Tetrahedron Letters No. 11, pp 913 - 916, 1975. Pergamon Press. Printed in Great Britain.

MOLECULAR STRUCTURE OF TRIMESITYLPHOSPHINE:
AN UNPRECEDENTED ENLARGEMENT OF VALENCE BOND ANGLES IN A PHOSPHINE

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(Received in USA 6 January 1975; received in UK for publication 5 February 1975)

The values of bond angles at phosphorus in all known simple acyclic phosphines range from slightly above 90°[1] to slightly below 104°.[2,3] We have found that the C-P-C bond angles in trimesitylphosphine assume values from 107.9° to 111.2° (average 109.7°), and thus significantly exceed the previously reported upper bound. To our knowledge, this extraordinary and unprecedented expansion of the valence bond angles, which is obviously due to nonbonded repulsive interaction among the three bulky mesityl (2,4,6-trimethylphenyl) groups,[4] represents the greatest flattening of the phosphorus pyramid in a phosphine on record.

Trimesitylphosphine (1) crystallizes from ethanol-chloroform as small acicular crystals. The crystal data for 1 are: triclinic, space group $P\bar{1}$, $a = 8.191(3)$, $b = 16.447(5)$, $c = 18.667(6)$ Å, $\alpha = 104.82(3)$, $\beta = 97.74(3)$, $\gamma = 100.07(3)$°, $Z = 4$. The intensity data were measured on a Hilger-Watts four circle diffractometer from a crystal which was 0.08 x 0.10 x 0.65 mm in size. Of the 8721 accessible reflections with $\theta < 76°$, 4964 were considered observed [$I > 2.5\ \sigma\ (I)$]. Since there are four molecules in a cell of symmetry $P\bar{1}$, there are two molecules in the unit cell which are not related by crystallographic symmetry. The structure was solved by a multiple solution procedure.[5] Block-diagonal least squares was used for the final cycles of refinement. The matrix was partitioned into only two blocks, one for each independent molecule. Anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but were not refined. The final discrepancy index is R = 0.065 for the 4964 observed reflections.

The conformations of the two independent molecules are shown in Figure 1. The average values of the bond lengths and the bond angles in each of the two molecules are given in Figure 2.

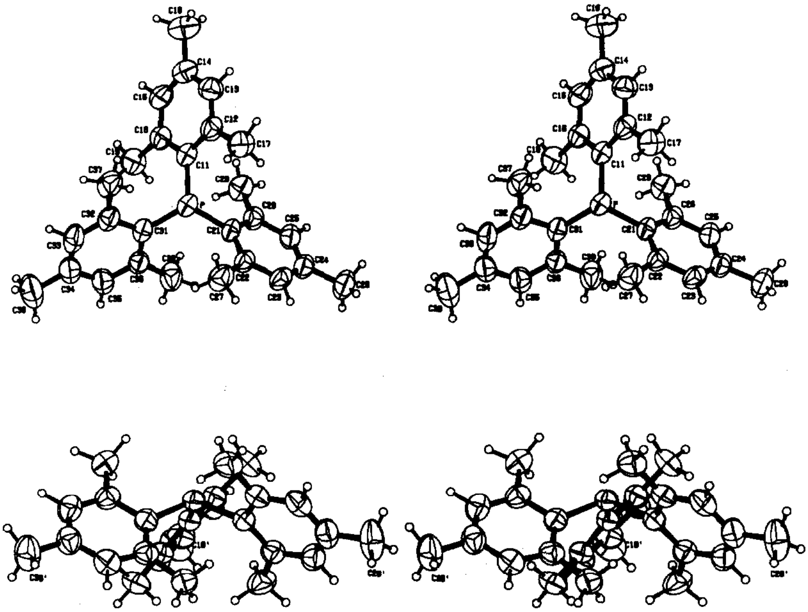

Figure 1. Stereodrawings of the two independent molecules of 1. The thermal ellipsoids are scaled to the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary size. The upper drawing is of the unprimed molecule viewed along its idealized three-fold axis from above the PC_3 pyramid. The lower drawing shows the primed molecule in a view normal to its three-fold axis.

