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Dipole Moments of the Methylethylphosphines

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The dipole moments of the methylethylphosphines have been determined by the Debye method in the gas phase. Values obtained are: $CH_3C_2H_5PH$, 1.28 ± 0.04 D; $(CH_3)_2C_2H_5P$, 1.31 ± 0.09 D; $CH_3(C_2H_5)_2P$, 1.58 ± 0.12 D. These results are found to be generally consistent with the Weaver–Parry model (1966) for variation in phosphine dipole moments with substituents.

Introduction

Earlier studies [1–5] of the dipole moments of alkylphosphines have been interpreted [6] to indicate that a significant and rational variation in the P–R group moment occurs as one goes from a primary to a secondary to a tertiary phosphine. The variation was ascribed as being due predominantly to the effect of the presence of the proton(s) on the electron distribution about phosphorus. Briefly, it was argued that the presence of a proton buried in phosphorus' electron cloud would enhance electron density near phosphorus, reducing any electron releasing tendencies of an alkyl group also bound to that phosphorus. The fewer the protons, the less would be this effect, so that an increasing release of electrons could occur as each proton is replaced by an alkyl group, giving rise to increasingly large P–C moments from RPH_2 to R_2PH to R_3P. These authors argued that this effect should be most notable in going from RPH_2 to R_2PH and less so from R_2PH to R_3P. This empirical model received support from a theoretical treatment by Kuznesof *et al.* [7].

Because the variation in P–R group moment was thought to be due predominantly to the primary, secondary, or tertiary character of the phosphine, it should be possible to predict the net dipole moment of a phosphine from the compoment group moments obtained from other molecules so long as the number of P–H bonds is consistent. To test this hypothesis, I have measured the dipole moments of the compounds methylethylphosphine, $CH_3(C_2H_5)PH$, dimethylethylphosphine, $(CH_3)_2C_2H_5P$, and methyldiethylphosphine, $CH_3(C_2H_5)_2P$, in the gas phase. Values for the P–H, P–CH_3, and P–C_2H_5 group moments have been reported previously [6] for both secondary and tertiary phosphines providing the data required for this test.

Results

Gas phase dielectric data (see Experimental section) were reduced by the Debye method to give values of 1.28 ± 0.04 D for $CH_3C_2H_5PH$, 1.31 ± 0.09 D for $(CH_3)_2C_2H_5P$, and 1.58 ± 0.12 D for $CH_3(C_2H_5)_2P$. The increasingly large standard deviations reflect the decreasing volatilities of the three compounds which renders the last compound especially difficult to measure because of the very small pressure variation obtainable and the short temperature range useful.

These values can be compared with those calculated using the P–R group moments previously reported [6] summed vectorially [8] at the angles reported for the methyl phosphines [1] in the absence of structural data for the compounds in question. These group moments and calculated resultants are given in Table I.

TABLE I. Bond Moments and Resultants for Methylethylphosphines.

	μPH	μPCH_3	μPC_2H_5	μ_r(sec)[a]	μ_r(tert)	μ_{obs}
$CH_3C_2H_5PH$	0.38	0.95	1.06	*1.29*	1.15	1.28 ± 0.04
$(CH_3)_2C_2H_5P$	–	0.83	0.94	1.42	*1.25*	1.31 ± 0.09
$CH_3(C_2H_5)_2P$	–	0.83	0.94	1.47	*1.30*	1.58 ± 0.12

[a] μ_r = resultant moment, sec: calculated for secondary phosphine, tert: for a tertiary phosphine.

The agreement with the appropriate calculated value (underlined in Table I) is excellent for $CH_3(C_2H_5)PH$, good for $(CH_3)_2C_2H_5P$ and poor for $CH_3(C_2H_5)_2P$. In fact in the latter case, the agreement is much better with the value calculated as if it were a secondary phosphine, that is using the larger P–R values. Unfortunately, this is not attributable to a clear failing of the model but may equally well be due to error in the measured dipole moment of triethylphosphine. Values reported for the dipole moment of triethylphosphine are given in Table II.

TABLE II. Reported Dipole Moments of $(C_2H_5)_3P$.

Value (D)	*Solvent*	*Data Reduction*
1.84 [9]	C_6H_{12}	conventional [10]
1.48 [11]	C_6H_6	conventional
1.45 [1]	C_6H_6	conventional
1.35 [1]	C_6H_6	elliptical cavity [12]
2.90 [13]	dioxane	conventional

