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]

Acknowledgment.—The generous support of this work by the National Science Foundation under Grant NSF G-21408 and by the National Institutes of Health (CA 07989-01) is gratefully acknowledged.

[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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Received September 10, 1965

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).

methylamine borane in benzene solution. They resolved their molecular moments into a series of bond moments which, by vector addition, predicted a value of 5.5 D. for ammonia borane or about 0.6 D. higher than the value measured in this laboratory in dioxane solution. Nöth and Beyer ascribed the difference between their predicted result and our experimental value to association of H_3NBH_3 in the dioxane solution. They further indicated that an experimental test of their thesis was rendered impossible by the fact that the insolubility of H_3NBH_3 in benzene prevents a measurement of the dipole moment of H_3NBH_3 under conditions comparable to those used by them for measuring the other alkylamine boranes.

Since the low vapor pressures of the amine boranes have precluded (at least up to this time) a vapor phase measurement of their dipole moments, possible solvent effects are of major importance in any systematic study of dipole moment trends for these molecules.

A theoretical analysis of solvent effects has been reported in a preceding paper.[3] In the present paper dipole moment values for ammonia borane, methylamine borane, dimethylamine borane, trimethylamine borane, and ammonia triborane are reported in several solvents. Solvent corrections have been made using the theoretical model. The data reveal unequivocally, and in contrast to the prediction of Nöth and Beyer, that the moment of ammonia borane is *not* higher than that of monomethylamine borane. Clearly a simple vector addition of bond moments comparable to that used by Nöth and Beyer is not adequate for an analysis of the electric moments of the amine boranes.

Experimental Section

1. Preparation of Amine Boranes.—Literature methods were used for the preparation of H_3NBH_3,[4] $(CH_3)_3NBH_3$,[5] and $H_3NB_3H_7$.[6] The latter compound was prepared by Dr. J. C. Carter in this laboratory.

The compound $(CH_3)_2NHBH_3$ was obtained through the courtesy of Callery Chemical Co. and was resublimed before use.

Monomethylamine borane, $CH_3NH_2BH_3$, formerly described[7] as an unstable material, was prepared in a stable form by the following procedure. A 50-mmole portion of pure B_2H_6 was added slowly at −78° to 15 ml of dry tetrahydrofuran. A 2-ml liquid sample of CH_3NH_2 was distilled into the diborane solution by freeezing the system with liquid nitrogen. A slush bath at −112°, placed around the reaction tube, allowed gradual warming of the reaction mixture to −45° over a 12-hr period. After the solvents and excess amine were removed at −45°, the reaction tube was warmed to 25° and large crystals of $CH_3N_2BH_3$ were slowly sublimed under vacuum into a cold finger held at 0°. Only about half of the total product could be sublimed to the cold finger in 1 week. *Anal.* Calcd for $CH_3NH_2BH_3$: H^-, 6.68; B, 24.10. Found: H^-, 6.64; B, 23.8; mp 58°.

The resulting stable white sublimate is soluble in diethyl ether and dioxane and dissolves with difficulty in benzene. It does not react with water at 50° but loses hydrogen from a 6 *M* HCl solution at 25°.

2. Drying of Solvents.—Because exclusion of water and other polar molecules is of major importance in preparation and manipulation of solutions, high-vacuum procedures or special techniques were used throughout.

Dioxane (Eastman) was refluxed with dilute HCl (about 1.5 *M*) for 12 hr; washing with KOH solution caused a phase separation. After several washings with KOH solution, the ether layer was dried by repeated treatment with KOH pellets and finally by refluxing with $LiAlH_4$. Traces of water were easily detected by measurement of the dielectric constant ($\epsilon = 2.205$ at 25°). The dried material was stored over $LiAlH_4$.

Benzene (reagent grade, Merck, Eastman, or Mallinckrodt) was refluxed with CaH_2. The dielectric constant of the dry sample did not vary by more than 0.001 and was taken as 2.273 (reference liquid).

Diethyl ether was dried over $LiAlH_4$. Its dielectric constant was 4.207.

