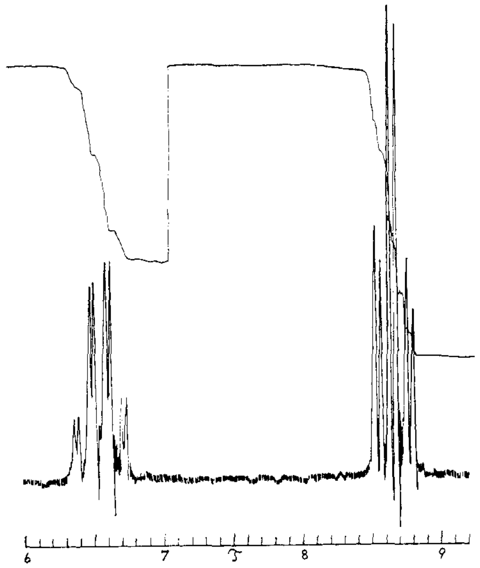
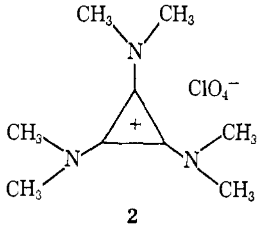


Figure 1. The 60-MHz spectrum of 1,2-bisdiethylamino-3-chlorocyclopropenyl perchlorate.

perchlorate was quantitatively obtained by the following procedures. Excess dimethylamine was added to tetrachlorocyclopropene in methylene chloride at 0° and stirred at this temperature for 5 hr and then at room temperature for 17 hr, and then refluxed for 3 hr. After cooling to room temperature, 70% perchloric acid was added to the solution followed by further stirring for several minutes. The organic layer was separated and dried over sodium sulfate. After removal of the solvent, trisdimethylaminocyclopropenyl perchlorate (**2**) was quantitatively obtained[6] [**2** ($C_9H_{18}N_3ClO_4$), $\tau^{\mathrm{CDCl_3}}$ 6.84 (sharp singlet with half-line width 0.3 Hz); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 233 mμ ($\log \epsilon$ 4.22)]. Comparison of the ir spectrum with the results of a normal coordinate analysis[7] indicates the expected D_{3h} symmetry for the trisdimethylaminocyclopropenyl cation. The



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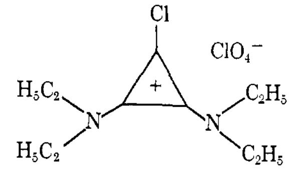
233-mμ band is assigned to an intramolecular charge-transfer band from the amino group to the cyclopropenyl ring by the modified Pariser–Parr–Pople type calculation (variable integrals method[8]) and solvent effect. Piperidine, morpholine, *N*-methylaniline, and *N*-ethylaniline have similarly been treated with tetrachlorocyclopropene to afford the corresponding triaminocyclopropenyl perchlorates (Ia, Ib, Ic, and Id, respectively) in quantitative yield [Ia [$C_{18}H_{30}N_3O_4Cl$], Y = N(C_6H_5); mp 146° dec; $\tau^{\mathrm{CF_3CO_2D}}$ 6.50 (m, 12 H), 8.25 (m, 18 H); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 237 mμ ($\log \epsilon$ 4.40); Ib [$C_{15}H_{24}N_3O_7Cl$], Y = N(C_6H_4)O; mp 270° dec; $\tau^{\mathrm{CDCl_3}}$ 6.30 (m, 12 H), 5.90 (m, 12 H); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 234 (4.37); Ic [$C_{24}H_{24}N_3O_4Cl$], Y = N(CH_3)C_6H_5; $\tau^{\mathrm{CDCl_3}}$ 6.70 (s, 9 H), 2.80 (m, 15 H); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 230 (4.18), 279 (4.45); Id [$C_{27}H_{30}N_3O_4Cl$], Y = N(C_2H_5)C_6H_5; $\tau^{\mathrm{CDCl_3}}$ 9.00 (t, 9 H), 6.60 (q, 6 H), 2.70 (m, 15 H); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 230 (4.18), 277 (4.30)]. Even in the reaction of diphenylamine, the triaminocyclopropenyl perchlorate was exclusively obtained. In contrast to the above cases, the reaction of diethylamine with tetrachlorocyclopropene afforded exclusively 1,2-bisdiethylamino-3-chlorocyclopropenyl perchlorate (**3**). As is seen in Figure 1, the nmr spectrum [$\tau^{\mathrm{CDCl_3}}$ 8.62 (a pair of triplets, 12 H), 6.50 (a pair of quartets, 8 H)] showed the existence of two kinds of ethyl groups whose magnetic environments are slightly different from each other, suggesting that the rotational barrier about the C–N bond is enhanced by the increased double bond character of the C–N linkage [$\lambda_{\max}^{\mathrm{CH_3CN}}$ 210 mμ (end absorption)]. Diisopropylamine has also afforded 1,2-bisdiisopropylamino-3-chlorocyclopropenyl perchlorate in 60–70% yield [$\tau^{\mathrm{CDCl_3}}$ 8.55 (doublet, 4 H), 6.00 (sesquitet, 24 H); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 235 (sh, $\log \epsilon$ 3.20), 210 mμ (end absorption)].



