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

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Dipole Moment Studies. IV. Trends in Dipole Moments

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

[2] D. K. Coles, W. E. Good, J. K. Bragg, and A. H. Sharbaugh, *Phys. Rev.*, **82**, 877 (1951).

[3] D. R. Lide, Jr., *J. Chem. Phys.*, **27**, 343 (1957); **20**, 1812 (1952).

[4] (a) D. R. Lide, Jr., and D. E. Mann, *ibid.*, **28**, 572 (1958); (b) *ibid.*, **29**, 914 (1958).

[5] C. A. Burrus, *ibid.*, **28**, 427 (1958).

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

character as one goes across the periodic table. Arguments utilizing the lone pair are not new.[7,8]

It should, however, be noted that the use of an electrostatic approach to chemical bonding led Bader to conclude, on the basis of electrostatic calculations, that the lone-pair orbital in ammonia must necessarily be close to 2s, and the three 2p orbitals must form bent bonds with the three hydrogens.

The contributions of the lone-pair electrons would be dependent in large measure upon the degree of hybridization and nuclear shielding, or, in alternate language, upon the charge distribution of the electron cloud. The relative influence of the proton as compared to an alkyl group can be examined from a variety of approaches and can be visualized in terms of a polarization model or a hybridization model.

In the polarization model the penetration of a proton into the electron cloud of a spherical ion results in two strong distortions: (1) a polarization or deformation of the electrons from spherical symmetry toward the proton and (2) a tightening of the charge cloud; the latter is clearly indicated experimentally by the decrease in molar refraction from the value of 9.0 cc for the chloride ion to 6.7 cc for HCl.[9,10] Because the alkyl group is larger than the proton and less able to penetrate, it has a larger effect on the polarization of the electron cloud (greater tendency to distort the cloud from the nitrogen toward carbon) but a significantly lower ability to tighten the over-all cloud around nitrogen. Restricting attention to that part of the charge cloud designated as the lone pair, the substitution of an alkyl group for a proton on nitrogen results in a loosening of the charge cloud and a concurrent distortion of the electrons toward the carbon. As a result, the lone pair will be more nearly centered on the nitrogen. The net effect is a lower moment for methylamine. It is, however, important to note that the cloud is now more polarizable and capable of stronger interaction with a very strongly polarizing positive center which can approach reasonably closely (*i.e.*, a proton). For this reason, methylamine is a stronger base than ammonia when the proton is the reference acid. On the other hand, with larger ions of lower polarizing power such as Cd^{2+}, one can interpret the evidence[11] as indicating that ammonia is slightly stronger as a base. Drago and Wayland[12] have also shown recently that the order of ΔH values for acid–base interactions of the alkylamines with various Lewis acids is clearly dependent upon the reference acid chosen. Base strength is thus more a measure of the ability of electrons to move under the influence of a polarizing field into position for bonding rather than a measure of the original distribution of electrons in the molecular ground state. Since the polarizing power of an approaching positive center is clearly related to its distance from the electron cloud, steric interference would show up in this manner.[13]

Again considering the size of the individual bond and electron-pair moments of methylamine as compared to ammonia, one would expect that the larger carbon–nitrogen distance and any electron donation by the CH_3 group would give rise to a larger bond moment for the $N-CH_3$ bond in methylamine than for the comparable N–H bond in ammonia.[14] This will be compensated, at least in part, by the shift toward carbon of both the lone-pair and the bonding electrons as a result of the general loosening of the charge cloud around the nitrogen. As a consequence, the carbon–nitrogen moment might well be expected to be comparable in size to the N–H moment which it replaced. The decrease in the *lone-pair moment* of methylamine would, however, account for the lower over-all moment of the molecule.

In hybridization language the foregoing concepts lead to the statement that the lone pair, with a lower moment, is less of an sp^3 hybrid and has more pure s character in methylamine than it has in ammonia. A qualitative discussion of the amines and related compounds in these terms has been given by Yoneda.[15] Such an argument leads to the conclusion that the H–N–H angle in methylamine, if steric and electrostatic distortion were comparable to those found in ammonia, should be smaller than the angle in ammonia because of the larger p character in the methylamine bonds. The H–N–H angles as determined by microwave spectroscopy are 107° for NH_3 and 106° for CH_3NH_2 (Table I). The difference, if significant, is consistent with the above proposal.