3. Handling Solutions. Preparation.—Samples of $(CH_3)_2NHBH_3$ or $(CH_3)_3NBH_3$ were sublimed from the vacuum system into a special density tube. The 15-mm cylindrical tube was about 20 cm long and was equipped at the top with two constricted necks, each terminating in a standard taper male joint by which the tube could be fastened to both the vacuum system and the amine borane storage unit. Without a two-necked tube, sublimation of the amine borane through the constriction was very difficult. For weighing, the tube was filled with dry N_2, wiped free of grease, and capped with outside glass caps. Solvent could be distilled into or out of the tube from the vacuum system.

Since H_3NBH_3 and $CH_6NH_2BH_3$ could not be sublimed through the constricted neck of the density tube, solid H_3NBH_3 or $CH_3NH_2BH_3$ was inserted in a nitrogen filled drybox into the neck above the constriction. After capping and weighing, the flask was rapidly fastened to the vacuum system, and the solute was washed in through the constriction using solvent which could be condensed above the solid. When the tube was filled to the constricted regions, it was removed from the vacuum line, capped, and thermostated at 25.00 ± 0.01° until the levels became stationary. The distance of the liquid above or below a fixed reference mark was measured with a cathetometer; then the exact volume was obtained from a calibration curve prepared earlier using pure solvent as the reference fluid.

To remove samples for measurement or dilution, one of the glass caps was replaced by a rubber serum bottle cap, and liquid was removed with a hypodermic syringe. If direct contact between the rubber cap and the solution were avoided, no solvent absorption correction was needed.

4. Measurement of Refractive Index.—Refractive index measurements were made with a high-precision Abbé refractometer, using light of wavelengths 5890, 5461, and 4358 A. No detectable difference was found between the dispersion of the solvent and solution, so the data were not extrapolated to infinite wavelength. Results recorded in Table II are for the sodium line at 5890 A. No solution decomposition occurred during measurement.

Dielectric constant measurements were obtained using the apparatus previously described.[1] Solutions were added and removed from the cell by syringe, so that the cell could be filled, emptied, rinsed and dried without altering in any way its position or electrical connections.

Results and Discussion

1. Dielectric Measurements.—Table I shows dielectric constant data for solutions of several of the amine boranes in dioxane, benzene, and ethyl ether. The grouping of the data indicates solutions made by dilution from the same samples of starting materials. The data were fitted to the equation $\Delta\epsilon = \epsilon' w + (\epsilon''/2)w^2$, in which $\Delta\epsilon$ is the difference between the dielectric constants of the solution and the pure solvent, w is the weight fraction of solute, and ϵ' and ϵ'' (designated thus because they are the limiting values of the

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

[4] S. G. Shore and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 8 (1958).

[5] A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 780 (1937).

[6] G. Kodama, R. W. Parry, and J. C. Carter, *ibid.*, **81**, 3534 (1959).

[7] E, Wiberg, *Naturwissenschaften*, **35**, 182 (1948).

TABLE I

DIELECTRIC CONSTANT DATA FOR AMMONIA BORANE AND METHYLAMINE BORANES IN DIOXANE, BENZENE, AND ETHYL ETHER

10^6w	$10^3\Delta\epsilon$ (obsd)	$10^3\Delta\epsilon$ (calcd)
Ammonia Borane in Dioxane		
5,150	506	505
2,972	297	296
1,421	144	143
7,066	683	683
3,201	319	319
1,039	106	105
2,720	268	272
1,378	139	139
Monomethylamine Borane in Dioxane		
5,753	396	395
8,494	579	579
3,644	250	251
3,391	232	234
1,208	86	84
Dimethylamine Borane in Dioxane		
7,366	382	379
3,830	197	197
9,843	507	507
5,099	266	262
1,882	96	97
9,860	505	507
4,200	215	216
Trimethylamine Borane in Dioxane		
7,275	273	274
7,034	265	265
2,613	97	97
958	35	35
5,385	202	201
Ammonia Triborane in Dioxane		
7,186	763	764
3,486	363	359
1,690	168	171