3

All of these aminocyclopropenyl perchlorates are soluble in polar solvents stable in the atmosphere and not hygroscopic. Especially the triaminocyclopropenyl perchlorates are very stable to water (even in hot) in contrast to trichloro- and triphenylcyclopropenyl perchlorates. The chemical behavior of the aminocyclopropenyl cations will be published soon.

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(6) No aminocyclopropenyl perchlorates have been found in the aqueous layer.

(7) To be published later.

(8) Z. Yoshida and T. Kobayashi, *Theor. Chim. Acta*, **19**, 377 (1970); *J. Chem. Phys.*, in press.

X-Ray Analysis of 1-Phenyl-4-phosphorinanone. Evidence for a Chair Conformation with an Axial Substituent[1]

Sir:

The principles of conformational analysis are increasingly being applied to saturated, six-membered heterocycles.[2,3] The system containing trivalent phosphorus (phosphorinane) remains little studied, however, and no direct evidence has been reported for the shape of the ring. Phosphorus is pyramidal and a high barrier to inversion makes possible in certain cases the isolation of stable configurational isomers. In the phosphorinane family, this property leads to the existence of separable cis,trans forms of 1,4-dialkyl-4-phosphorinanols.[4] No direct determination of the position (axial or equatorial) adopted by a substituent on phosphorus in such systems has been reported. We have performed the first X-ray single-crystal analysis

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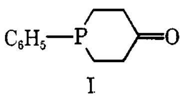
(1) Supported in part by U. S. Public Health Service Research Grant No. CA-05507 from the National Cancer Institute.

(2) E. L. Eliel, *Accounts Chem. Res.*, 3, 1 (1970).

(3) C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, 4, 39 (1969).

(4) H. E. Shook, Jr., and L. D. Quin, *J. Amer. Chem. Soc.*, **89**, 1841 (1967).

of a phosphorinane derivative (1-phenyl-4-phosphorinanone (I)); the shape of the ring is clearly revealed, and the position of the phenyl group established. While the results apply strictly to the solid state, there is increasing



I

evidence for other systems that the conformation found in the crystal corresponds closely to one of the major conformers in solution.[2,3,5]

Crystals of I were obtained[6] from a melt (mp 42.5–43.5°, lit. 43–44°) and sealed in a thin-walled capillary. There are eight units of $C_{11}H_{13}OP$ in the orthorhombic unit cell, space group $Pbca$, with dimensions $a = 8.95$, $b = 21.99$, $c = 10.63$ Å. Three-dimensional data were recorded by equiinclination Weissenberg photography of the 0–8kl layers and visually estimated. The structure was solved by the heavy-atom method and the atomic parameters (anisotropic temperature factors for P, C, O; isotropic for H) refined by full-matrix least-squares calculations[7] to a conventional R of 0.073 over 1368 reflections. The most important dimensions are given in the legend of Figure 1 which shows the molecular conformation.

