Investigation of the Reaction of Benztrifuroxan with Triphenylphosphine

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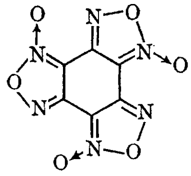
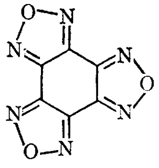
REDUCTION of benztrifuroxan (I) with trialkyl phosphites has been found to give crystalline 1 : 1 molecular complexes of benztrifurazan (II) with the corresponding trialkyl phosphates.[1]



(I)



(II)

In contrast, the reaction of benztrifuroxan (I) with triphenylphosphine is complex, and gives no benztrifurazan (II). The product is a mixture of triphenylphosphine oxide with a large number of coloured compounds, which are difficult to separate. Four of these, a dark green, a lighter green, a red, and a yellow compound, have been obtained as crystalline solids, and all contain nitrogen and phosphorus.

The physical data for the compounds gave little information. The compounds decomposed on analysis and in the inlet to the mass spectrometer. Spectroscopic data indicated the presence of P–Ph groups in all the compounds, and N–H or O–H groups in the red compound.

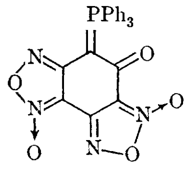
As only small quantities were available, it was decided to examine the compounds by X-ray crystallography. The structure analyses of the dark green and the red compounds are reported here.

Crystal data: *dark green compound.* Triclinic pinacoidal, $a = 15{\cdot}44$, $b = 11{\cdot}63$, $c = 10{\cdot}35$ Å; $\alpha = 114{\cdot}12°$, $\beta = 96{\cdot}63°$, $\gamma = 120{\cdot}63°$; *space group* $P\bar{1}$; Cu-K_α radiation $D_m = 1{\cdot}378$ g.cm.$^{-3}$, which gave an estimated molecular weight of 549 and two molecules per unit cell. From the structure analysis, the formula is $C_{30}H_{21}N_4O_5P$; $M = 548$; $Z = 2{\cdot}005$; $\mu = 13{\cdot}6$ cm.$^{-1}$ 2,500 independent reflections were measured visually from equi-inclination Weissenberg photographs.

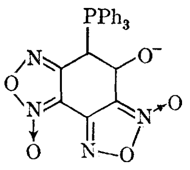
Crystal data: *red compound.* Triclinic pinacoidal; $a = 9{\cdot}59$, $b = 10{\cdot}82$, $c = 11{\cdot}81$ Å; $\alpha = 96{\cdot}70$, $\beta = 94{\cdot}90$, $\gamma = 90{\cdot}83$; space-group $P\bar{1}$; Cu-K_α radiation. $D_m = 1{\cdot}477$ g. cm.$^{-3}$, which gave an estimated molecular weight of 503 and two molecules per unit cell. From the structure analysis, the formula is $C_{24}H_{17}N_6O_5P$; $M = 502$; $Z = 2{\cdot}007$; $\mu = 15{\cdot}44$ cm.$^{-1}$ 3670 independent reflections were measured visually from equi-inclination Weissenberg photographs.

In both analyses, the positions of the phosphorus atom and three phenyl groups were established from a three-dimensional Patterson function "sharpened to point atoms at rest". The remaining atoms were located from a series of F_0 syntheses. The trial structures, with individual isotropic temperature-factors, were refined by a least-squares method that used a block-diagonal approximation to the full matrix with cross terms from atoms in chemically distinct units. The reliability factor R is 16% for both compounds, and the bond length e.s.d's are $\ngtr 0{\cdot}02$ Å. Refinement is to be continued with anisotropic temperature-factors.

The molecular structure of the dark green compound (Figure 1) may be formulated as (III) or (IV).