10^6w	$10^3\Delta\epsilon$ (obsd)	$10^3\Delta\epsilon$ (calcd)
Monomethylamine Borane in Benzene		
8,559	288	
3,818	152	
2,329	101	
Dimethylamine Borane in Benzene		
25,530	784	
12,141	393	
3,031	111	
8,063	276	
5,630	200	
2,548	97	
5,957	211	
2,708	103	
Trimethylamine Borane in Benzene		
21,006	676	675
11,931	378	381
6,210	196	197
2,816	89	89
15,974	545	544
3,216	101	102
2,036	67	64
Dimethylamine Borane in Ethyl Ether		
10,091	525	527
5,822	305	307
2,699	142	143
16,533	850	851
7,903	420	415
Trimethylamine Borane in Ethyl Ether		
10,034	374	374
5,137	189	189

TABLE II

VALUES OF DIPOLE MOMENTS IN DIFFERENT SOLVENTS CALCULATED USING SEVERAL DIFFERENT THEORETICAL MODELS

Solute	Solvent	ϵ'	ϵ''	$n^{2\prime}$	v'	μ_{conv}	μ_{sph}	μ_{ell}	b/a
NH_3BH_3	Dioxane	101.89	−1480	0.30	0.43	5.03	4.99	5.05	0.92
$CH_3NH_2BH_3$	Dioxane	69.69	−371	0.10	0.39	5.02	5.03	5.15	c
$(CH_3)_2NHBH_3$	Dioxane	51.31	32	−0.04	0.50	4.94	4.99	4.99	1.00
$(CH_3)_3NBH_3$	Dioxane	36.73	250	−0.09	0.49	4.66	4.74	4.69	1.08
$NH_3B_3H_7$	Dioxane	99.56	1898	0.39	0.38[a]	6.73	6.63	6.98	0.70
$CH_3NH_2BH_3$	Benzene	(assocd)		−0.21					
$(CH_3)_2NHBH_3$	Benzene	(assocd)		−0.27					
$(CH_3)_3NBH_3$	Benzene	31.57	55	−0.32	0.32[b]	4.62	4.72	4.67	1.08
$(CH_3)_2NHBH_3$	Ethyl ether	53.37	−231	0.28	0.08[b]	4.07	5.19	5.19	1.00
$(CH_3)_3NBH_3$	Ethyl ether	36.29	197	0.19	0.07[b]	3.73	4.90	4.79	1.08

[a] Estimated from structural parameters. [b] Estimated from corresponding dioxane values. [c] $b/a = 0.74$ for component of μ along major axis ($b = c < a$) and 1.35 along minor axis ($a = c < b$).

first and second derivatives of ϵ with prespect to w) are constants to be evaluated. The third column of Table I shows, for comparison, the $\Delta\epsilon$ values recalculated from the equation using the experimental values of ϵ' and ϵ'', fitted from the data and shown in Table II. The method has an advantage of not giving undue weight to points in the very dilute region.

The square of the refractive index and the specific volume were regarded as linear with weight fraction, and their slopes (with uncertainties of about ±0.05) are shown in the columns designated $n^{2\prime}$ and v' in Table II. There was no observed deviation from linearity within these limits. The uncertainties in ϵ' are of the order of ±0.1 to ±0.3.

The association of the mono- and dimethylamine boranes in the benzene solution is demonstrated by the dielectric constant measurements in this solvent, shown graphically in Figure 1, in which the ratio $\Delta\epsilon/w$ is plotted against w. Normal behavior is shown by trimethylamine borane which gives a straight line with intercept ϵ' and slope $\epsilon''/2$. The data for the associated solutes $(CH_3)_2NHBH_3$ and $(CH_3)NH_2BH_3$ are qualitatively consistent with the freezing point measurements of Nöth and Beyer, but not with their dielec-