The $P–C_2H_5$ values used were those obtained in ref. 1, $\mu[P(C_2H_5)_3] = 1.35$ D. Clearly, any of the others listed would give a higher sum and more nearly agree with the experimental result of this work. Since the methylphosphine moments were all determined in the gas phase, these values can be used with considerable confidence. In fact, it is possible to make the reverse calculation, to determine $\mu_{P-C_2H_5}$ from the present work and the μ_{P-CH_3} moments and thereby to check the reported values for the ethylphosphines. When this is done for $HP(CH_3)C_2H_5$ a value for $\mu_{P-C_2H_5}$ of 1.03 D is obtained. For $P(CH_3)_2C_2H_5$ a value of 1.05 D is obtained and with $PCH_3(C_2H_5)_2$ a value of 1.20 D is found to give an average value of 1.13 D for $\mu_{P-C_2H_5}$ in the tertiary phosphines. The value calculated for $HP(C_2H_5)_2$ using $\mu_{P-Et} = 1.03$ D, 1.35 D, is virtually identical to that obtained experimentally in benzene solution, 1.36 D [1]. The value calculated for $P(C_2H_5)_3$ using $\mu_{P-Et} = 1.13$ D is 1.6 D which is in fair agreement with the conventionally calculated values of Cumper *et al.* [11], and of Kodama, *et al.* [1]. In fact when a value of 1.05 D is used, obtained from the more reliable data for $P(CH_3)_2C_2H_5$ alone, the resultant is 1.51 D which is in quite good agreement with these two reported values for $P(C_2H_5)_3$. This observation casts some doubt, however, on the validity of the correction to an elliptical solute cavity used by the latter in this case [1], perhaps a result of difficulty in estimating the appropriate ellipse parameters. It is very difficult to reconcile the values of reference 9 and 13 to the present experiment. The results obtained in dioxane are, in fact, sufficiently inconsistent with the benzene solution values, which are in turn reasonable values compared with the moments of trialkylphosphines obtained in the gas phase [$P(CH_3)_3$ [4], $P(CH_3)_2C_2H_5$, and $P(CH_3)(C_2H_5)_2$] as to suggest that a specific association between the phosphines and dioxane may exist which distorts those data. By contrast dioxane was shown to be a superior solvent to benzene for dipole determinations of the amine boranes [14], demonstrating once again that considerable care must be taken in selecting a solvent for dipole moment studies in solution.

There remains at least one further necessary test to determine the validity, or at least the utility, of the model proposed by Weaver and Parry [6], namely a high confidence evaluation of the dipole moment of triethylphosphine. Because its low volatility makes this evaluation by the Debye method extremely difficult, a determination by microwave spectroscopy appears to be in order.

Experimental

Apparatus

IR spectra were recorded with a Beckman IR-20A spectrometer, NMR spectra with a Varian XL-100-12 instrument in the CW mode at 40.5 MHz (^{31}P) and with Varian A60-A and 360-A instruments at 60 MHz (^1H). Chemical shifts are referred to 85% H_3PO_4 and TMS (+ = downfield). All spectra were recorded at ambient temperature. Mass spectra were obtained with a Perkin Elmer-Hitachi RMU-6E spectrometer at 70 eV. Results reported are the principal peaks in the hydrocarbon clusters; proton loss was apparent in each cluster as expected. Relative intensities and assignments are given in parentheses. Dielectric data were obtained at various temperatures for gas samples using a heterodyne beat system previously described [15]. The apparatus was modified only to the extent that Teflon valves were used to isolate the system to minimize the absorption of the compounds in the valve grease.

Materials

Phosphine samples were prepared using standard high vacuum techniques as described below. CH_3PCl_2 and $C_2H_5PCl_2$ were obtained from Ethyl Corp. and were vacuum distilled before use.

$C_2H_5(CH_3)PH$ was prepared by means of the reaction sequence

$$PH_3 \xrightarrow{Na} NaPH_2 \xrightarrow{CH_3I} CH_3PH_2 \xrightarrow{Na}$$

$$NaHPCH_3 \xrightarrow{C_2H_5Br} C_2H_5(CH_3)PH,$$

all in liquid ammonia solution. The product was purified by the preparation of its hydrochloride salt, filtration, then displacement of the pure secondary phosphine by NH_3 from which separation was readily accomplished on the vacuum line. The sample's purity was indicated by a linear vapor pressure curve [log P (mm) = –1612/T + 7.81] constant vapor pressure following partial distillation, and the absence of extraneous peaks in the NMR spectra. It was characterized by its vapor density molar mass (calcd. 76, found 80), its IR and NMR spectra. The IR spectrum consists of the anticipated CH fingerprints and a strong band at 2275 cm^{-1} characteristic of the P–H function. Other peaks are observed in the gas phase (45 mm, 7.5 cm cell) at 2960(s), 2925(vs), 2830(s), 1430(s), 1380(sh, m), 1290(w), 1235(w), 1045(s), 990(vs), 865(s), 685(s), 620(sh, m). The NMR spectra are conclusive. The ^{31}P spectrum consists of a doublet ($^1J_{PH}$ = 188 Hz, lit. [16] 191 Hz) centered at –79.0 ppm (lit. [15] –77.0, –77.5). Each member of the doublet is further split into a sextet ($^2J_{PH}$ = 12.7 Hz) of quartets ($^3J_{PH}$ = 3.2 Hz) by the CH_3 and CH_3CH_2 protons and by the CH_3 protons of the ethyl group, respectively. The ^1H spectrum consists of a doublet of sextets ($^3J_{HH}$ = 7 Hz) due to the pH proton centered at δ = 2.85 (assuming $^1J_{PH}$ = 188, above) with the upfield member of the doublet obscured by the CH_2 multiplet at δ = 1.38. The CH_3 multiplet is centered at δ = 1.03. The pattern and intensities of the 10 resolved lines in these overlapping multiplets is entirely consistent with the coupling values obtained from the ^{31}P spectrum. The total area ratio of the CH_3, CH_2, and 1/2 PH proton multiplet to the lower 1/2 PH sextet was measured as 17.8:1, calcd., 17.0:1.

