate anion is bonded octahedrally to six oxygen atoms. A hydrogen atom was unambiguously located within bonding distance of the nitrogen atom in the cation. Important molecular parameters are: P–O = 1.723 (4), 1.706 (4) Å; N–H = 0.94 (8), H . . . O = 2.36 (7) Å, O–P–O(ring) =  $91.4$  (2)°. The nonbonding transannular O . . . O distance is 2.454 (5) Å.

The unusual ring degradations of spirocyclophosphazenes to spirophosphoranes or spirophosphates in the presence of *o*-aminophenol or catechol and triethylamine have been described previously.<sup>2–6</sup> In one

such reaction, tris(*o*-phenylenedioxy)cyclotriphosphazene (I) reacts rapidly with catechol and triethylamine to yield ammonia and a white, crystalline spirophosphorane (II) or spirophosphate (III) anion.<sup>2,3</sup> Some uncertainty existed with respect to the correct

(1) A preliminary report of this work has appeared: H. R. Allcock and E. C. Bissell, *J. Chem. Soc., Chem. Commun.*, 676 (1972).

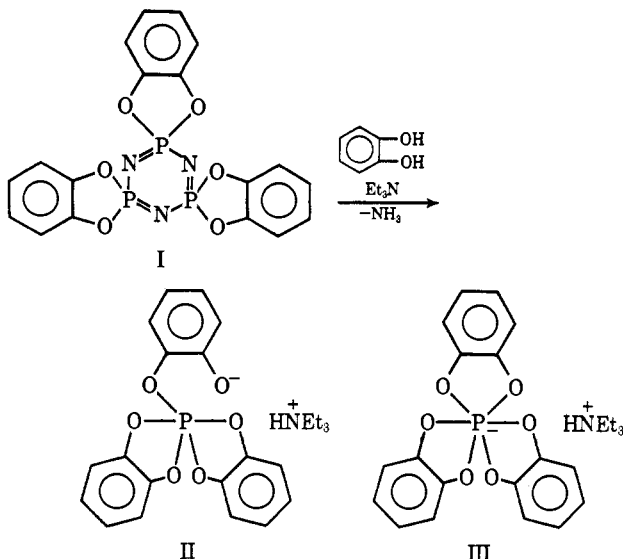
(2) H. R. Allcock, *J. Amer. Chem. Soc.*, **85**, 4053 (1963).

(3) H. R. Allcock, *ibid.*, **86**, 2591 (1964).

(4) H. R. Allcock and R. L. Kugel, *J. Chem. Soc., Chem. Commun.*, 1606 (1968).

(5) H. R. Allcock and R. L. Kugel, *J. Amer. Chem. Soc.*, **91**, 5452 (1969).

(6) H. R. Allcock, "Phosphorus-Nitrogen Compounds," Academic Press, New York, N. Y., 1972, Chapter 14.



formulation of the anion. For example, the ultraviolet spectrum, mass spectrum, and degradation reactions favored the classical pentacoordinate phosphorus structure, II, but infrared spectra of the solid were consistent with structure III.<sup>3</sup> The hexacoordinate phosphorus formulation (III) was also suggested by recent infrared and <sup>31</sup>P nmr data.<sup>7</sup>

With these facts in mind, we have performed an X-ray single crystal study on this compound and have obtained unambiguous evidence for the presence of the hexacoordinate anion (III). This constitutes the first X-ray crystallographic evidence that hexacoordinate organophosphate anions exist as stable entities.

### Experimental Section

**Preparation of Crystals.** Triethylammonium tris(*o*-phenylenedioxy)phosphate (III) was prepared by the procedure described previously.<sup>3</sup> Crystals of this compound were grown by slow evaporation of solvent from a dimethyl sulfoxide solution. The crystals obtained were hexagonal prisms elongated in the direction of the unique axis.

