TABLE VI

A COMPARISON OF DIFFERENT METHODS FOR CALCULATING DIPOLE MOMENTS IN SOLUTION USING NONSPHERICAL CAVITIES

	Data[a]				Calculated dipole moments by method of					
Compd	T, °K	ϵ	Density, g/cc	P_{E+A}	Scholte[7]	LeFevre[11]	Abbot[8]	Buckley[9]	This work[b]	Gas
$CHCl_3$	393	4.813	1.489	24.8	1.08	0.99	0.92	0.92	1.00	1.01
C_6H_5Cl	302.2	5.475	1.096	31.5	1.63	1.67	1.80	1.82	1.71	1.70
$C_6H_5NO_2$	298	34.89	1.199	37.2	5.04	4.93	5.44	5.45	5.15	4.27

[a] From ref 11. [b] Values differ slightly from those in Table III because of use of different experimental data.

Comparison with Other Methods

In order to observe the effect of varying the assumptions as to the nature of the cavity and the anisotropy correction, it is of interest to compare our results with those of previous workers, all of whom used somewhat different procedures. However, this presents some difficulty since the published results are not strictly comparable because of variations in the original data. Some of the methods used data not ordinarily obtained as part of a normal dipole measurement. Some are applied to pure liquids only, and others to dilute solutions.

LeFevre and Rao[11] compared their results for three compounds–chloroform, chlorobenzene, and nitrobenzene—with Scholte's[7] results. Since these compounds represent nearly the extremes in eccentricity, a considerable range in polarity, and include one which shows large deviations from all of the equations, they appear to be a good selection for comparison on a limited basis. Table VI shows these values of Scholte and Le Fevre and Rao, along with values calculated from these same basic data and using the same shape parameter by the methods of Abbot and Bolton,[8] Buckley and Maryott,[9] and by the present method.

The important conclusions to be drawn would appear to be: (1) If the correction is made for cavity shape alone without including the anisotropy in polarizability, the result will be over-corrected as in the work of Abbot and Bolton and Buckley and Maryott. (2) The use of a cavity size much smaller than the apparent molecular volume, as in the work of Scholte, does not lead to any improvement in agreement with gas values. From a theoretical point of view, the results of LeFevre and Rao should be superior to the others since values for the individual polarizabilities along the minor axes were introduced, but the difference from this work where these effects are averaged is not great.

The best results for nonassociated liquids are obtained by using for cavity volumes the average molecular volume and by including anisotropy of polarization along the dipole axis.

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Dipole Moment Studies. II. The Dipole Moments of the Ethylphosphines

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The dipole moment of monoethylphosphine, as measured in the gas phase with a high-precision heterodyne beat apparatus, is 1.17 ± 0.02 D. The moments of monoethyl-, diethyl-, and triethylphosphine, measured in benzene solution and corrected for solvent effect, are 1.15 ± 0.05, 1.36 ± 0.06, and 1.35 ± 0.05 D., respectively. These data plus microwave values for CH_3PH_2 and $(CH_3)_3P$ lead to a value of 1.22 ± 0.05 D. for the dipole moment of dimethylphosphine. This compares favorably with a recently reported experimental value of 1.23 D. The moment of the ethyl–phosphorus bond is about 0.11 D. larger than that of the corresponding methyl–phosphorus bond. It is assumed that the size of the carbon–phosphorus moment increases as one goes from trialkylphosphine to monoalkylphosphine while the size of the phosphorus–hydrogen moment remains constant in the series.

At the time that this study was initiated, the literature contained no reliable dipole moment data for the *alkyl*phosphines. On the other hand, a study of the Stark effect in the microwave region of phosphine, PH_3, had permitted Sirvetz and Weston[1] to obtain a dipole moment value of 0.579 ± 0.012 D. for PH_3. More recently, using microwave techniques, Kojima, Breig, and Lin[2] obtained a value of 1.100 ± 0.010 for CH_3PH_2, while Lide and Mann,[3] also using microwave methods, obtained a value of 1.192 ± 0.005 for $(CH_3)_3P$. In cases where microwave methods are applicable, a large amount of detailed data of high precision is obtained.

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(1) M. H. Sirvetz and R. E. Weston, *J. Chem. Phys.*, **21**, 898 (1953).

(2) T. Kojima, E. Breig, and C. C. Lin, *ibid.*, **35**, 2139 (1961).