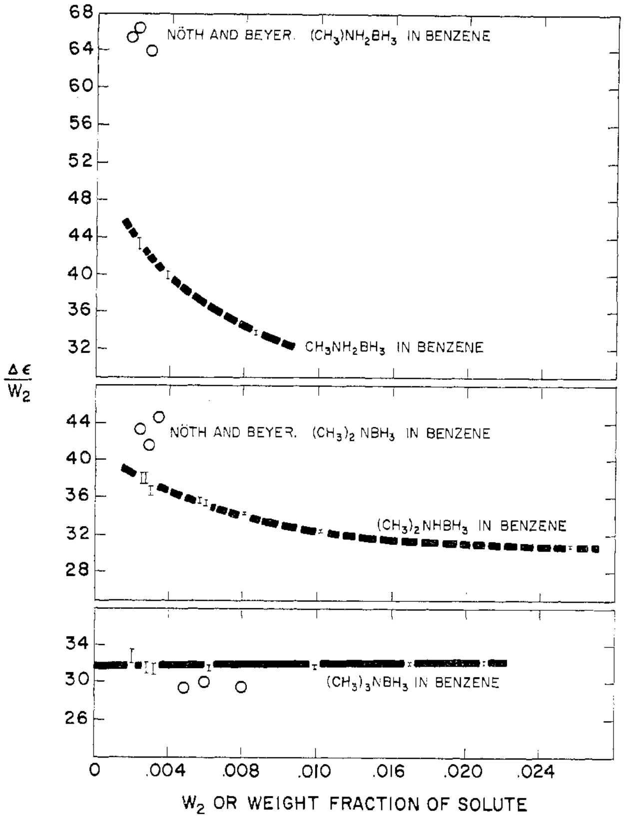

Figure 1.—Dielectric constant measurements, for mono-, di-, and trimethylamine boranes in benzene solution. The change in slope indicates association. (Values of Nöth and Beyer are given for comparison.)

tric constant measurements, which are also shown in Figure 1.

It is of interest to note that the slope of the trimethylamine borane line appears to be slightly positive. It is significant that a slight positive slope is expected from theory for a normal nonassociated solute. On the other hand, the ammonia borane line shows a slightly negative slope in dioxane (Figure 2) suggesting weak molecular association in the dioxane solution. It is, however, apparent from the figures that the slope is clearly not enough to influence the dipole measurement seriously or to preclude extrapolation of the measured quantities to infinite dilution. Monomethyl- and dimethylamine boranes show slight evidence for association in the dioxane solution (Figure 2); dimethylamine borane in diethyl ether shows some slight evidence for association (Figure 3).

In contrast to the above observations in dioxane and dimethyl ether solutions, the values obtained by us for $(CH_3)NH_2BH_3$ and $(CH_3)_2NHBH_3$ in *benzene solution* (Figure 1) are distorted so seriously by association that a realistic extrapolation of the curves to infinite dilution is impossible. The values obtained for $(CH_3)NH_2BH_3$ and $(CH_3)_2NHBH_3$ in dioxane solution suggest that the benzene solutions could reasonably extrapolate to values of about 61 and 45, respectively, but such numbers are not unambiguously obtained from the benzene data alone.

