

Electron Diffraction Study of Monomethyl- and Dimethylphosphine*

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The structural parameters of gaseous monomethyl- and dimethylphosphine were determined by the sector-microphotometer method of electron diffraction. Center of gravity bond distances and standard errors for the two molecules were, respectively: $r_{CP} = 1.858 \pm 0.003$ Å and 1.853 ± 0.003 Å; $r_{CH} = 1.094 \pm 0.008$ Å and 1.097 ± 0.007 Å; $r_{PH} = 1.423 \pm 0.007$ Å and 1.445 ± 0.02 Å. The angles P—C—H were $109.6 \pm 1^\circ$ and $109.8 \pm 0.7^\circ$. In dimethylphosphine the angle C—P—C was $99.2 \pm 0.6^\circ$. The methyl groups were found to be in staggered conformations. The distances and root-mean-square amplitudes of vibration agreed well with the values determined in recent studies of phosphine and trimethylphosphine.

INTRODUCTION

THE series of molecules PH_3 , PH_2CH_3 , $\text{PH}(\text{CH}_3)_2$, and $\text{P}(\text{CH}_3)_3$ plays a prominent role in theories of coordination complexes. The stabilities of complexes of the phosphines have been correlated with such properties of the free phosphine molecules as dipole moments, bond angles and hybridization, steric factors and other properties which, in turn, have been related to the assumed structure of the molecules.¹⁻⁴ An investigation of the structures of the molecules has never been made, however. A program was undertaken, accordingly, to study the series by the sector-microphotometer method of electron diffraction. The results for PH_3 ⁵ and $\text{P}(\text{CH}_3)_3$ ⁶ have already been reported and compared with spectroscopic studies^{7,8} of the molecules. The structure determinations for PH_2CH_3 and $\text{PH}(\text{CH}_3)_2$ are presented in the following.

PROCEDURE

Samples of monomethyl- and dimethylphosphine were generously provided by Professor R. W. Parry of the University of Michigan. Electron diffraction patterns were recorded on Kodak medium lantern slides with an apparatus described earlier,⁹ using 40-kv

electrons and an r^3 sector. Experimental procedures followed those previously published.¹⁰ Indices of resolution, $R = M_{\text{expt}}(s)/M_{\text{theor}}(s)$, of 0.88 and 0.92 were obtained with monomethylphosphine for the 10-cm and 25-cm camera data, respectively. Corresponding indices of 0.79 and 0.83 were obtained with dimethylphosphine. The deviations from unity resulted principally from a uniform delocalization of the specimen throughout the camera chamber, and corrections were made for the effect.¹¹ Corrections ranged from 0 to 0.002 Å.

The data were processed by a procedure closely resembling several described previously.^{12,13} The Gaussian damping function used in the radial distribution integrand had a value of 0.1 at $s = 31$. Included in the analysis were corrections for non-nuclear scattering and the failure of the Born approximation. For the latter correction the phase shifts calculated by Ibers and Hoerni¹⁴ were used. The shifts suggested by Bartell and Brockway^{12,15} are too small at small s . Fourier integral termination errors were corrected with the aid of an analytic approximation discussed elsewhere.⁶

Final parameters were deduced by fitting the experimental radial distribution function, $f(r)$, with Gaussian peaks by the method of steepest ascents.¹⁶ The regions from 0.90 to 1.55 Å, 1.70 to 2.00 Å, and 2.15 to 2.80 Å were fitted independently, and the results showed that the areas of the various regions were consistent. This is reflected in the least squares output of the index of resolution (adjusted to the 10-cm data) which, for the three regions was 0.878, 0.876, and 0.875 for monomethylphosphine and 0.801, 0.788, and 0.787 for dimethylphosphine. Root-mean-square deviations between experimental and calculated $f(r)$ curves decreased with r , approximately as $0.022r^{-1}$ and $0.030r^{-1}$

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³ R. W. Parry and R. N. Keller, Chapter 3 in *The Chemistry of the Coordination Compounds* (Reinhold Publishing Corporation, New York, 1956), pp. 123-129.

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⁵ L. S. Bartell and R. C. Hirst, J. Chem. Phys. **31**, 449 (1959).