(3) D. R. Lide and D. E. Mann, *ibid.*, **29**, 914 (1958).

As yet, no microwave values for the ethylphosphines are available in the literature.

This paper reports a study of the dipole moments of ethyl-, diethyl-, and triethylphosphines in benzene solution using heterodyne beat methods. Ethylphosphine was also measured in the vapor state. Solution measurements have been corrected for solvent effects using methods outlined in the first paper of this series.[4] The corrected solution value for $C_2H_5PH_2$ shows excellent agreement (0.02 D.) with the gas phase measurement. Accordingly, corrected values for diethyl- and triethylphosphines are likewise believed to be of high reliability. The values obtained are: $C_2H_5PH_2$, 1.17 ± 0.01 D. (gas phase); $C_2H_5PH_2$, 1.15 ± 0.05 D. (solution); $(C_2H_5)_2PH$, 1.36 ± 0.06 D. (solution); and $(C_2H_5)_3P$, 1.35 ± 0.05 (solution). (Above solution values have been corrected for solvent effect.)

An earlier value of 1.84 D. for $(C_2H_5)_3P$, measured in cyclohexane solution and reported in 1959,[5] is *not* consistent with the above values or with the microwave data. It is also inconsistent with our analysis of bond moments using both microwave and heterodyne beat values.

Experimental Section

1. **Materials. a.**—Monoethyl- and diethylphosphine were prepared in a conventional vacuum system by the method of Wagner and Burg[6] using the reactions

$$PH_3 + Na \xrightarrow{NH_3(l)} NaPH_2 + {}^1/{}_2H_2$$

$$NaPH_2 + C_2H_5I \longrightarrow NaI + C_2H_5PH_2$$

$$C_2H_5PH_2 + Na \xrightarrow{NH_3(l)} NaC_2H_5PH + {}^1/{}_2H_2$$

$$NaC_2H_5PH + C_2H_5I \longrightarrow (C_2H_5)_2PH + NaI$$

Products were purified by vacuum distillation. Procedures and characterization data are described elsewhere.[7]

b.—Reagent grade benzene was dried by refluxing with calcium hydride and distilling in the vacuum line.

2. **Gas Phase Measurements on $C_2H_5PH_2$.**—The orientation polarization of $C_2H_5PH_2$ was determined in the gas phase using a high-precision heterodyne beat apparatus constructed by Dr. Henry Habgood in the laboratory of Professor K. Fajans. A detailed description of the apparatus, its calibration, and its use are given elsewhere and are available on request.[8] Corrections were made for the inductance of the leads and plates as determined from the frequency dependence of the capacitance and for the deformation of the sample cell at reduced pressures. Some idea of the reliability of the values may be obtained by comparing the measured value of 7.36 cc for the molar polarization of CO_2 with literature values of 7.34,[9,10] 7.35,[11,12] 7.46,[13] and 7.54.[14]

Measurements were taken at four temperatures with 10 to 16 measurements at each temperature and at pressures ranging from 100 to 600 mm. The resulting $\Delta C/P$ values were extrapolated to zero pressure to correct for deviation from ideal gas behavior.

3. **Measurements in Solution. a. Preparation of Solutions.**—A weighed quantity of phosphine in a sealed glass bulb was introduced into a calibrated thick-bottom volumetric flask of 25-ml capacity. The flask was half-filled with dry benzene and the bulb was crushed with a glass rod inserted through the mouth of the flask. Solution adhering to the rod was washed into the flask with dry benzene; then solvent was added to bring the volume up to 25 ml. During these operations the flask was bathed in a stream of dry nitrogen to minimize contamination of the liquid with moisture and oxygen.

b. Dielectric Measurements.—The dielectric constant of each solution was measured using previously described techniques.[15]

c. Density Measurement.—The flask, solution, and glass fragments were weighed. After the dielectric constant measurement had been completed on the solution, the liquid was removed from the flask, but all glass fragments were carefully retained inside. The flask and glass pieces were carefully rinsed several times with dry benzene, then dried and weighed. The flask was then filled with dry benzene up to the mark and weighed again. From these weights and the density of pure benzene, the density of the solution was obtained.