The availability of highly precise structural and dipole data for the methylamines from microwave spectroscopy makes possible a semiquantitative formulation of these concepts using only a limited number of supportable assumptions. Structural and dipole data are summarized in Table I.[16]

The geometry of methylamine is like that of methylphosphine.[8] (See Figure 1, ref 17.) Lide's values for the dipole moment components along the axes of rotation are $\mu_a = 0.304$ and $\mu_c = 1.247$. These values along with the value of 3.5° for ϵ, the angle between the N–C axis and the principal axis of rotation, provide striking confirmation of the ideas just developed. The resultant moment vector, calculated from μ_a and μ_c is found to make almost equal angles with the three bonds, so that the bond moments of N–H and $N-CH_3$ must be nearly equal. If no moment is assumed for the

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[7] (a) C. A. Coulson, "Valence," Oxford University Press, Oxford, 1952, p 207; (b) J. A. Pople, *Proc. Roy. Soc.* (London), **A202**, 323 (1950); (c) A. B. F. Duncan and J. A. Pople, *Trans. Faraday Soc.*, **49**, 217 (1953).

[8] R. F. W. Bader, *J. Am. Chem. Soc.*, **86**, 5070 (1964); R. F. W. Bader and G. A. Jones, *Can. J. Chem.*, **41**, 586 (1963); R. F. W. Bader and G. A. Jones, *J. Chem. Phys.*, **38**, 2791 (1963).

[9] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, 1945, p 54.

[10] "Landholt-Börnstein Tabellen," Vol. II, Part 8, 6th ed, 1962, pp 6–873.

[11] C. S. Spike and R. W. Parry, *J. Am. Chem. Soc.*, **75**, 2728 (1953).

[12] R. S. Drago and B. B. Wayland, *ibid.*, **87**, 2571 (1965).

[13] H. C. Brown, H. Bartholomay, and M. D. Taylor, *ibid.*, **66**, 435 (1944).

[14] In this model the CH_3^+ group is regarded as a unit. The moments of the three C–H bonds are regarded as part of the $N-CH_3$ moment.

[15] H. Yoneda, *Bull. Chem. Soc. Japan*, **31**, 708 (1958).

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

[17] G. Kodama, J. R. Weaver, J. LaRochelle, and R. W. Parry, *Inorg. Chem.*, **5**, 710 (1966).

TABLE I

STRUCTURAL PARAMETERS FOR METHYLAMINES

Amine property	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
N–H distance	1.012 ± 0.004 A	1.011 A (3)	1.011 A[a]	
N–C distance	. . .	1.474 A (3)	1.474 A[a]	1.472 ± 0.008 A (4)
H–N–H angle	107° (2)	105.9° (3)	. . .	. . .
H–N–C angle	. . .	112.0° (3)	112°[a]	. . .
C–N–C angle	. . .	. . .	109°[a]	108.7 ± 1.0 (4)
ϵ	. . .	3.5°	. . .	. . .
μ_{total}	1.47 (2)	μ_a = 0.304 (3) μ_c = 1.247 (3) μ_T = 1.283 (3)	μ_T = 1.03 (16)	0.612 ± 0.003 (4)
β	119.5°	128.7°	130.1°	. . .
Quadrupole coupling constant	−4.08 Mc	−4.5 to −4.9 Mc (Z comp)	. . .	−5.47 Mc

[a] Interpolated from values for methyl- and trimethylamine.

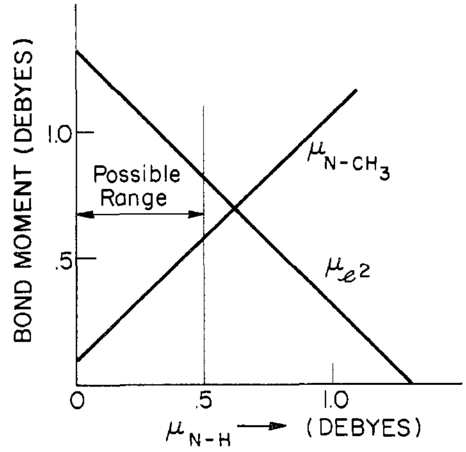

Figure 1.—Possible assignment of bond and lone-pair moments consistent with observed data.

lone pair in methylamine, the bond moments are μ_{N-H} = 1.30 D. and μ_{N-CH_3} = 1.37 D.

