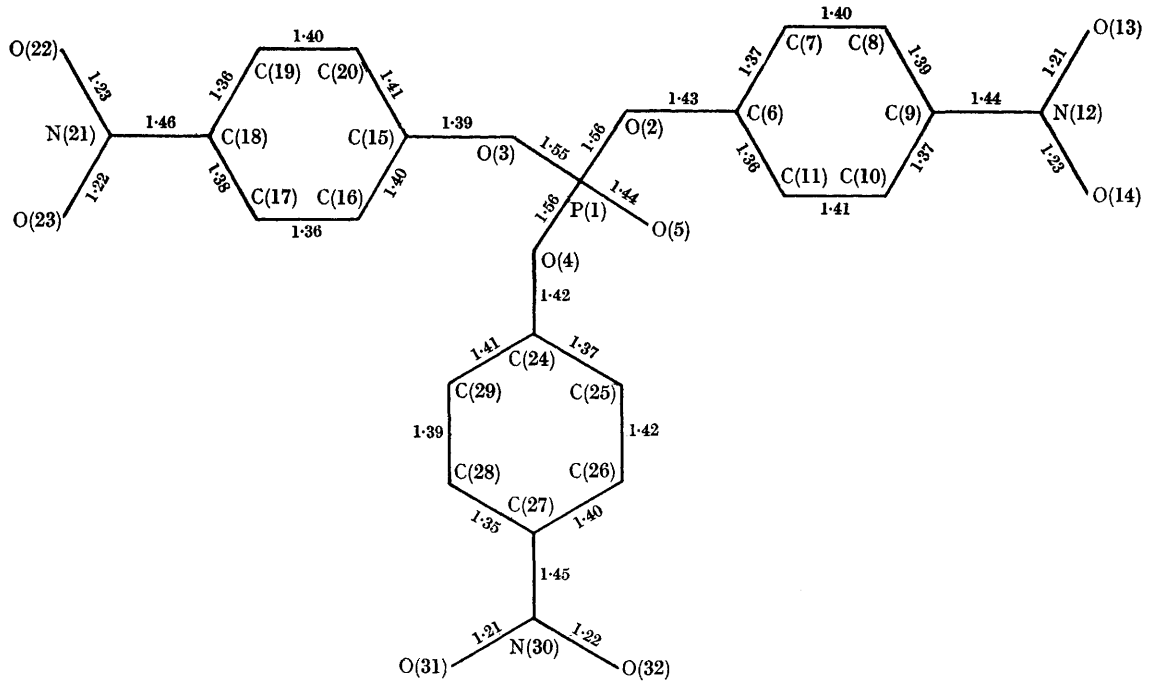
The Crystal and Molecular Structure of Tri-*p*-nitrophenyl Phosphate

By MAZHAR-UL-HAQUE and CHARLES N. CAUGHLAN
(*Department of Chemistry, Montana State University, Bozeman, Montana* 59715)

THE effect of electron-attracting substituents on phenyl phosphates is of interest in considering the kinetics and mechanisms of hydrolysis of the organic phosphates. It has been shown that the hydrolysis of monoaryl phosphates shows acid catalysis only if an electron-attracting substituent is present on the aryl group.[1] Apparently the hydrolysis of tri-*p*-nitrophenyl phosphate has not been reported but both the kinetics and the structure of triphenyl phosphate have been studied[1,2] and thus a comparison of triphenyl phosphate with tri-*p*-nitrophenyl phosphate is significant.

An *X*-ray study of tri-*p*-nitrophenyl phosphate gave the following results: $(C_6H_4NO_2)_3PO_4$, M = 461·28, monoclinic, $a = 17{\cdot}36, b = 8{\cdot}49, c = 12{\cdot}97$ Å, $\beta = 91{\cdot}35°$, $D_m = 1{\cdot}594$ g. cm.$^{-3}$, $Z = 4$, $D_c = 1{\cdot}602$. Space Group $P2_1/c$ (No. 14); $\mu = 1{\cdot}37$ cm.$^{-1}$ for Mo-K_α radiation.



FIGURE

The intensities of 1350 independent reflections were measured with a diffractometer using Mo-K_α radiation and the structure solved from the Patterson function. The structure was refined by least-squares analysis, using anisotropic temperature factors, to a final R of 7·2%. The structure with bond distances is shown in the Figure. The phosphate bond angles are O(2)–P(1)–O(3) = 105°; O(2)–P(1)–O(4) = 101°; O(2)–P(1)–O(5) = 117°; O(3)–P(1)–O(4) = 102°; O(3)–P(1)–O(5) = 112°; O(4)–P(1)–O(5) = 117°. The average standard deviations are 0·015 Å for bond distances and 0·4° for bond angles. There appear to be no significant differences in the P–O or C–O bond lengths of tri-*p*-nitrophenyl phosphate and triphenyl phosphate but none of the O–P–O bond angles are as small as the 96·6° reported in triphenyl phosphate.[2]

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[1] P. W. C. Barnard, C. A. Bunton, D. Kellerman, M. M. Mhala, B. Silver, C. A. Vernon, and V. A. Welch, *J. Chem. Soc.* (*B*), **1966**, 227; C. A. Bunton, D. Kellerman, K. G. Oldham, and C. A. Vernon, *ibid.*, p. 292.
[2] G. W. Svetich and C. N. Caughlan, *Acta Cryst.*, 1965, **19**, 645.