$(CH_3)_2C_2H_5P$ was prepared by means of the reaction of CH_3MgBr with $C_2H_5PCl_2$ in diethylether. The sample was purified by formation of the hydrochloride, recrystallization, then displacement with NH_3 followed by distillation on the vacuum line. The purity of the sample was demonstrated by a linear vapor pressure curve [log P (mm) = –1726/T + 7.91], by the absence of extraneous NMR peaks and by the absence of unexpected mass spectral peaks. The IR spectrum shows the expected hydrocarbon fingerprints. Peaks are observed at 2960(vs), 2890(vs), 2820(m), 1420(s), 1320(sh, w), 1280(w), 1000(m), 960(m), 925(s), 875(m), 680(s). Vapor density molar mass: calcd 90, found 92. Mass spectrum: 90 (96, $C_4H_{11}P^+$, mol. ion), 75 (86, $C_3H_8P^+$), 62 (100, $C_2H_7P^+$), 46 (70, CH_3P^+), 34.2 (metastable, loss of CH_4 from $C_2H_7P^+$) and 22.5 (metastable, loss of PH_3 from $C_3H_8P^+$). NMR spectra confirm the identity of the compound. The ^{31}P spectrum consists of a peak at –48.6 ppm (lit. [17], –51, –48.5 ppm) whose fine structure was not resolved. The ^1H spectrum consists of a multiplet at δ = 1.23 and one at δ = 0.97, relative intensities 1:1.95. This pattern is consistent with that expected assuming coupling constants to be approximately the same as those found for $CH_3C_2H_5PH$.

$CH_3(C_2H_5)_2P$ was prepared and purified as described for $(CH_3)_2C_2H_5P$ except that CH_3PCl_2 and C_2H_5MgBr were used. Vapor pressure: log P (mm) = –1878/T + 7.93. IR spectrum: 2960(s), 2920(s), 2890(m), 1455(m), 1430(m), 1380(w), 1285(w), 1235(m), 1045(w), 1005(m), 860(m), 745-(w), 700(w), 670(w). Vapor density molar mass: calcd 104, found 110. Mass spectrum: 104 (72, $C_5H_{13}P^+$, mol ion), 89 (42, $C_4H_{10}P^+$), 76 (100, $C_3H_9^+P^+$), 61 (47, $C_2H_6P^+$), 48 (77, CH_5P^+), 41 (19, $C_3H_5^+$). NMR spectra confirm the compound's identity. The ^1H spectrum consists of multiplets at δ = 1.25 (area 1) and δ = 0.97 (area 0.84). The area ratio compares well with the value estimated assuming coupling values the same as in $CH_3C_2H_5PH$ of 0.9. The ^{31}P spectrum consists of a peak at –35.2 ppm with unresolved fine structure which compares well with the literature value of –34 ppm [17].

Molar Polarizations

The orientation polarizations of the phosphines were determined in the gas phase as described previously [15]. Measurements were made at 7 or 8 temperatures with 15–30 measurements at each temperature at pressures ranging from 2–30 mm Hg for $CH_3(C_2H_5)_2P$, 5–65 mm Hg for $(CH_3)_2C_2H_5P$, and 5–70 mm Hg for $CH_3C_2H_5PH$ in an effort to keep the pressures well under the equilibrium vapor pressures of the compounds. The resulting data at each temperature were extrapolated to zero pressure to correct for deviation from ideal gas behavior. For $CH_3C_2H_5PH$, P_T = (25.78 ± 1.96) + (10028 ± 592); temperature range 285.56–322.54 K. For $(CH_3)_2C_2H_5P$, P_T = (25.92 ± 4.42) + (10482 ± 1345)/T; temperature range 291.06–322.08 K. For $CH_3(C_2H_5)_2P$, P_T = (18.83 ± 6.92) + (15155 ± 2136)/T; temperature range 297.55–327.53 K. The electric dipole moments were obtained from the slopes of P_T = A + B/T as μ = 0.012812 B, the standard Debye method [18]. Error limits are standard error.

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