Further Investigation of the Reaction of Benztrifuroxan with Triphenylphosphine

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IT has been reported[1,2] that amongst the products of the reaction of triphenylphosphine with benztrifuroxan (I) in toluene is a high-melting yellow crystalline solid. The structure of this compound has been determined.

Crystal data: triclinic needles, $a = 8{\cdot}864$, $b = 13{\cdot}502$, $c = 25{\cdot}534$ Å; $\alpha = 97{\cdot}92°$, $\beta = 99{\cdot}13°$, $\gamma = 111{\cdot}47°$; Cu-K_α radiation, $\mu = 11{\cdot}28$ cm.$^{-1}$; $D_m = 1{\cdot}2975$ g.cm.$^{-3}$, D_c for $2(C_{60}H_{45}N_6O_6P_3)$,-$CH_3C_6H_5$, 1·30049 cm.$^{-3}$. Space group $P\bar{1}$, 6218 independent reflections were measured visually from equi-inclination Weissenberg photographs.

The positions of the three phosphorus atoms were unambiguously established from a three-dimensional Patterson function "sharpened to point atoms at rest." The 75 light atom positions were located from an F_0 synthesis phased on the three phosphorus positions. The trial structure, with individual isotropic temperature factors, was refined by a method of least-squares that used a block diagonal approximation to the full matrix with cross terms from atoms in chemically distinct units. A difference synthesis calculated when the reliability factor R was 20% showed that the crystals contained a clathrate toluene molecule at sites disordered about a centre of symmetry.

The R factor is now 16%, the bond length e.s.d.'s are $\ngtr 0{\cdot}02$ Å and the refinement is continuing.

The molecular structure (Figure) may be formulated as (II).

The interatomic distances in the phenyl groups are in the range of accepted values, and the temperature factors for the atoms in the central ring, are similar to the temperature factors of both, the nitrogen atoms bonded to the ring and the carbon atoms bonded to the phosphorus.

The P=N bond lengths vary between 1·54 and

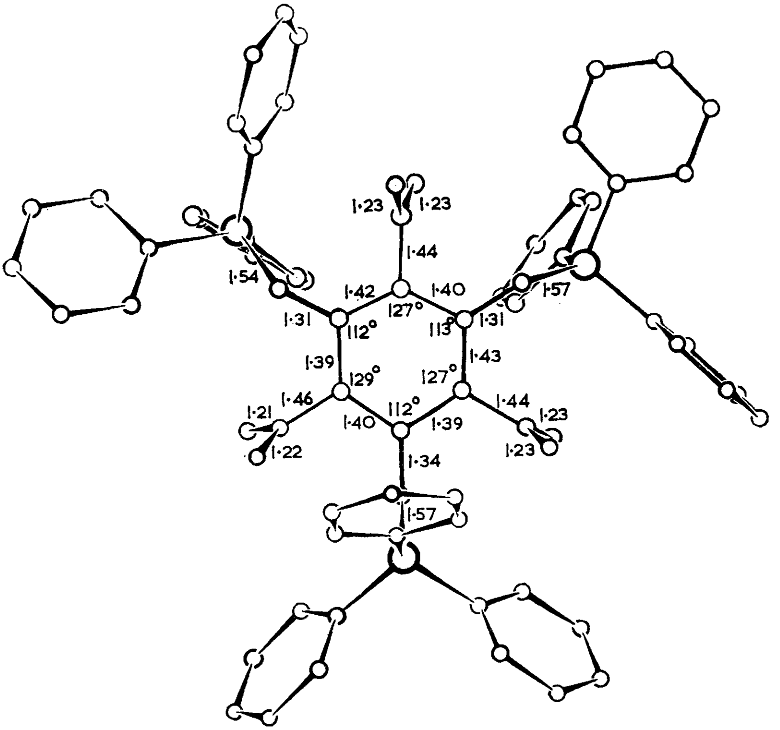
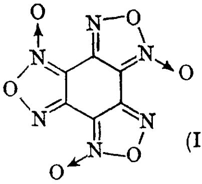


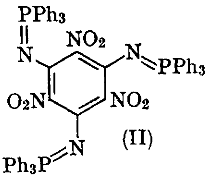
FIGURE. *Yellow compound* (II) *projected perpendicular to the least-squares best plane of the central carbon ring. The interatomic distances are in Å units.*

1·57 Å and compare with an average phosphorus to nitrogen distance of 1·59 Å in $(PNCl_2)_3$,[3] and of 1·62 Å at the phosphorus atom bonded to the phenyl groups in *gem*-$P_3N_3Cl_4Ph_2$.[4]

The average angle in the C–N=P system is 137° and is distorted from the 120° of sp^2 hybridization by a $p\pi$–$d\pi$ interaction between the nitrogen lone pair and an available *d* orbital on phosphorus, which would tend to give a linear system.[5] There is also some delocalization of the ring system over this nitrogen,[6] as the C–N distances are intermediate in value between 1·43 Å for C–N[7] and 1·24 Å for C=N.[1]



(I)



(II)

The planes through the nitro-groups are almost at right-angles to the plane of the central C_6 ring and these groups make no abnormally short contacts to the other substituents; the central ring, however, is considerably distorted. This effect has been observed in other atomatic nitro-compounds.[8] It has been suggested[9] that the distortion is caused by repulsions of the σ-bonding electrons and not by π-bond interactions.

The yellow compound, which may be considered as a stable Wittig intermediate, is important in the understanding of the complex reactions of triphenylphosphine with benztrifuroxan.

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