X-Ray Crystal and Molecular Structure of Triethylammonium Tris(*o*-phenylenedioxy)phosphate

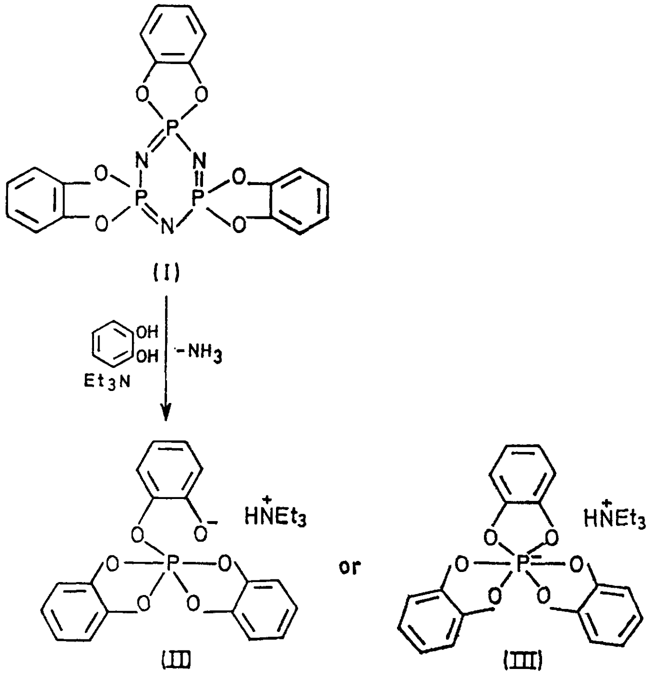
By H. R. ALLCOCK* and E. C. BISSELL

(*Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania* 16802)

Summary An *X*-ray crystal-structure analysis of triethylammonium tris(*o*-phenylenedioxy)phosphate (III) has confirmed the presence of a hexaco-ordinate phosphorus anion; the molecular structure and crystal packing arrangement are described.

TRIS(*o*-PHENYLENEDIOXY)CYCLOTRIPHOSPHAZENE (I) reacts rapidly with catechol and triethylamine to yield a white, crystalline compound with elemental and spectroscopic analyses consistent with structure (II) or (III).[1]

Spectroscopic analyses of solutions of the product were consistent with structure (II), but i.r. spectra of the crystalline solid suggested the hexaco-ordinate phosphate structure, (III). Recently, i.r. and ^{31}P n.m.r. data have been used to favour hexaco-ordinate structures for several spirophosphates, including the anion of (III).[2]



We have now completed an X-ray single crystal investigation of (III) which has confirmed the presence of an octahedral arrangement of bonds at phosphorus. Intensity data were collected in the 2θ scan mode on a Picker FACS-I system, with the use of Mo-K_α radiation. Prior to data collection, the unit cell parameters were refined by least squares techniques using the settings for eight hand-centered reflections. Crystals of (III) are trigonal with the space group $P\bar{3}$. The lattice constants are: $a = 12{\cdot}046$ (13), $c = 8{\cdot}744$ (12) Å, with $Z = 2$. The structure determination and initial refinements were effected with the use of 600 unique reflections observed at the 2σ level based on counting statistics. The structure was solved by Patterson methods and refined to $R = 8{\cdot}9\%$ with anistropic thermal factors for the phosphorus, oxygen, nitrogen and carbon atoms. A difference synthesis at this stage revealed several of the hydrogen positions.

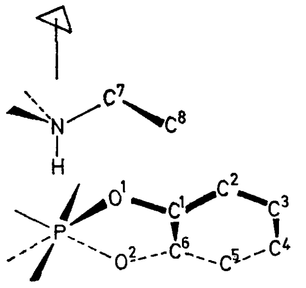


FIGURE 1. *Arrangement of the anion–cation unit at one of the three-fold special postions.*

The spirophosphate anion and the triethylammonium cation are both located along the three-fold axes, *d*, with adjacent sets of ions being related by an inversion point. The molecular parameters within each radial arm of the cation and the anion are defined by the notation shown in Figure 1. Each N–C(7)–C(8) unit in the cation has an opposite chirality to, and lies in a staggered position above, the O(1)–C(1) arrays in the anion (Figure 2). Bond lengths (Å): P–O(1) = 1·723(7), P–O(2) = 1·711(8), O(2)–C(6) = 1·36(1), O(1)–C(1) = 1·34(1), N–C = 1·51(1), C(7)–C(8) = 1·55(2), N–H = 0·99†, H · · · O(1) = 2·32†, H · · · P = 2·90†. Bond angles (°): O(1)–P–O(2) = 91·3(3), O(1)–P–O (non-ring) = 87·7, 88·2, 92·9(4), P–O(1)–C(1) = 111·9(6), P–O(2)–C(6) = 112·4(6), O(1)–C(1)–C(6) = 113·1(9), O(2)–C(6)–C(1) = 111·3, (9), C(7)–N–C(7) = 110·2(7), N–C(7)–C(8) = 111·7(9), C(7)–N–H = 108·7(7).

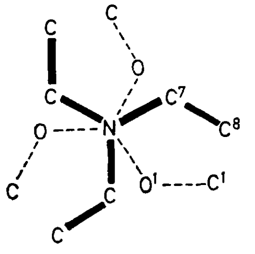


FIGURE 2. *Disposition of radial arms of the triethylammonium unit relative to the adjacent bonds of the spirophosphate anion. Opposite chiralities of both ions are found at the other special position.*

Four points are noteworthy about this structure. First, the presence of the octahedral geometry in the anion has been confirmed. Presumably, the preferred stability of structure (III) over that of structure (II) reflects both the facility with which phosphorus can expand its octet and the symmetry advantages of this arrangement in the solid state. Second, the *o*-phenylenedioxyphosphole unit is essentially planar. Third, the unambiguous location of a hydrogen atom linked directly to nitrogen and pointed along *z* toward phosphorus reflects a preferred steric disposition of the cation. Furthermore, the distance between this hydrogen atom and the three proximal oxygen atoms of the anion is only 2·32 Å, and the possibility exists that the structure is stabilized by hydrogen bonding. Finally, although the model illustrated in Figure 2 converged rapidly during least squares refinement, the first Fourier had indicated a nearly equal occupancy of the two possible conformations of the cation (the one shown in Figure 2, and the model with opposite cation chirality). The thermal parameters for C^7 in the second model diverged rapidly during the least squares treatment, but the existence of this conformation cannot be disregarded. Molecular models suggest that both packing arrangements are acceptable, and a static disorder model appears possible. Refinement to examine this possibility is currently in progress.

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† From interpolated hydrogen position from difference Fourier.

[1] H. R. Allcock, *J. Amer. Chem. Soc.*, 1963, **85**, 4050; 1964, **86**, 2591.

[2] D. Hellwinkel and H.-J. Wilfinger, *Chem. Ber.*, 1970, **103**, 1056.