**Crystal Data.** The unit cell is trigonal with  $a = 12.046$  (13) and  $c = 8.744$  (12) Å measured at 25° using diffractometer settings for eight reflections centered on the  $K\alpha$  peak of Mo X radiation ( $\lambda$  0.71069 Å) followed by two cycles of least-squares refinement. Other crystal data include  $V = 1099$  Å<sup>3</sup>,  $D_m = 1.381$  g cm<sup>-3</sup> (by flotation at 25° in carbon tetrachloride and chlorobenzene),  $Z = 2$ ,  $D_c = 1.382$  g cm<sup>-3</sup>, molecular weight 457.4, and  $\mu_{MoK\alpha} = 1.74$  mm<sup>-1</sup>. The space group is  $P\bar{3}$  ( $C_{3h}^1$ , no. 147).

**Collection and Reduction of Data.** A crystal with the approximate dimensions  $0.30 \times 0.07 \times 0.07$  mm, was placed on a Picker FACS-I system for data collection. The mount was such that no specific orientation was employed in order to reduce the likelihood of multiple reflections. The source was powered at 48 kV and 14 mA using Mo X radiation, zirconium filtered in the diffracted beam.

Data were collected in the  $\theta$ - $2\theta$  scan mode with a scan rate of 2°/min for  $2\theta \leq 27$  and 1°/min for  $27^\circ < 2\theta \leq 47^\circ$ . Backgrounds of 20 sec were measured on each side of the scan. The scaling of intensities necessitated by the change of scan rate was achieved by derivation of the mean ratio of the sum of net intensities of three standard reflections. These were monitored throughout the data collection.

Net intensities were derived by the formula  $I = (CTS - (B1 + B2) ST/40)$ , where CTS represents total counts, B1 and B2 background counts, ST the scan time in seconds, and 40 the total time (sec) spent in the counting of backgrounds. In order to separate the data into observed and unobserved sets, the criterion  $I \geq 2.5 \sigma(I)$  was used, where  $\sigma(I)$  is the standard deviation derived from counting statistics by the formula  $\sigma(I) = (CTS + (ST/20)^2 (B1 + B2)/2)^{1/2}$ , where 20 (sec) is the time spent on an individual background measurement, and other symbols are as defined above.

(7) D. Hellwinkel and H.-J. Wilfinger, *Chem. Ber.*, **103**, 1056 (1970).

By this criterion 529 of the 1098 unique reflections measured were observed. These data were corrected for Lorentz and polarization effects, and observed structure factors were derived by setting  $F_o = (I')^{1/2}$ . At this point  $\sigma(F_o)$  was assigned a value of 1.1, 1.0, or 1.2 depending on whether the second term of the expression for  $\sigma(I)$  was negligible, similar to, or very large compared to the first term. Because of the very small linear absorption coefficient (1.74 mm<sup>-1</sup>) and the size of the crystal, no correction for absorption was necessary.

**Solution and Refinement of the Structure.** The structure was solved by interpretation of the locations of only a few strong vectors in a three-dimensional Patterson synthesis. An octahedral arrangement of oxygen around phosphorus was confirmed by a single octahedron of P-O vectors about the origin. The location of this group along the threefold axis,  $d$ , of the space group was given by an exceptionally large vector along the Harker line  $1/3 \ 2/3 \ w$ . A Fourier synthesis based on phosphorus and two oxygen positions revealed the locations of the remaining atoms of the spirophosphate unit. The triethylammonium cation was also located in this map. However, two possible positions for the methylene carbon atom indicated the likelihood of disorder with respect to the chirality of this group. The asymmetric unit of structure consists of one third of the cation and anion.

In the early stages of least-squares refinement each of the two positions for the methylene carbon atom was examined. In one model the isotropic thermal parameter for this atom became very large, and in the other it did not. Using isotropic thermal parameters, a crystallographic  $R$  factor of 0.114 resulted from three cycles of refinement. Use of anisotropic thermal parameters reduced the  $R$  factor to 0.089 after two cycles.