It is seen from Figure 1 that the dielectric values of

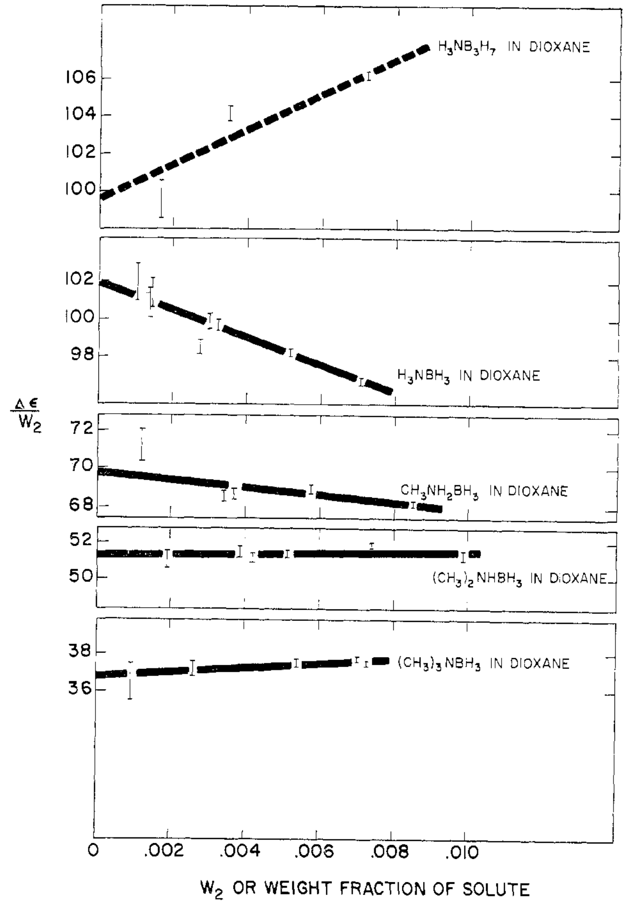

Figure 2.—Dielectric constant measurements for ammonia borane and methylamine boranes in dioxane solution.

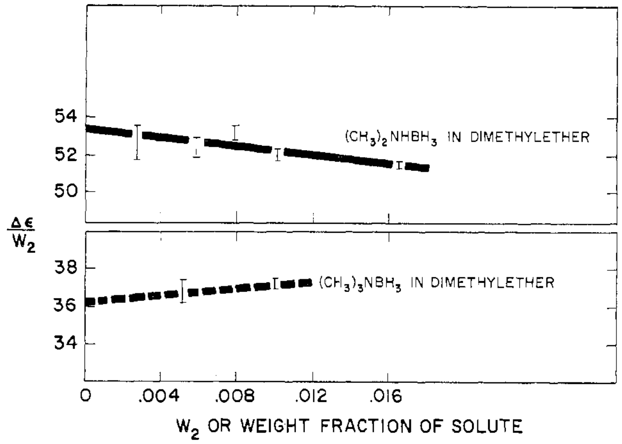

Figure 3.—Dielectric constant measurements for di- and trimethylamine boranes in dimethyl ether.

Nöth and Beyer for $(CH_3)NH_2BH_3$ and $(CH_3)_2NHBH_3$ in benzene solution are much higher than those obtained in this laboratory for solutions of comparable concentration. The values recorded are, in fact, close to those which would be expected in solvents where little association of $CH_3NH_2BH_3$ and $(CH_3)_2NHBH_3$ occurred (*i.e.*, dioxane). In view of both the cryoscopic work of Nöth and Beyer in benzene and our own dielectric measurements in benzene solution, the dielectric data of Nöth and Beyer are difficult for us to rationalize.

2. Conventional Dipole Calculations.—The dipole moments of H_3NBH_3, $CH_3NH_2BH_3$, $(CH_3)_2NHBH_3$, $(CH_3)_3NBH_3$, and $H_3NB_3H_7$ were calculated from solution data where possible. For the cases of $CH_3NH_2BH_3$ and $(CH_3)_2NHBH_3$ in benzene solution, association precluded straightforward calculations from the data available.

Several theoretical models were used to calculate the values shown in Table II. Values labeled μ_{conv} were obtained using two standard relationships based on the Debye equation.[8]

To obtain orientation polarization values from total polarization, the electronic polarization was taken as 12 cc for ammonia borane with an increment of 4.5 cc for each methyl group. These values are consistent with atomic refraction values and with the smoothed out values calculated from the measured n^2. The atomic polarization was taken as 5% of the electronic component. These latter values are not critical since a difference of 1 cc in the polarization changes the calculated moment by only 0.005 D. The moments calculated by different conventional methods without solvent correction agreed to within ±0.01 D. The result for trimethylamine borane is 0.04 D. lower in benzene than in dioxane. In diethyl ether the moment calculated for $(CH_3)_3NBH_3$ by the conventional procedure without solvent correction is about 0.9 D. lower than in benzene.