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⁷ C. C. Loomis and M. W. P. Strandberg, Phys. Rev. **81**, 798 (1951); H. H. Nielsen, J. Chem. Phys. **20**, 759 (1952); V. M. McConaghie and H. H. Nielsen, *ibid.* **21**, 1836 (1953); M. H. Sirvetz and R. E. Weston, Jr., *ibid.* **21**, 898 (1953).

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for the monomethyl and dimethyl compounds respectively. The magnitude of the deviations corresponded to about 0.5% of the value of the main PC peak. Thus, the contribution of random intensity errors to the uncertainty in the PC distances is apparently only 0.001 Å, as was found also in the case of trimethylphosphine.⁶

Standard errors were calculated as described elsewhere.^{16,17} They include all known sources of error except those associated with the imperfectly understood uncertainties in the approximations of electron scattering theory. Standard errors quoted for bond angles correspond solely to uncertainties in the "center of gravity" r_g values¹⁸ from which the angles were calculated and not to possible interpretational uncertainties associated with the operational definition of the angle. In the case of the P—C—H angles, account was taken of the effect of the uncertainty in the $\text{C}\cdots\text{H}_p$ peaks which could not be resolved from the stronger $\text{P}\cdots\text{H}_c$ peaks.

DISCUSSION OF RESULTS

Experimental and theoretical intensity functions are compared in Fig. 1. Experimental radial distribution

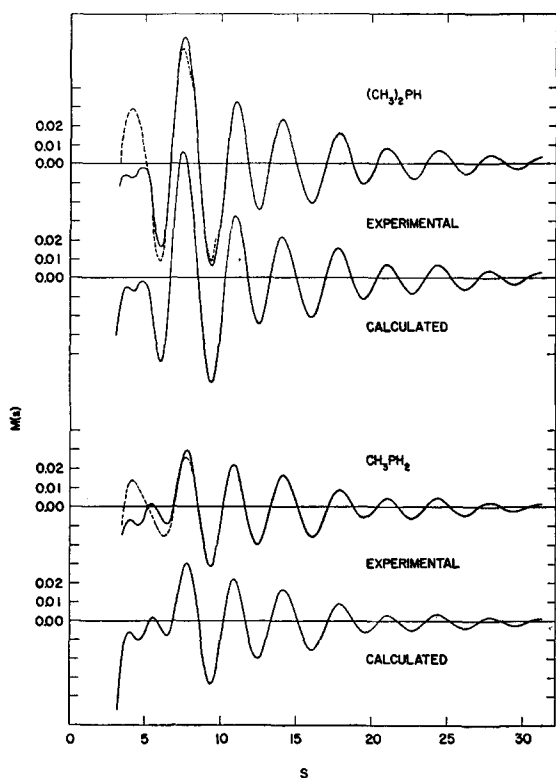


FIG. 1. Reduced intensity curves for monomethyl- and dimethylphosphine. The solid lines represent the total scattering function, $M(s) = (I_M/I_B) - 1$ and the dashed lines represent the nuclear scattering functions, $M_c(s)$. The calculated curves have been multiplied by the experimental index of resolution.

¹⁷ R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.* **81**, 3491 (1959).

¹⁸ The term r_g corresponds to $r_p(0)$ of L. S. Bartell, *J. Chem. Phys.* **23**, 1219 (1955).

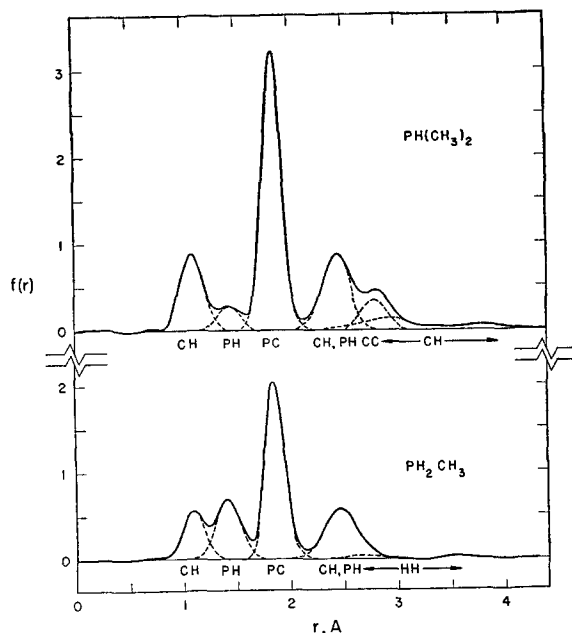


FIG. 2. Experimental radial distribution functions for monomethyl- and dimethylphosphine.