If the moment of the lone pair is included, the experimental components of the moment along the rotational axes of the molecule are given by

$$\mu_a = \mu_{N-CH_3} \cos \epsilon + 2\mu_{N-H} \cos \frac{\text{HNH angle}}{2} \cos (\beta + \epsilon) - \mu_{e2} \cos (\alpha - \epsilon)$$

$$\mu_c = 2\mu_{N-H} \cos \frac{\text{HNH angle}}{2} \sin (\beta + \epsilon) + \mu_{N-CH_3} \sin \epsilon + \mu_{e2} \sin (\alpha - \epsilon)$$

where μ_a = the moment along the principal rotational axis; μ_c = the moment along the rotational axis perpendicular to μ_a and closest to the N–H resultant (see Figure 1, ref 17); μ_{N-H}, μ_{N-CH_3} = bond moments along N–H and N–CH_3 bonds, respectively; μ_{e2} = moment of lone pair; β = angle between the N–CH_3 bond and the *resultant* of the *two* N–H bonds; α = angle between the C–N bond and the lone-pair vector; ϵ = angle between N–CH_3 axis and the rotational axis a.

For methylamine cos β = cos (CNH angle)/cos (HNH angle/2) and β = 128.7°; μ_a, μ_c, HNH angle, CNH angle, and ϵ are available as experimental values.[3]

Placing these values in the above two expressions for μ_a and μ_c, one obtains two equations with four unknowns—μ_{N-CH_3}, μ_{N-H}, μ_{e2}, and α. A value for α can be estimated as follows. In ammonia the angle between the lone pair and each of the bonds, assuming a symmetrical model, can be calculated and is found to be 112°. Taking the same value for the angle between the lone-pair moment and the nitrogen–hydrogen bonds in methylamine, one obtains for α, the angle between the lone pair and the nitrogen–carbon bond, a value of 103°. Since the model requires some distortion of the charge cloud for the lone pair in the direction of the nitrogen–carbon bond, this value obtained from geometric arguments is reasonable. With the assignment of a value of α, the only remaining unknowns in the two equations are the components μ_{N-CH_3}, μ_{N-H}, and μ_{e2}. Taking any one of those as a parameter, the other two can be expressed in terms of it.

$$\mu_{N-CH_3} = 0.971\mu_{N-H} + 0.96$$

$$\mu_{e2} = -0.965\mu_{N-H} + 1.260$$

These relationships are plotted in Figure 1, where it is evident (1) that μ_{N-CH_3} remains about 0.08 to 0.09 D. larger than μ_{N-C} throughout the entire range of possible values of μ_{N-H} and (2) that any change in the assignment of μ_{N-H} and μ_{N-CH_3} is compensated by a change in μ_{e2} in the opposite direction.

Certain limitations on the range of possible values shown in Figure 1 can be established by independent arguments. If it is agreed that the hydrogen must remain positive, μ_{N-H} must be positive. On the other hand, if one assumes that all of the dipole moment in trimethylamine is due to N–CH_3 bonds one obtains a maximum value of μ_{N-CH_3} in trimethylamine of 0.59 D. The close agreement in N–C bond lengths in methylamine and trimethylamine (in contrast to the phosphines in which the change of bond moment is reflected by a change in length of 0.02 A) suggests that the N–C bond moment should be assigned the same value in methylamine as in trimethylamine. The range of possible values in Figure 1 is thus restricted to the region $\mu_{\mathrm{N-H}} = 0$ to 0.50, with $\mu_{\mathrm{e}2}$ falling between 0.75 and 1.25 D. This representation reflects the following two points: (1) that the exact division of the charge cloud into bonding and lone-pair electrons is arbitrary[18] but (2) *that to rationalize the experimental data a consistent model is obtained only if the largest contribution to the electric moment is assigned to the lone pair.* Several theoretical treatments support this assignment.[7,19]

Lide[3] has suggested that the similarity in bond lengths and in quadrupole coupling components in the N–H direction in ammonia and methylamine indicates that the N–H bonds in these two molecules should have identical bond moments. As noted above a similar conclusion for the N–CH_3 bonds in methylamine and trimethylamine can be drawn. If it is assumed that both of these bond moments remain constant throughout the series of compounds, interesting comparisons can be made between the lone-pair moments of each of the four molecules. For dimethylamine, accurate values for structural paramenters are apparently not available in the literature, but they can be interpolated with reasonable confidence (Table I). Figure 2 shows the variation in $\mu_{\mathrm{e}2}$ for three possible pairs of $\mu_{\mathrm{N-H}}$ and $\mu_{\mathrm{N-CH_3}}$ values.