Values for amine boranes corrected for solvent effects by an application of the methods given in the first paper of the group are shown in Table II. The column headed μ_{sph} assumes the solute molecule to be spherical and shows the deviation from the conventional equation due to the incorrect formulation of the reaction field. For the data from the dioxane and benzene solutions the largest deviations are 0.1 D., but in the polar solvent ether there is an increase in the calculated moment of more than 1 D. The column μ_{ell} shows the result assuming an ellipsoidal cavity with an eccentricity as shown in the last column. The ellipsoidal correction ranges from +0.35 D. for ammonia triborane in dioxane to −0.11 D. for trimethylamine borane in ether. There is good agreement between the result for trimethylamine borane in dioxane and benzene, but the results for the ether solutions are 0.1 to 0.2 D. high. This is similar in magnitude to the discrepancy between the dipole moment of ether itself as calculated from data for the pure liquid and from data for the vapor phase.[3]

It is of interest that both μ_{sph} and μ_{ell} show a maximum for monomethylamine borane, while μ_{conv} values for ammonia borane and monomethylamine borane are the same size. In contrast to the postulate of Nöth and Beyer, no evidence of any type suggests that ammonia borane has a larger dipole moment than methylamine borane. In fact, all of the available evidence indicates that the reverse is true; methylamine borane has a somewhat higher dipole moment than ammonia borane. This fact is particularly damaging to any obvious correlation of dipole moments based on simple vector addition of bond dipole moments.

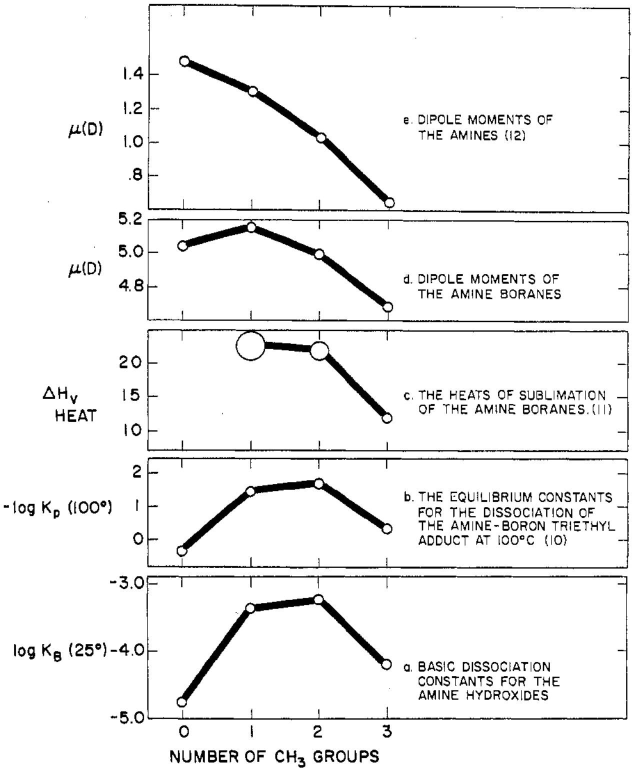

Figure 4.—Variation of properties of methylamines as hydrogens are replaced by methyl groups.

The maximum at methylamine borane is reminiscent of the fact that many other properties of the alkylamines show a maximum as one goes through members of the series. For example, the basic dissociation constants of the amine hydroxides and the stability constants for the boron trimethyl adducts show a maximum at dimethylamine with methylamine being very close to the maximum. This behavior is in contrast to the dipole moments of the free amines themselves which decrease regularly with increasing methyl substitution. The curve showing the variation in dipole moment of the amine boranes would appear to be almost intermediate in form between the curve showing the dipole moments of the free amines and the curve showing the interaction of the free electron pairs in chemical systems, Figure 4 (*i.e.*, the p*K* values and stability constants).

Incipient behavior of this type appears also in the p*K* values of the N-methyl- and O-methylalkylhydroxylamines and in the available heat of sublimation values for the amine boranes.[9]

Since the dipole moments of the free amines decrease regularly from ammonia to trimethylamine,[10] it is not immediately obvious why coordination of a BH_3 group on the free electron pair of each amine should produce

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(8) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., Amsterdan, 1952, p 305, eq 9.37 and 9.38..

(9) E. R. Alton, R. D. Brown, J. C. Carter, and R. C. Taylor, *J. Am. Chem. Soc.*, **81**, 3550 (1959); T. C. Bissot, R. W. Parry, and D. H. Campbell, *ibid.*, **79**, 796 (1957).

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

such different effects. A model to rationalize the foregoing facts along with others is presented in the next paper.

Acknowledgment.—Financial support of a portion of this work by the National Science Foundation under Grant NSF G-21408 is gratefully acknowledged.