functions are shown in Fig. 2. For dimethylphosphine the data clearly indicate that the methyl groups are in staggered conformations, with a barrier to rotation about the P—C bond probably in excess of 1 kcal/mole. A much more accurate value of 2.6 ± 0.5 kcal/mole was reported for the analogous barrier in trimethylphosphine by Lide and Mann⁸ according to a microwave investigation. In the case of monomethylphosphine the data at all stages of refinement persistently exhibited $\text{H}\cdots\text{H}$ interactions indicative of a staggered conformation for the methyl groups. The interactions were not much stronger than the noise level of the data, however, so no quantitative assessment of the rotational barrier could be made.

The structural parameters determined in this investigation are listed in Table I with the parameters found in parallel electron diffraction investigations of phosphine⁵ and trimethylphosphine.⁶ The root-mean-square amplitudes of vibration appear to be of reasonable magnitudes. The distances and angles agree well among the molecules, with no more than the expected number of results differing from corresponding ones by amounts in excess of the standard errors.

A trend that appears significant is the decrease in the P—C bond length as the number of methyl groups increases. Although the total standard errors are about two parts per thousand, the random uncertainty appropriate in the comparison of the P—C bonds is only about one part per thousand. The shift between monomethyl- and trimethylphosphine is substantially larger than this, being about six parts per thousand. Recently, in another paper, the author¹⁹ proposed ten-

¹⁹ L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960).

TABLE I. Electron diffraction results and standard errors. Distances r_0 and amplitudes l are in Angstrom units.

		P(CH ₃) ₃ ^a	PH(CH ₃) ₂ ^b	PH ₂ CH ₃ ^b	PH ₃ ^c
P—C	r_0	1.846 \pm 0.003	1.853 \pm 0.003	1.858 \pm 0.003	...
	l	0.054 \pm 0.003	0.053 \pm 0.003	0.055 \pm 0.003	...
C—H	r_0	1.091 \pm 0.006	1.097 \pm 0.007	1.094 \pm 0.008	...
	l	0.073 \pm 0.006	0.080 \pm 0.007	0.082 \pm 0.008	...
P—H	r_0	...	1.445 \pm 0.02	1.423 \pm 0.007	1.437 \pm 0.004
	l	...	0.070 \pm 0.02	0.077 \pm 0.008	0.085 \pm 0.008
C...C	r_0	2.800 \pm 0.005	2.821 \pm 0.010
	l	0.084 \pm 0.005	0.088 \pm 0.008
P...H	r_0	2.455 \pm 0.006	2.452 \pm 0.008	2.452 \pm 0.014	...
	l	0.110 \pm 0.006	0.114 \pm 0.007	0.124 \pm 0.010	...
\angle CPC		98.6 \pm 0.3°	99.2 \pm 0.6°
\angle PCH		110.7 \pm 0.5°	109.8 \pm 0.7°	109.6 \pm 1°	...
\angle CPH		...	(96.5° assumed)	(96.5° assumed)	...
Methyl config.		Staggered	Staggered	Staggered	...

^a Reference 6.^b This investigation.^c Reference 5.

tative potential energy functions to describe C...C, C...H and H...H intramolecular van der Waals interactions in hydrocarbon molecules. It is interesting, although of uncertain significance, that the forces derived from these functions imply both the direction and general magnitude of the trend observed in the phosphines. The trend in P—C bonds is opposite to that reported for Si—C bonds in an electron diffraction study of mono-, di-, and trimethylsilanes,²⁰ but in good agreement with recent, more precise microwave studies of mono-²¹ and dimethylsilane.²²

None of the other parameters show significant trends over the series. It may be noted that the P—H bond length, determined here in terms of r_0 , is 0.01 Å to 0.02 Å higher than the spectroscopic r_0 values found for various isotopic species of phosphine in infrared and microwave studies.⁷ This is apparently attributable to

the operational difference between the parameters r_0 and r_0^5 . The C—H bonds appear to be about 0.02 Å shorter than those in the *n*-hydrocarbons butane through heptane,²³ and in the methyl groups in isobutylene,¹⁹ but 0.01 Å longer than the C—H bonds in ethylene.²⁴ The explanation of this result must await further research.

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