At this point the largest residual in a difference Fourier was 0.8 e/Å<sup>3</sup>, and this corresponded to the other position for the methylene carbon of the cation. In addition, five of the ten hydrogen atoms were easily located in this map at electron densities ranging from 0.28 to 0.38 e/Å<sup>3</sup>.

A static disorder model was indicated for the methylene carbon atom. Accordingly an additional carbon position was added to the model, isotropic thermal parameters were reassigned to all atoms, and occupancy factors were varied for the two methylene carbon positions. No hydrogen atoms were included at this time. The occupancy factors converged to 0.87(5) and 0.24(5) respectively for  $C_7$  and  $C_{7'}$ . These values were normalized to 0.779 and 0.221 and were not varied in further refinements. Using isotropic thermal parameters for the static disorder model, the  $R$  factor was 0.099. After two cycles with the use of anisotropic thermal parameters,  $R$  was 0.073.

At this stage a difference Fourier confirmed the positions of the five previously located hydrogen atoms. The hydrogen atoms on methylene carbon  $C_7$  and methyl carbon  $C_8$  were located at electron densities from 0.26 to 0.41 e/Å<sup>3</sup>. The ten hydrogen atoms were added to the model, with occupancy factors equal to that of  $C_7$  for the five affected by the  $C_7$ - $C_{7'}$  disorder. This model consisted of anisotropic thermal parameters for the 13 nonhydrogen atoms and isotropic thermal parameters for the ten hydrogen atoms. All positional and thermal parameters, except those constrained by space group symmetry, were varied simultaneously during the last cycles of refinement. In the last cycle, the thermal parameter of one hydrogen atom changed by one-half of its esd, while all other shifts were considerably less than this. Both the crystallographic  $R$  factor and the weighted  $R$  factor,  $R_w = ((\sum w(|F_o| - |F_c|)^2) / (\sum w|F_o|^2))^{1/2}$ , had values of 0.043 for the model just described. A final difference Fourier had a maximum residual of 0.15 e/Å<sup>3</sup>.

In refinement, the quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(F_o)$  and  $\sigma(F_o)$  was defined earlier. The scattering factors for P, O, N, and C were those of Ibers<sup>8</sup> while, for H, the values given by Stewart, Davidson, and Simpson<sup>9</sup> were used. No corrections for anomalous dispersion were made and no extinction parameters were added to the model.

Table I lists observed and calculated structure factors.<sup>10</sup> Tables

(8) J. A. Ibers, Ed., "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 201-207.

(9) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(10) Table I will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-3154. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

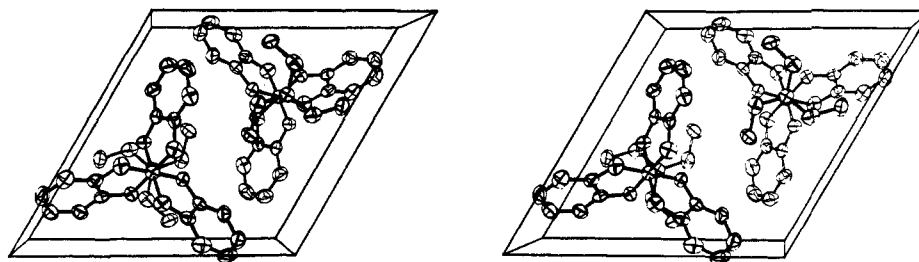
Figure 1. Stereoscopic representation of the unit cell of III viewed down the *c* axis.