The chair conformation for the phosphorinane ring is established by this analysis. Of particular note is the *axial* orientation of the phenyl group. By adoption of this conformation, considerable overcrowding of the phenyl ring and diaxial protons results. Relief from the nonbonded interactions is gained by tilting away of the phenyl ring and by some flattening of the phosphorinane ring at phosphorus. The former is manifested in the phosphorus displacement of 0.29 Å from the least-squares plane through the phenyl-ring carbon atoms (root-mean-square deviation 0.005 Å), the displacement being to the opposite side of the plane from the other atoms of the phosphorinane ring. It is not immediately obvious why the axial rather than equatorial position is adopted by the phenyl ring. Transannular dipole–dipole interactions have been invoked to explain the relatively large population of axial conformer present in 4-hydroxy-[8] and 4-chlorocyclohexanones.[9] In seeking an explanation for the present observations, it would be of interest to establish the preferred conformation in other phosphorinane derivatives wherein such an interaction could not exist.

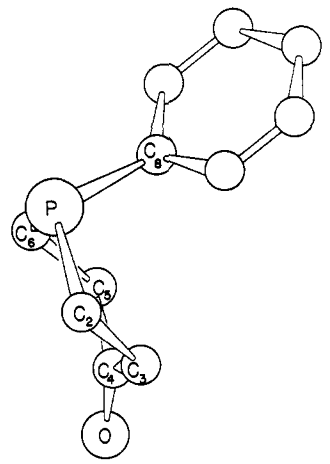


Figure 1. Conformation of 1-phenyl-4-phosphorinanone. Molecular dimensions are $P–C_2 = 1.837$, $P–C_6 = 1.838$, $P–C_8 = 1.837$, $C_2–C_3 = 1.527$, $C_3–C_4 = 1.499$, $C_4–C_5 = 1.496$, $C_5–C_6 = 1.530$, $C_4–O = 1.209$, average phenyl C–C = 1.393 Å; $C_2PC_6 = 98.2°$, $C_2PC_8 = 103.9°$, $C_6PC_8 = 101.8°$, $PC_2C_3 = 117.0°$, $PC_6C_5 = 115.9°$, $C_2C_3C_4 = 114.7°$, $C_3C_4C_5 = 117.7°$, $C_4C_5C_6 = 112.8°$, $C_3C_4O = 121.1°$, $C_5C_4O = 121.2°$. Standard deviations of distances are ±0.005 Å for P–C bonds and ±0.006 Å for C–C bonds, while for angles they are ±0.2° and ±0.4° for CPC and CCC angles, respectively. Torsion angles are $PC_2C_3C_4 = 49.8°$, $C_2C_3C_4C_5 = -53.0°$, $C_3C_4C_5C_6 = 56.1°$, $C_4C_5C_6P = -56.3°$, $C_2PC_6C_5 = 47.6°$, $C_6PC_2C_3 = -44.3°$.

From an nmr study of several phosphines, Albrand, *et al.*,[10] have developed a valuable relation between $^2J_{PCH}$ and the dihedral angle α, defined by the plane of the atoms P, C, and H, and the plane containing the P–C bond and the ternary axis of the bonds from the phosphorus. This relation was then used to assign the conformation of I in solution. In their interpretation, they eliminated the possibility of axial phenyl, maintaining that such a conformation obviously would have equal values of α for both axial and equatorial protons, and therefore equal values for $^2J_{PCH}$. The finding of unequal $^2J_{PCH}$ values (± 10 and ∓ 1 Hz) was interpreted on the basis that I existed in either a chair or a boat conformation, with some distortion due to the CPC angle (assumed to be *ca.* 100°), and that the phenyl substituent was equatorial. The present study has revealed that the conformation adopted by the phosphorinane ring has torsion angles about phosphorus considerably smaller than the value reported[11] for cyclohexane (54.5°), causing values for α as defined by Albrand, *et al.*, to differ regardless of the orientation of the P substituent. Therefore, the $^2J_{PCH}$ values with an axial substituent *need not* be equal. Without knowledge of the torsion angles, such relationships do not appear to be capable of unambiguously defining the preferred conformation of I. It is noteworthy that the proton on phosphorus in phosphorinane itself has been reported from nmr studies to occupy the axial position.[12]

Further X-ray and nmr structural studies are in progress to attempt to elucidate the relationship between conformation and substitution pattern among phosphorinane derivatives.

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(6) Prepared by the method of R. P. Welcher, G. A. Johnson, and V. P. Wystrach, *ibid.*, 82, 4437 (1960).

(7) Listings of observed and calculated structure amplitudes for 1-phenyl-4-phosphorinanone will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

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