Results

Results of the vapor phase measurements are shown in Table I. C_s is the capacitance of the evacuated condenser, $(\Delta C/P)_{P=0}$ is the ratio of the increase in the condenser reading to the pressure (extrapolated to zero pressure and corrected by a factor of 0.9838 for inductance of the leads and plates), and P is the molar polarization calculated according to

TABLE I

DATA FOR MEASUREMENT OF DIPOLE MOMENT OF $C_2H_5PH_2$ IN VAPOR PHASE

T, °K	C_s, $\mu\mu f$	$(\Delta C/P)_{P=0}$, $10^3 \times \mu\mu f/mm$	P, cc
302.51	1016.2	8.297	51.34
313.03	1016.4	7.867	50.37
324.67	1016.6	7.346	49.36
331.94	1016.8	7.208	48.92

$$P = \frac{RT}{3C_s}\left(\frac{\Delta C}{P}\right)_{P=0}$$

derived from the Clausius–Mosotti equation. A least-squares treatment of P *vs.* $1/T$ gave

$$P = 23.66 \pm 0.03 + \frac{8365 \pm 290}{T}$$

The dipole moment obtained from the slope is 1.17 ± 0.02 D.

Results of the solution measurements are summarized in Table II. α and β, the coefficients of the change in dielectric constant and density with mole fraction of solute, were obtained by the formulas

$$\alpha = \frac{\Sigma\epsilon - n\epsilon_0}{\Sigma x} \qquad \beta = \frac{\Sigma d - nd_0}{\Sigma x}$$

where n is the number of measurements and the subscript zero indicates pure solvent. This method of

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[4] J. R. Weaver and R. W. Parry, *Inorg. Chem.*, **5**, 703 (1966).

[5] G. Klages and R. Langpape, *Z. Elektrochem.*, **63**, 533 (1959).

[6] R. I. Wagner and A. B. Burg, *J. Am. Chem. Soc.*, **75**, 3869 (1953).

[7] J. T. Yoke, III, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1954.

[8] H. W. Hagbood, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1951.

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[10] R. J. W. LeFevre, and P. Russell, *Trans. Faraday Soc.*, **43**, 374 (1947).

[11] H. E. Watson, G. G. Rao, and K. L. Ramaswamy, *Proc. Roy. Soc.* (London), **A143**, 558 (1933).

[12] K. B. McAlpine and C. P. Smyth, *J. Am. Chem. Soc.*, **55**, 453 (1933).

[13] A. Van Itterbeck and J. Spaepen, *Physica*, **10**, 173 (1943).

[14] J. Clay and F. Van der Maesen, *ibid.*, **15**, 467 (1949).

[15] J. R. Weaver, S. R. Shore, and R. W. Parry, *J. Chem. Phys.*, **29**, 1 (1958).

TABLE II

DATA FOR CALCULATION OF DIPOLE MOMENTS OF ETHYLPHOSPHINES IN SOLUTION

	α	β	P	$1.10R$	μ_{conv}	Cavity shape	μ_{ell}
$C_2H_5PH_2$	1.63 ± 0.14	−0.123	48.8 ± 2.2	23.6	1.11 ± 0.05	$b = c = 0.85a$	1.15 ± 0.05
$(C_2H_5)_2PH$	2.64 ± 0.24	−0.140	73.7 ± 3.5	34.1	1.39 ± 0.06	$a = b = c/1.3$	1.36 ± 0.06
$(C_2H_5)_3P$	2.80 ± 0.20	−0.187	87.1 ± 2.9	44.2	1.45 ± 0.05	$b = c = 1.55a$	1.35 ± 0.05

TABLE III

STRUCTURAL PARAMETERS OF THE METHYLPHOSPHINES

	PH_3	CH_3PH_2	$(CH_3)_2PH$	$(CH_3)_3P$
P–C distance	...	1.858 ± 0.003 (18) 1.863 (2)	1.853 ± 0.003 (18)	1.846 ± 0.003 (18) 1.841 ± 0.003 (3)
P–H distance	1.437 ± 0.004 (18) 1.418 (1)	1.423 ± 0.007 (18) 1.414 (2)	1.445 ± 0.002 (18)	...
C–H distance	...	1.094 ± 0.008 (18) 1.093 (2)	1.097 ± 0.007 (18)	1.091 ± 0.006 (18) 1.090 (assumed) (3)
C- -C nonbonded	...	...	2.821 ± 0.010 (18)	2.800 ± 0.005 (18)
P- -H nonbonded	...	2.452 ± 0.014 (18)	2.452 ± 0.008 (18)	2.455 ± 0.006 (18)
∠CPC	...	...	99.2 ± 0.6° (18)	98.6 ± 0.3° (18) 99.1 ± 0.2° (3)
∠CPH	...	97.5° (2) (assumed)	96.5° (18) (assumed)	...
∠HPH	93.3° (1)	93.4° (2)	...	...
∠PCH	...	109.6 ± 1° (18)	109.8 ± 0.7 (18)	110.7 ± 0.5° (18)
∠HCH	...	109.75° (2)		107° (3)
ϵ	...	2° $\mu_a = 0.958 \pm 0.005$ D. $\mu_c = 0.591 \pm 0.010$ D.		...