Table II. Fractional Crystal Coordinates

Atom	<i>x</i>	<i>y</i>	<i>z</i>
P	-0.3333	0.3333	0.2129 (3)
O <sub>1</sub>	-0.2384 (4)	0.3017 (4)	0.3319 (4)
C <sub>1</sub>	-0.2306 (5)	0.1985 (6)	0.2804 (6)
C <sub>2</sub>	-0.1616 (6)	0.1506 (6)	0.3494 (8)
C <sub>3</sub>	-0.1663 (8)	0.0434 (8)	0.2813 (10)
C <sub>4</sub>	-0.2390 (8)	-0.0129 (7)	0.1537 (10)
C <sub>5</sub>	-0.3079 (8)	0.0382 (7)	0.0833 (8)
C <sub>6</sub>	-0.3025 (6)	0.1445 (6)	0.1493 (6)
O <sub>2</sub>	-0.3624 (4)	0.2073 (4)	0.0976 (4)
N	-0.3333	0.3333	0.6593 (9)
C <sub>7</sub>	-0.4241 (9)	0.1983 (8)	0.7137 (9)
C <sub>7'</sub>	-0.2919 (30)	0.2360 (29)	0.7106 (29)
C <sub>8</sub>	-0.3841 (11)	0.1050 (8)	0.6597 (10)
H <sub>1</sub>	-0.3333	0.3333	0.5513 (93)
H <sub>2</sub>	-0.1097 (58)	0.1896 (58)	0.4521 (68)
H <sub>3</sub>	-0.1197 (68)	0.0100 (69)	0.3369 (75)
H <sub>4</sub>	-0.2339 (53)	-0.0778 (7)	0.0919 (60)
H <sub>5</sub>	-0.3647 (64)	-0.0015 (63)	0.0002 (83)
H <sub>7a</sub>	-0.4172 (83)	0.2064 (85)	0.8465 (103)
H <sub>7b</sub>	-0.5074 (60)	0.1817 (59)	0.6569 (68)
H <sub>8a</sub>	-0.4442 (72)	0.0368 (76)	0.6808 (79)
H <sub>8b</sub>	-0.3240 (93)	0.0934 (99)	0.6923 (109)
H <sub>8c</sub>	-0.3759 (67)	0.1064 (69)	0.5268 (91)

II and III present the positional and thermal parameters, respectively, for the 23 atoms of the asymmetric unit. Bond distances and angles of the molecular units are given in Tables IV and V.

## Results and Discussion

**Structure of the Anion.** The present crystallographic results demonstrate unambiguously that the tris(*o*-

Table IV. Bond Distances (Å)

P-O <sub>1</sub>	1.723 (4)	N-H <sub>1</sub>	0.94 (8)
P-O <sub>2</sub>	1.706 (4)	C <sub>2</sub> -H <sub>2</sub>	1.06 (6)
O <sub>1</sub> -C <sub>1</sub>	1.368 (7)	C <sub>3</sub> -H <sub>3</sub>	0.96 (7)
C <sub>1</sub> -C <sub>2</sub>	1.367 (9)	C <sub>4</sub> -H <sub>4</sub>	0.98 (6)
C <sub>2</sub> -C <sub>3</sub>	1.397 (11)	C <sub>5</sub> -H <sub>5</sub>	0.95 (7)
C <sub>3</sub> -C <sub>4</sub>	1.371 (12)	C <sub>7</sub> -H <sub>7a</sub>	1.20 (11)
C <sub>4</sub> -C <sub>5</sub>	1.398 (11)	C <sub>7</sub> -H <sub>7b</sub>	1.05 (7)
C <sub>5</sub> -C <sub>6</sub>	1.376 (9)	C <sub>8</sub> -H <sub>8a</sub>	0.79 (8)
C <sub>6</sub> -C <sub>1</sub>	1.387 (8)	C <sub>8</sub> -H <sub>8b</sub>	0.88 (9)
O <sub>2</sub> -C <sub>6</sub>	1.358 (7)	C <sub>8</sub> -H <sub>8c</sub>	1.16 (8)
N-C <sub>7</sub>	1.512 (9)		
N-C <sub>7'</sub>	1.552 (30)	H <sub>1</sub> ...O <sub>1</sub>	2.36 (7)
C <sub>7</sub> -C <sub>8</sub>	1.505 (13)	N...O <sub>1</sub>	3.176 (8)
C <sub>7'</sub> -C <sub>8</sub>	1.471 (32)		

phenylenedioxy)phosphate anion exists as an octahedral structure in the solid state. Figures 1 and 2 illustrate the general arrangement of the anion and cation in the crystal structure. The spirophosphate anion and the triethylammonium cation are both located along the threefold axes, *d*, with adjacent sets of ions being related by an inversion point.