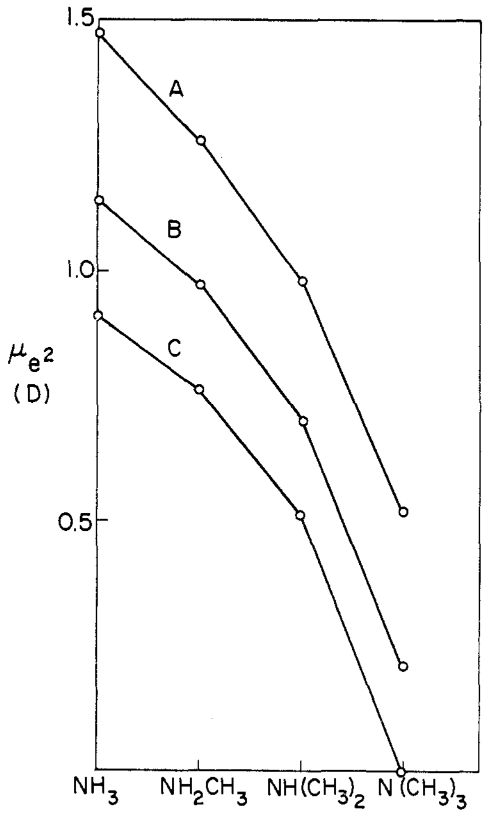

Figure 2.—Lone-pair moments for several assumed values of $\mu_{\mathrm{N-H}}$. A: $\mu_{\mathrm{N-H}} = 0$, $\mu_{\mathrm{N-CH_3}} = 0.09$. B: $\mu_{\mathrm{N-H}} = 0.30$, $\mu_{\mathrm{N-CH_3}} = 0.39$. C: $\mu_{\mathrm{N-H}} = 0.50$, $\mu_{\mathrm{N-CH_3}} = 0.59$.

The variation of $\mu_{\mathrm{e}2}$ in Figure 2 is extremely interesting and has significant possibilities for the interpretation of the problem of base strength. It is observed that the sharpest fall in $\mu_{\mathrm{e}2}$, that is, the most pronounced *shift of the center of the lone-pair charge cloud* toward the nitrogen nucleus, occurs with the removal of the *last* hydrogen. This may well be a major factor in the decrease in base strength from dimethylamine to trimethylamine. From ammonia to dimethylamine a "loosening effect" predominates, and the base strength increases. Since the change in p*K* from ammonia to methylamine is larger than that for any other p*K* change in the series and since the change in the lone-pair moment from ammonia to methylamine is not unusually large, one must conclude that in terms of this model the *loosening effect* is largest with the replacement of the first hydrogen; subsequent replacements bring about smaller alterations.

It is also of interest to compare the value for the difference in bond moments between the N–CH_3 bond and the N–H bond with the difference in bond moment between the C–CH_3 and C–H bonds. The dipole moment of the propane molecule has been measured as 0.083 D.[20] If this value is apportioned between two C–CH_3 and C–H vectors, one obtains $\mu_{\mathrm{C-CH_3}} - \mu_{\mathrm{C-H}} = \pm 0.07$ D. If it is assumed that the direction of the moment is such that both CH_3 and H are positive and that the C–CH_3 moment is larger than the C–H moment, the difference of 0.07 is very close to the difference of 0.09 for $\mu_{\mathrm{N-CH_3}} - \mu_{\mathrm{N-H}}$. Apparently, the presence of the polarizable lone pair provides sufficient shielding of the nitrogen nucleus to make the bonds in the amines quite similar to those in the hydrocarbons.

The Alkylphosphines

It is of interest to see how the preceding arguments for the methylamines relate to the alkylphosphines. The low dipole moment of phosphine itself indicates that, in contrast to the large lone pair in ammonia, the lone-pair contribution in phosphine must be very small. Such a result is consistent with the conclusion from the nmr coupling constant which shows the P–H bond to have almost pure p character.[21] The phenomenon can be rationalized in terms of the larger size and greater polarizability of phosphines which makes the P–H bond almost as long as the N–C bond and permits the lone pair to be nearly centered on the phosphines.

As in the case of the amines, the replacement of a proton with an alkyl group should (1) loosen the electron cloud making the lone pair more readily available and (2) produce greater charge separation and higher dipole moment along the bond as a result of any electron-releasing tendencies and the larger internuclear distance in the P–CH_3 bonds. In the case of the amines,

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[18] This statement is true of an orbital model as well as the polarization model since the assignment of a basic set of orbitals for the representation is arbitrary.

[19] W. E. Moffitt, *Proc. Roy. Soc.* (London), **A202**, 548 (1950).

[20] D. R. Lide, *J. Chem. Phys.*, **33**, 1514 (1960).

