Crystal and Molecular Structure of 2,2,3,4,4-Pentamethyl-1-phenylphosphetan 1-Oxide($C_{14}H_{21}PO$)

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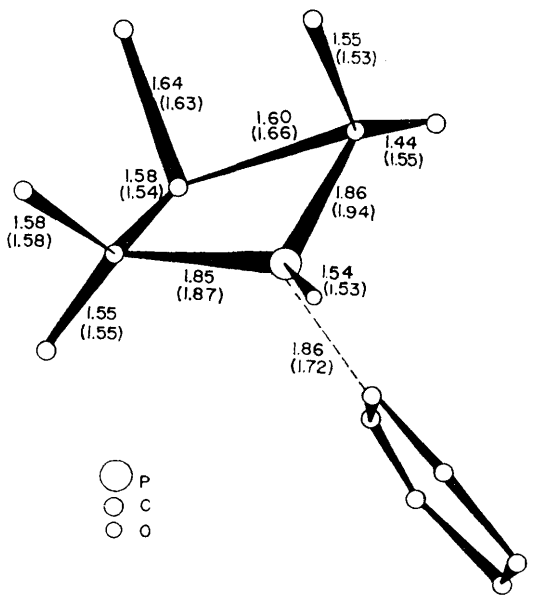
THE structure of 2,2,3,4,4-pentamethyl-1-phenylphosphetan 1-oxide was determined in order to understand the bonding and reactions at the phosphorus atom. Cremer and Chorvat[1] synthesized this compound and proposed its structure on the basis of n.m.r. studies.†

Crystals of 2,2,3,4,4-pentamethyl-1-phenylphosphetan-1-oxide† are orthorhombic, space group $Pca2_1$, $a = 12{\cdot}34$, $b = 15{\cdot}91$, and $c = 14{\cdot}9$ Å, $Z = 8$ with two crystallographically unrelated molecules in the asymmetric unit. Intensity data were collected on a General Electric XRD-5 diffractometer equipped with single-crystal orienter using a scintillation counter for detector. Zirconium-filtered Mo-radiation was used. Intensities were measured with a θ—2θ scan, counting background on each side of the peak. The intensities of 943 reflections were above background. The structure was solved by locating two independent phosphorus atoms from the Patterson and Fourier syntheses. Refinement, not yet complete, has reduced R to 10·5% for all observed intensities. The structure, with pertinent bond distances, is shown in the Figure. The bond angles around both phosphorus atoms are much distorted from tetrahedral, ranging from 81·8—118·0° in one case and 84·8—126·2° in the other, the small angles being those in the heterocyclic rings. The carbon angles in the rings are 85·0 (88·1), 102·6 (102·1), and 84·3 (82·6°). The phenyl groups are normal with the carbon–carbon distances averaging 1·40 Å and the angles 120°. The phosphorus–oxygen distance is long for a phosphoryl bond. Average standard deviations are



FIGURE

† Crystals were supplied bp Dr. Cremer, Illinois Institute of Chemical Technology, Chicago.

0·03 Å for the bond distances and 1·5° for bond angles.

The four-membered ring is not planar in either molecule. In one molecule P and C(3) are 0·09 and 0·12 Å above the best least-squares plane, while C(2) and C(4) are 0·11 Å below the plane, and in the other P and C(3) are 0·11 and 0·16 Å below, while C(2) and C(4) are 0·13 and 0·14 Å above the plane. In 2,3,4-trimethylpentane-2,4-phosphinic acid monohydrate the departure from planarity is the same.[2] The dihedral angles between P–C(2)–C(3) and P–C(4)–C(3) are 19·7 and 24·8° respectively and the dihedral angles between C(10)–P–O(16), and C(2)–P–C(4), are 91·1 and 90·8° respectively for the two molecules. In both molecules the methyl group at C(3) is *cis* to the phenyl ring.

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[1] S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 1967, **32**, 4066; S. E. Cremer and R. J. Chorvat, *Tetrahedron Letters*. 1968, **4**, 413.

[2] D. D. Swank and C. N. Caughlan, *Chem. Comm.*, 1968, 1051.