It seems clear that the hexacoordinate structure at phosphorus in III provides more favorable opportunities for delocalization of the negative charge than does the alternative pentacoordinate structure, II. However, some slight distortion from a perfect octahedral arrangement is found. Both bonds which involve O<sub>1</sub> are longer than those which involve O<sub>2</sub>, and the O-P-O angles differ by as much as 5.4°. The O<sub>1</sub>-P-O<sub>1'</sub> angle

Table III. Thermal Parameters (Å<sup>2</sup>)

Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>	Eq B
P	0.042 (2)	0.042 (2)	0.023 (1)	0.021 (1)	0.0	0.0	2.81 (5)
O <sub>1</sub>	0.041 (3)	0.042 (3)	0.031 (2)	0.025 (2)	-0.007 (2)	-0.006 (2)	2.86 (7)
C <sub>1</sub>	0.032 (3)	0.038 (4)	0.040 (3)	0.012 (3)	0.007 (3)	0.006 (3)	3.10 (12)
C <sub>2</sub>	0.043 (4)	0.058 (5)	0.057 (4)	0.029 (4)	0.007 (3)	0.005 (4)	4.03 (14)
C <sub>3</sub>	0.057 (5)	0.064 (5)	0.091 (6)	0.039 (4)	0.020 (5)	0.014 (5)	5.27 (16)
C <sub>4</sub>	0.077 (6)	0.042 (5)	0.083 (6)	0.028 (5)	0.039 (5)	-0.001 (3)	5.36 (15)
C <sub>5</sub>	0.064 (5)	0.049 (5)	0.045 (4)	0.021 (4)	0.012 (4)	-0.001 (3)	4.43 (14)
C <sub>6</sub>	0.040 (4)	0.037 (4)	0.038 (3)	0.012 (3)	0.012 (3)	-0.002 (3)	3.29 (12)
O <sub>2</sub>	0.061 (3)	0.052 (3)	0.032 (2)	0.029 (3)	-0.011 (2)	-0.014 (2)	3.77 (8)
N	0.044 (5)	0.044 (5)	0.021 (4)	0.022 (3)	0.0	0.0	2.87 (16)
C <sub>7</sub>	0.048 (6)	0.057 (6)	0.043 (5)	0.019 (5)	0.000 (5)	0.014 (5)	4.16 (29)
C <sub>7'</sub>	0.075 (25)	0.052 (22)	0.038 (16)	0.047 (22)	-0.022 (18)	-0.010 (17)	3.8 (1.4)
C <sub>8</sub>	0.072 (6)	0.041 (5)	0.072 (5)	0.031 (5)	0.015 (5)	0.006 (4)	4.77 (15)
H <sub>1</sub>							1.6 (1.7)
H <sub>2</sub>							4.8 (1.5)
H <sub>3</sub>							6.9 (2.0)
H <sub>4</sub>							4.0 (1.4)
H <sub>5</sub>							6.0 (1.9)
H <sub>7a</sub>							7.6 (2.4)
H <sub>7b</sub>							1.8 (1.3)
H <sub>8a</sub>							2.9 (2.0)
H <sub>8b</sub>							6.1 (3.3)
H <sub>8c</sub>							4.7 (1.7)

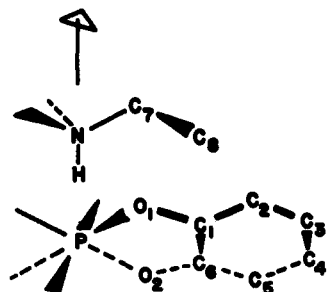


Figure 2. Relative disposition of the anion and cation complex in III.