averaging avoids giving undue weight to the most dilute region. Within the rather large limits of random error, there was no observable deviation from linearity of the ϵ *vs.* x plots. All concentrations were in the range of 0.001–0.016 mole fraction, with most of the values below 0.010.

Calculation of the conventional dipole moment by Hedestrand's equation,[16] which for benzene at 25° may be written $P = 0.3411M + 14.71\alpha - 30.53\beta$, gave values for the molar polarization as shown under P. Molar refractions were obtained from the group refraction values of Smyth[17] with 10% added to allow for atomic polarization. The conventional moments were then obtained as $\mu_{\text{conv}} = 0.2212\sqrt{P - 1.10R}$.

To correct for the solvent effect, structural parameters were used to estimate cavity shapes with results as shown in Table II. In each case a is the axis in the direction of the moment and b and c are axes perpendicular to a. There is, of course, considerable uncertainty as to the behavior of the ethyl groups. Average values between the most extended and most compact positions were assumed. The corrected moment was obtained using a formula equivalent to eq 21b of ref 4

$$\mu_{\text{ell}} = \left[\frac{(2\epsilon + 1)(\epsilon + 2)}{9\epsilon} \frac{1 - FD}{\sqrt{1 - FC}}\right]\mu_{\text{conv}}$$

in which F, C, and D are defined in eq 2, 5, and 6 of ref 4.

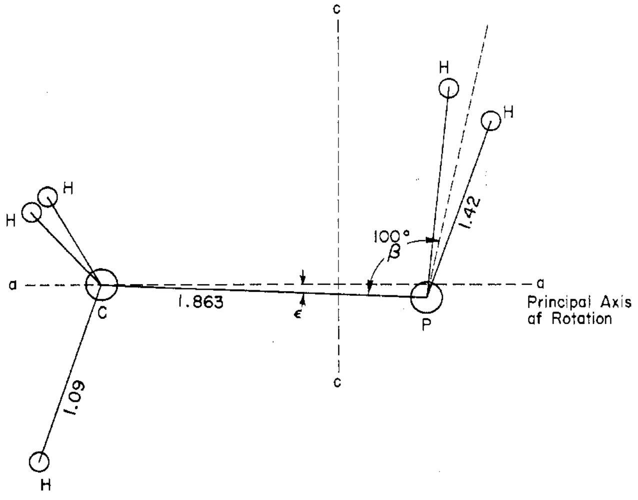

Figure 1.

Discussion

Structural parameters for the methylphosphines have been obtained by microwave methods and by Bartell using electron diffraction.[18] Values from all sources are summarized in Table III. A particularly interesting feature of the microwave study of CH_3PH_2 is that the components of the dipole moment along the rotational axes of the molecule are obtained directly from the experimental data. These values, along with the appropriate structural information and over-all dipole moment values, can then be used as the basis for a bond moment analysis of each molecule. Appropriate angles and axes for CH_3PH_2 are shown in Figure 1.

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(16) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., Houston, Texas, 1952, p 305.

(17) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 409.

(18) L. S. Bartell and R. C. Hirst, *J. Chem. Phys.*, **31**, 449 (1959); L. S. Bartell and L. O. Brockway, *ibid.*, **32**, 512 (1960); L. S. Bartell, *ibid.*, **32**, 832 (1960).

If one considers that the dipole moment for $P(CH_3)_3$ is the resultant of three $P–CH_3$ moments and the value for PH_3 is the resultant of three P–H moments, one obtains by straightforward geometry[19] a P–H moment of 0.356 D. and a $P–CH_3$ moment of 0.83 D.