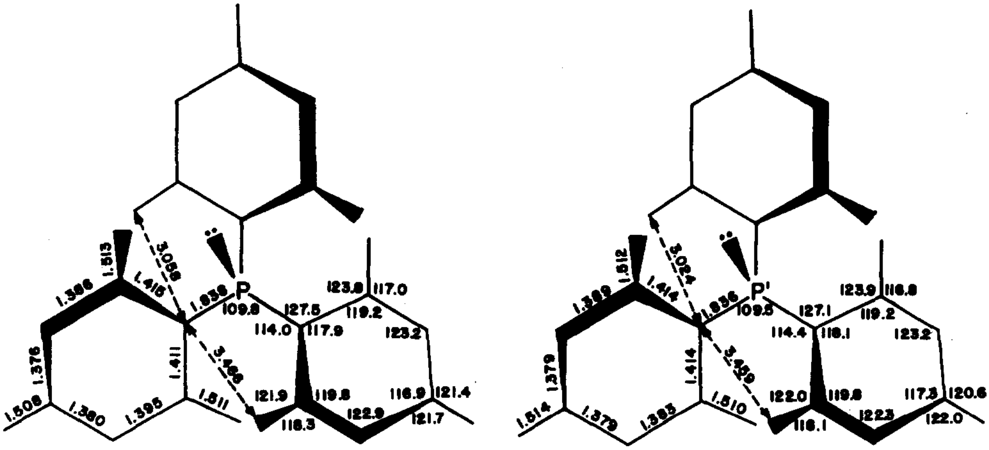

Figure 2. The average values of the bond lengths and bond angles in the unprimed molecule (left) and the primed molecule (right) of 1. Each value is the average of the three independent, but structurally equivalent, values in the given molecule.

Dihedral angles between each phenyl ring and its reference plane (the plane defined by the P-C bond and the idealized three-fold axis of the PC_3 unit) are listed in Table I and the individual C-P-C angles are shown in Table II. Examination of Table I shows that, whereas the primed molecule has approximate C_3 symmetry, the other independent molecule deviates significantly from C_3 symmetry. The variation in the angle of twist of the mesityl groups about their C-P bonds, however, does not appear to affect the size of the C-P-C angle. There are no significant differences in the six mesityl groups when one compares equivalent parameters. The mean of the nine standard deviations, each calculated for the average of six chemically equivalent lengths, is 0.007 Å. The mean of the twelve standard deviations calculated for the C-C-C angles is 0.5°.

Table I. Dihedral Angles (degrees) between the Planes of the Phenyl Rings and the Corresponding Reference Planes.

Ring	Angle	Average
C(11) ,..., C(16)	43.3	43.7
C(21) ,..., C(26)	37.7	
C(31) ,..., C(36)	50.1	
C(11)',..., C(16)'	44.8	44.5
C(21)',..., C(26)'	44.6	
C(31)',..., C(36)'	44.1	
all six rings		44.1

Table II. Central Angles (degrees) about the Phosphorus Atoms.

Atoms	Angle	Average
C(11) - P - C(21)	108.5	109.8
C(21) - P - C(31)	111.2	
C(31) - P - C(11)	109.7	
C(11)'- P - C(21)'	110.1	109.5
C(21)'- P - C(31)'	110.6	
C(31)'- P - C(11)'	107.9	
all six C-P-C angles		109.7

Acknowledgment. We thank the National Science Foundation (MPS74-18161) for support of this work.

References and Notes

1. For example, F-P-F = 91.5° in dimethylaminodifluorophosphine (E. D. Morris, Jr. and C. E. Nordman, Inorg. Chem., 8, 1673 (1969)) and C-P-H = 91.9° in trifluoromethylphosphine (I. Y. M. Wang, C. O. Britt, A. H. Cowley, and J. E. Boggs, J. Chem. Phys., 48, 812 (1968)).
2. The C-P-C bond angles in triphenylphosphine are 103.57°, 102.07°, and 103.34° (J. J. Daly, J. Chem. Soc., 3799 (1964)).
3. The C_1-P_2-C_{Ph} angle in ethylene-1-(diphenylphosphino)-1-(triphenylphosphonium)-2-(diphenylamino)-2-(phenylamide) is 108.2° (F. K. Ross, L. Manojlovic-Muir, W. C. Hamilton, F. Ramirez, and J. F. Pilot, J. Amer. Chem. Soc., 94, 8738 (1972)).
4. As in the case of trimesitylmethane; see preceding communication.
5. G. Germain, P. Main, and M. M. Woolfson, Acta Cryst., B26, 274 (1970).