Table V. Bond Angles (deg)

Five-Membered Ring		Exocyclic Angles at Phosphorus	
O <sub>1</sub> -P-O <sub>2</sub>	91.4 (2)	O <sub>1</sub> -P-O <sub>1(3)</sub>	87.3 (2)
P-O <sub>1</sub> -C <sub>1</sub>	110.9 (3)	O <sub>2</sub> -P-O <sub>2(2)</sub>	88.6 (2)
P-O <sub>2</sub> -C <sub>6</sub>	111.7 (4)	O <sub>1</sub> -P-O <sub>2(3)</sub>	92.7 (2)
O <sub>1</sub> -C <sub>1</sub> -C <sub>6</sub>	112.8 (5)	O <sub>1</sub> -P-O <sub>2(-3)</sub>	178.7 (2)
O <sub>2</sub> -C <sub>6</sub> -C <sub>1</sub>	113.2 (5)		
Phenylene Ring		Triethylammonium Cation	
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	116.8 (7)	C <sub>7</sub> -N-C <sub>7(3)</sub>	110.6 (4)
C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	117.5 (7)	C <sub>7</sub> -N-C <sub>7'(3)</sub>	112.1 (9)
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	121.7 (7)	N-C <sub>7</sub> -C <sub>8</sub>	111.9 (7)
C <sub>5</sub> -C <sub>6</sub> -C <sub>1</sub>	120.9 (7)	N-C <sub>7</sub> -C <sub>8</sub>	111.7 (2.0)
C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	120.8 (6)	C <sub>7</sub> -N-H <sub>1</sub>	108.4 (4)
C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub>	122.3 (6)		
C <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub>	122 (3)	N-C <sub>7</sub> -H <sub>7a</sub>	105 (5)
C <sub>2</sub> -C <sub>3</sub> -H <sub>2</sub>	121 (3)	N-C <sub>7</sub> -H <sub>7b</sub>	100 (4)
C <sub>3</sub> -C <sub>4</sub> -H <sub>3</sub>	114 (4)	H <sub>7a</sub> -C <sub>7</sub> -H <sub>7b</sub>	120 (6)
C <sub>4</sub> -C <sub>5</sub> -H <sub>3</sub>	124 (4)	C <sub>8</sub> -C <sub>7</sub> -H <sub>7a</sub>	109 (5)
C <sub>5</sub> -C <sub>6</sub> -H <sub>4</sub>	124 (3)	C <sub>8</sub> -C <sub>7</sub> -H <sub>7b</sub>	110 (4)
C <sub>6</sub> -C <sub>1</sub> -H <sub>5</sub>	119 (4)	C <sub>7</sub> -C <sub>8</sub> -H <sub>8a</sub>	103 (6)
O <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	124.8 (5)	C <sub>7</sub> -C <sub>8</sub> -H <sub>8b</sub>	130 (6)
O <sub>2</sub> -C <sub>6</sub> -C <sub>1</sub>	126.0 (5)	C <sub>7</sub> -C <sub>8</sub> -H <sub>8c</sub>	111 (4)
		H <sub>8a</sub> -C <sub>8</sub> -H <sub>8b</sub>	99 (8)
		H <sub>8a</sub> -C <sub>8</sub> -H <sub>8c</sub>	105 (6)
		H <sub>8b</sub> -C <sub>8</sub> -H <sub>8c</sub>	105 (7)

is narrowed and the O<sub>2</sub>-P-O<sub>2'</sub> angle is widened. These distortions represent a slight shift of the oxygen octahedron along the crystallographic threefold axis toward the cation. Consequently, all three phenylenedioxyphosphole groups are displaced slightly above the plane occupied by the phosphorus atom with an angle of elevation of 4.5°. These distortions can be visualized either as a response to the electrostatic attraction between the three proximal oxygen atoms (with a delocalized negative charge) and the cation or as a result of hydrogen bonding. The same factors are presumed to be responsible for the slight nonplanarity of the phenylenedioxyphosphole fused ring unit.<sup>11</sup> Specifically, O<sub>1</sub> is somewhat displaced toward H<sub>1</sub>, although the remaining atoms in the phenylenedioxyphosphole unit are close to the mean plane.