Microwave studies on NH_3 and CH_3NH_2 have shown that the N–H bond lengths are the same in the two molecules, and Lide,[20] after a comparison of distances and nuclear quadrupole coupling constants in NH_3 and CH_3NH_2, concluded that the N–H bonds in the two molecules are identical. A careful examination of Table III shows no systematic variation in P–H distances in the different alkylphosphines. It then seems reasonable to extrapolate Lide's conclusion to the alkylphosphines and assume that the P–H bond remains the same through the series. A constant value of 0.36 D. for the P–H bond moment will be used. The validity of the assumption is supported by an independent experimental measurement. If one uses the known geometry of the phosphines and the known dipole moment vectors along the rotational axes of methylphosphine, independent values of the $P–CH_3$ and P–H moments can be calculated.

The P–H moment obtained is 0.38, which is in excellent agreement with the value 0.36 given above. On the other hand, the value of 1.06 obtained for the methyl–phosphorus moment is significantly higher than the value 0.83 obtained from $P(CH_3)_3$. This difference is held to be real and will be related in paper IV to the C–P bond lengths of 1.863 A in CH_3PH_2 and 1.841 A in $(CH_3)_3P$.

By a treatment analogous to that used for $(CH_3)_3P$ and by assuming that $(C_2H_5)_3P$ and $(CH_3)_3P$ have identical C–P–C bond angles, one can calculate the ethyl–phosphorus moment in triethylphosphine as 0.94 D. This value is about 0.11 D. larger than the methyl–phosphorus moment in $(CH_3)_3P$. It is then reasonable to assume that the ethyl–phosphorus moment in $(C_2H_5)PH_2$ is also 0.11 D. larger than the methyl–phosphorus moment in $(CH_3)PH_2$. The resulting value of 1.17 D. for $P–C_2H_5$ can be combined with the known PH moment and the geometry of the molecule to calculate an independent value of 1.19 D. for $C_2H_5PH_2$. The agreement with the measured value is good (μ = 1.17 D.).

Since the value of the alkyl–phosphorus moment decreases from mono- to di- to trialkylphosphines, it is necessary to calculate the $C_2H_5–P$ moment in the secondary phosphine from the measured moment of $(C_2H_5)_2PH$. The value obtained is 1.06 D. This result was used to predict a value for $(CH_3)_2PH$. If one assumes that the methyl–phosphorus moment in $(CH_3)_2PH$ is about 0.11 D. smaller than the 1.06 D. given above, a value of 0.95 D. is obtained for the methyl–phosphorus moment in $(CH_3)_2PH$. The latter result in conjunction with the P–H moment of 0.36 and the known geometry of the molecule predicts a value of 1.22 ± 0.05 D. for the moment of dimethylphosphine. The independent recent experimental value for this molecule is 1.23 D.[21]

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[19] For these symmetric molecules, the relation is: resultant = component × $\sqrt{3 + 6 \cos (\text{angle X–P–X})}$.

[20] D. R. Lide, Jr., *J. Chem. Phys.*, **27**, 350 (1957).

[21] R. Nelson, *ibid.*, **39**, 2382 (1963).

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Dipole Moment Studies. III. The Dipole Moments of the Methylamine Boranes

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Dipole moments of ammonia borane, methylamine borane, dimethylamine borane, trimethylamine borane, and ammonia triborane have been measured in several solvents. After correction for solvent effects, the following values were obtained: NH_3BH_3, 5.05; $CH_3NH_2BH_3$, 5.15; $(CH_3)_2NHBH_3$, 4.99; $(CH_3)_3NBH_3$, 4.69; $NH_3B_3H_7$, 6.98 D. The foregoing variations must be rationalized by any acceptable model. Additive bond moments are not adequate for representation of the data.

In an earlier paper from this laboratory[1] the dipole moment of ammonia borane was reported as 4.9 D. in dioxane solution, but the early data were not sufficiently extensive to permit a careful consideration of solvent effects in the measurement. In a subsequent precision study of the dipole moments of the alkylamine boranes in this laboratory, possible solvent effects again made an interpretation of the data difficult.

The problem is illustrated by a 1960 paper of Nöth and Beyer,[2] who also measured the dipole moments for methylamine borane, dimethylamine borane, and tri-

[1] J. R. Weaver, S. G. Shore, and R. W. Parry, *J. Chem. Phys.*, **29**, 1 (1958); Technical Report 59-207, Wright Air Development Center, May 1959, pp 69–78.

[2] H. Nöth and H. Beyer, *Chem. Ber.*, **93**, 928, 939 (1960).