(III)



(IV)

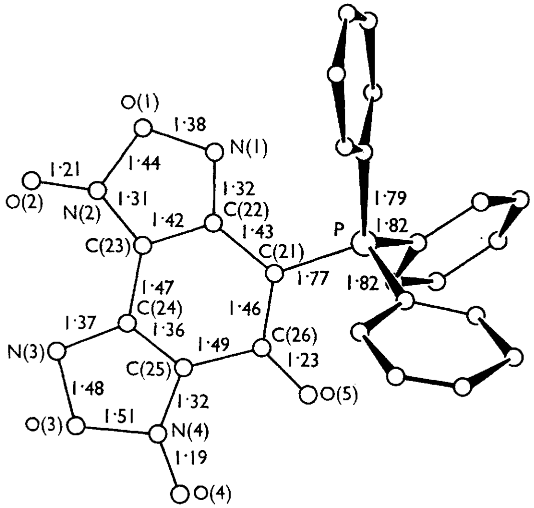
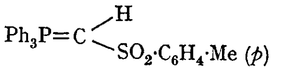


FIGURE 1.

The dark green compound (III) *projected perpendicular to the least-squares best plane of the carbon ring of the benztrifuroxan fragment. The interatomic distances are in Å units.*

The interatomic distances in the phenyl groups are in the range of accepted values, and those in the furoxan rings agree with the values recently published for benztrifuroxan.[2] The P–C bond lengths vary between 1·77 and 1·82 Å; these are similar to the P–C lengths in structure (V),[3]



$$\mathrm{Ph_3P{=}C}\genfrac{}{}{0pt}{}{\diagup\mathrm{H}}{\diagdown\mathrm{SO_2{\cdot}C_6H_4{\cdot}Me}\ (p)} \qquad \text{(V)}$$

except that in contrast to the latter, no one length is significantly shorter than any other. The bond lengths in the C(21)–C(26)–O(5) system are very similar to those in the quinones.[4] The correct representation for the compound is probably (III) ⟷ (IV). The crystals contain two molecules of benzene of crystallisation in each unit cell.

The dark green compound is probably formed by an aromatic substitution by triphenylphosphine. Similar reactions have been reported for 2,5-dichloro-*p*-benzoquinone[5] and recently for *o*-dinitrobenzene.[6]

The red compound (Figure 2) is a hydrogen-bonded complex of triphenylphosphine oxide and an unusual difurazan (VI).

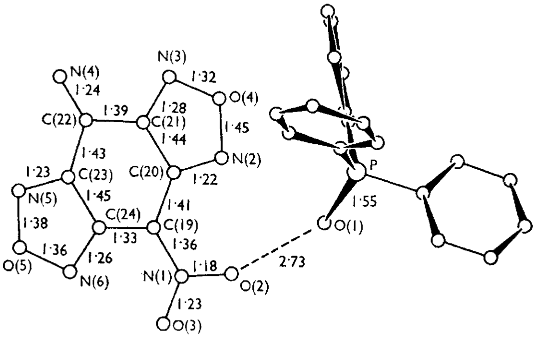
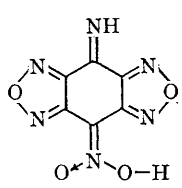


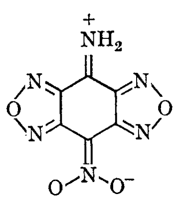
FIGURE 2.

The hydrogen bonded complex found in the red compound (VI) *projected perpendicular to the least-squares best plane of the bentrifuroxan fragment. The interatomic distances are in Å units.*

The interatomic distances in the triphenylphosphine oxide are similar to those of triphenylphosphine;[7] the P=O distance is 1·55 Å. The bond lengths in the furazan rings, which are very different from those reported in a two-dimensional analysis of benzofurazan,[8] are consistent with double bonds between carbon and nitrogen and single bonds between nitrogen and oxygen. The C–C bonds in the furazan rings correspond to the "single" bonds in quinones[4] and the C–C bond in dimethylglyoxime.[9] The C–N bond lengths not in the furazan rings are in agreement with structure (VI) rather than its tautomer(VII). The short



(VI)



(VII)

O–O contact (2·73 Å) between the phosphoryl and nitro-groups is presumed to be a hydrogen bond. Other physical data indicated that the compound can exist in the tautomeric form (VII) in solution.

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