It is instructive to compare the molecular parameters found for the anion in III with those derived from a related pentacoordinate phosphorane. The crystal and molecular structure of 2,2,2-triisopropoxy-4,5-(2',2''-biphenylene)-1,3,2-dioxaphospholene (IV) has been determined.<sup>12,13</sup> The P-O bond lengths in that compound vary from 1.58 to 1.75 Å, with the two bonds

(11) The nonplanarity was detected during the final stages of refinement, and this observation thus differs from the result described in a preliminary report.<sup>1</sup>

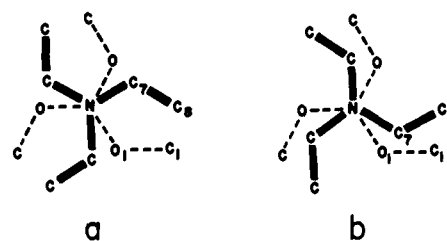


Figure 3. The two anion-cation packing arrangements that result from the two possible locations of C<sub>7</sub> (viewed down the *c* axis). Arrangement a represents the principal contributor to the structure.

which form part of the five membered ring having values of 1.751 and 1.633 Å. The values found in III (1.723 and 1.706 Å) fall in a similar range and are slightly longer than the average P-O bond in the pentacoordinate species. The endocyclic O-P-O angles are similar in the two compounds (91.4° in III and 89° in IV).

The fact that the endocyclic O-P-O bond angle is close to 90° implies that virtually no ring strain is exerted at phosphorus. Similarly, the endocyclic angle at oxygen of 110.9° is sufficiently close to the expected value that no ring strain is indicated here either. However, appreciable angular distortions from 120° are evident at the point of fusion of the five- and six-membered rings. For example, the angle O<sub>1</sub>-C<sub>1</sub>-C<sub>2</sub> is 124.8°, O<sub>1</sub>-C<sub>1</sub>-C<sub>6</sub> is 112.8°, and C<sub>2</sub>-C<sub>1</sub>-C<sub>6</sub> is 122.3° and these values are ascribed to the restrictions of the five-membered ring. The O<sub>1</sub>...O<sub>2</sub> transannular distance is 2.454 (5) Å, which is shorter than 3.0 Å, the sum of the accepted van der Waals radii.<sup>14</sup> The exocyclic O<sub>1</sub>...O<sub>2</sub> distance is only slightly longer (2.481 (5) Å), whereas the exocyclic O<sub>1</sub>...O<sub>1</sub> and O<sub>2</sub>...O<sub>2</sub> distances are shorter still, with values of 2.383 (7) Å.

**Structure of the Cation.** The conformation of the cation unit is illustrated in Figures 1 through 3a, and the molecular parameters are listed in Tables IV and V. An important result from this work was the unambiguous location of a hydrogen atom linked directly to nitrogen and pointed along *c* toward phosphorus. The nitrogen-hydrogen distance is 0.94 Å, as expected for covalent bonding. By contrast, the P...H distance is 2.90 Å and the O<sub>1</sub>...H distance is 2.36 Å, both outside the limits required for direct covalent bonding. However, the oxygen-hydrogen distance is sufficiently short that the possibility of hydrogen bonding as a stabilization force cannot be excluded.

**Relative Arrangement of Anion and Cation.** Figures 1 through 3 illustrate the preferred relative disposition of the anion and cation units. Opposite chiralities of adjacent units in the two ions are found (Figure 3a). However, as discussed in the Experimental Section, evidence was also obtained for the presence of a static disorder system in which the packing arrangement shown in Figure 3b was also present. Molecular models indicate that both arrangements provide satisfactory packing systems, and this provides an explanation for the fact that both structures are found in the crystal.

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