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Dipole Moment Studies. IV. Trends in Dipole Moments

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Received September 10, 1965

As one replaces the hydrogen atoms on ammonia with methyl groups, the dipole moment *falls* from a value of 1.47 D. for NH_3 to 0.61 D. for both $N(CH_3)_3$ and $N(C_2H_5)_3$. The corresponding replacements in the phosphines result in an *increase* from 0.58 D. for PH_3 to 1.19 D. for $P(CH_3)_3$ and 1.35 D. for $P(C_2H_5)_3$. The dipole moments of the amine boranes rise to a maximum at $H_2NCH_3BH_3$ and fall to a minimum at $(CH_3)_3NBH_3$. All of the foregoing facts may be rationalized in terms of a model which predicts a high lone-pair moment for ammonia and a rapid decrease in lone-pair moment as the polarizability of the central atom is increased. Base strength is related to both the lone-pair moment and the electron-cloud polarizability. In the phosphines the lone-pair moment is of little significance. The model provides a reasonable basis for interpretation of the data on the amine boranes.

Chemical evidence such as the strength of acids and bases is usually assumed to indicate that the electron-releasing propensity of a methyl or ethyl group is larger than that of a hydrogen atom in the same position. For example, the increase in basic strength as one goes from ammonia to dimethylamine is usually interpreted in terms of the inductive effects of the methyl group. It is then rather surprising to find that the dipole moment of ammonia is 1.47 D., that of CH_3NH_2 is 1.28 D., that of $(CH_3)_2NH$ is 1.03 D., and that of $(CH_3)_3N$ is 0.612 D. If indeed the alkyl group promoted electron release and formation of a *more positive carbon* at a *greater distance* from the nitrogen (1.47 A for the carbon–nitrogen distance as compared to 1.01 A for the hydrogen–nitrogen distance), an increase in the dipole moment rather than a decrease would be clearly expected.

If, on the other hand, one were to postulate that, contrary to the chemical evidence, the alkyl group is more electron withdrawing than is the hydrogen atom, the dipole moment trends in the alkylamines could be understood in simple terms, but the opposite trends in the phosphines, an increase in moment from PH_3 to $P(CH_3)_3$, would pose equally troublesome problems. The foregoing contrast in dipole trends with alkyl substitution is found not only for nitrogen and phosphorus derivatives but also for oxygen and sulfur derivatives as well as for fluorine and chlorine compounds.

A further anomaly in trends is found in the data for the alkylamine boranes reported earlier in this series.[1] The new precision data for ammonia borane and methylamine borane indicate clearly that a maximum in moment is found at methylamine borane; this apparent anomaly is a fact of nature which must be rationalized by any acceptable model for electron interaction.

In the past 15 years, unusually precise dipole data for NH_3,[2] NH_2CH_3,[3] $N(CH_3)_3$,[4a] $(CH_3)_3P$,[4b] H_3P,[5] and CH_3PH_2[6] have been obtained from microwave data. In an excellent set of papers Lide[3,4] carefully analyzed the Stark effect in the microwave spectrum of methylamine and deuteriomethylamine to obtain precise values for dipole moment components along the axes of the molecules. A similar analysis has been completed more recently by Kojima, Breig, and Lin[6] for methylphosphine. The availability of these fine data plus the data for the ethylphosphines and amine boranes given earlier have prompted the construction of the following model for rationalization of the trends of dipole moments in different systems.

The Alkylamines

If the dipole moment of ammonia were assumed to be the resultant of three nitrogen–hydrogen vectors, a value of 1.31 D. for each N–H bond would be required to reproduce the experimental value of 1.47 D. for the molecule. If negative charge were assumed to be distributed in a spherically symmetrical pattern about the nitrogen, a charge of -0.82 would be required on the nitrogen atom. A similar treatment for water would require a charge of -0.64 on oxygen and for HF would require a value of -0.43 on fluorine. It would appear that a model which avoids spherical charge distribution as required by the additivity of bond moments and which postulates a considerable contribution from lone pairs of electrons would fit better with normal chemical concepts of the changes in electronegativity or ionic

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