Crystal and Molecular Structure of the 1:1 Complex of Benzotrifurazan and Triethyl Phosphate

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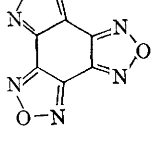
BENZOTRIFUROXAN is reduced in good yield to the corresponding trifurazan by trialkyl phosphites; the product is isolated as a colourless crystalline 1 : 1 complex of benzotrifurazan (I) and the trialkyl phosphate.[1] Molecular weight determinations suggest that the component molecules of this complex remain associated in solution.[2]


(I)

The three-dimensional X-ray diffraction patterns for the trimethyl, triethyl, and tri-isopropyl phosphate complexes have been observed photographically at 20°. All show thermal diffuse scatter and a sharp temperature cut off at a Bragg angle of $\approx 40°$. The diffraction patterns have so far defied detailed interpretation.

The triethyl phosphate complex has been examined at low temperature. On cooling the crystals, the number of observed X-ray reflections increases and their relative intensities are greatly altered without change in space group or significant change in cell dimensions. The most significant alterations in intensity occur above the melting point of triethyl phosphate ($-52°$).

Crystal data (at $-120°$): monoclinic needles, $a = 7{\cdot}702$, $b = 8{\cdot}869$, $c = 13{\cdot}131$ Å; $\alpha = \beta = 90°$, $\gamma = 107{\cdot}0°$; $D_m = 1{\cdot}4040$ g. cm.$^{-3}$ (at 20°), D_c for $2(C_{12}H_{15}N_6O_7P)$, $1{\cdot}4137$ g. cm.$^{-3}$; Mo-K_α radiation $\mu = 1{\cdot}460$ cm.$^{-1}$; space group $P2_1$, 1030 independent reflections were measured on a Hilger and Watts linear diffractometer.

The structure was determined from a 'sharpened'

Patterson function and F_0 syntheses using the 'heavy-atom method'. Because of the approximate mirror plane at $Z = \frac{1}{4}$ (Figure 1) the structure was refined with constraints.[3,4] With individual isotropic temperature factors the reliability factor R is now 15% and the refinement is continuing.

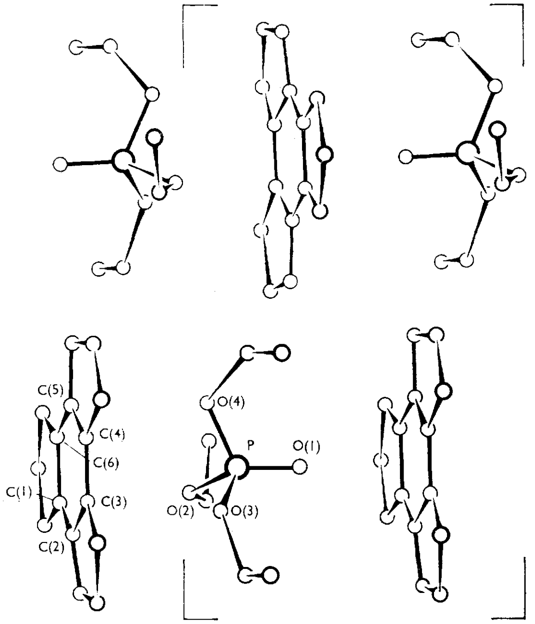


FIGURE 1.

The structure is shown projected perpendicular to [0 1 0] in Figure 1, and projected on to the least-squares best plane of benzotrifurazan in Figure 2.

The phosphate ester and the benzotrifurazan molecules form alternating stacks parallel to *a*. There are no close contacts between atoms in adjacent stacks, but within the stacks the P=O bond is almost co-incident with the three-fold axis of the nearest benzotrifurazan molecule and the oxygen atom 0(1) is only 2·49 Å from the plane of this molecule. The oxygen atoms 0(2), 0(3), and 0(4) are respectively 3·08, 3·11, and 2·97 Å from carbon atoms C(1), C(3), and C(5) of a second benzotrifurazan molecule (Figure 2b). The close approach of oxygen atom 0(1) to the plane of the C_6 ring suggests a specific interaction between the ring π-electron system and this phosphate ester oxygen. Shifts of the order 20 cm.$^{-1}$ have been observed in the P=O stretching frequency. However the visible and u.v. spectrum of the complex is the sum of the spectra of the components and there is no spectroscopic evidence for intramolecular charge transfer. The benzene–iodine complex has a formally similar structure.[5]

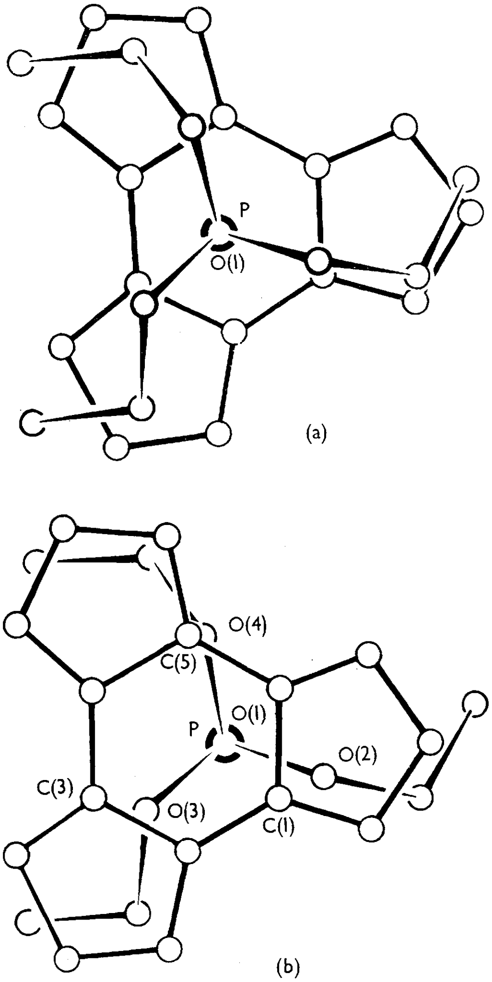


FIGURE 2.

In the benzotrifurazan molecule the intra-heterocyclic and extra-heterocyclic C–C bonds were constrained by analogy to benzotrifuroxan[6] to be 1·43 and 1·44 Å respectively with standard deviations of 0·03 Å, but despite this constraint, at the end of the present refinement, the average values of these bond lengths are 1·46 and 1·41 Å respectively. The C=N bond lengths were constrained to be 1·33 Å with a standard deviation of 0·03 Å and have remained at this value. The average N–O bond length is 1·40 Å. This is another example of the π character of a multicyclic conjugated system collecting on the periphery of the rings.[7]

The bond lengths in the phosphate ester, P=O of 1·45 Å and the mean value for P–O of 1·56 Å are in good agreement with those found in triphenyl phosphate.[8]

We thank the (U.S.) National Institutes of Health for financial support to T.S.C.

(*Received, April* 10*th*, 1968; *Com.* 441.)

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