[21] H. S. Gutowsky, D. W. McCall, and C. P. Slicter, *ibid.*, **21**, 279 (1953).

the second phenomenon tending to increase the moment was counterbalanced by a shift of the lone electron pair inward toward more spherical distribution, a move which not only reduced the size of the lone-pair moment but also brought the N–CH_3 moment back very close to the original N–H values. In the case of the phosphines, with little or no lone-pair moment, loosening the electron cloud by substitution of a methyl group for a proton again makes the lone pair more readily available in chemical systems. Further, it produces a much larger bond dipole for P–CH_3 as compared to P–H—for reasons outlined in point 2 above. As a result of charge loosening, a relatively small shift of charge takes place from phosphorus toward carbon as more alkyl groups are added, making the moment of the P–CH_3 bond slightly smaller as one goes from H_2PCH_3 (1.06 D.) to $P(CH_3)_3$ (0.83 D.). This change, however, is small when one considers the large increase in the P–CH_3 moment as compared to the P–H moment. Since there is no decrease in a lone-pair moment in the phosphines to offset the large increase in molecular moments due to the P–CH_3 bond, the molecular moments of the alkylphosphines increase as hydrogens are replaced by alkyl groups. The calculated bond moments for the methyl- and ethylphosphines are summarized in Table II.

Table II

The Calculated Bond Moments for Methyl- and Ethylphosphines

	μ_{PH}	μ_{PCH_3}	$\mu_{PC_2H_5}$
PH_3	0.36	...	...
RPH_2	0.38	1.06	1.17
R_2PH	(0.38)	0.95	1.06
R_3P	...	0.83	0.94

Significant points indicated in Table II are: (1) a nearly constant moment for the μ_{P-H} bonds in the series, (2) a decrease in the P–CH_3 moment as one goes from methylphosphine to trimethylphosphine (see above discussion), and (3) a difference of 0.1 D. between the P–C_2H_5 bond moment and the P–CH_3 bond moment. The latter point deserves comment. Since the CH_3 of the ethyl group is not in the direction of the bond, but presumably at an average angle of 71° with this direction, the difference is too large to ascribe simply to the difference between C–CH_3 and C–H moments (estimated earlier as 0.07 D.). An extra inductive effect by the *ethyl* group is indicated.

The Amine Boranes

The foregoing ideas are illustrated quite simply and beautifully by the dipole moments of the amine boranes shown graphically in Figure 3. Both the size of the moments in these molecules (5.0 D.) and a consideration of vector addition of individual bond moments show that the measured moment will be dominated by the moment components in the N–B direction.

The coordination of the lone pair to the boron should greatly change the environment of the groups on the nitrogen, making the absolute bond moments of N–H and N–CH_3 somewhat larger. Perhaps one might also observe a greater difference between them. However, the fact that these bonds will be at or near the tetrahedral angle will reduce their contribution to the molecular moment and justify focusing major attention on the moment of the N–B bond.[22] The coordination of a BH_3 group to the projecting electron pair of ammonia will perturb it outward and shift negative charge away from the nitrogen and toward the boron. The result is a much larger dipole moment for H_3NBH_3 (5.0 D.) than for H_3N (1.5 D.) where the undistorted lone pair makes the major contribution to the measured value for the free base.

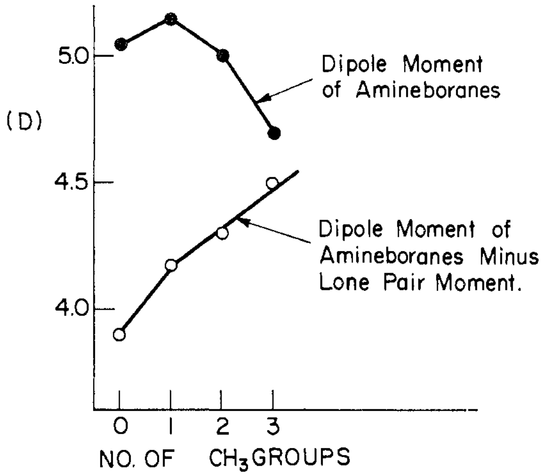

Figure 3.—The dipole moments of the amine borane corrected for the lone-pair moments of the free amines. The difference gives a relative measure of the "loosening effect" of methyl substitution.

When an alkyl group is substituted in place of a hydrogen atom to give methylamine, the charge cloud is loosened and some of the lone-pair charge is shifted toward the methyl group, thus reducing the lone-pair moment in methylamine. (The value for μ_{e^2} drops from 1.14 to 0.97.[23]) Exactly the same effect is anticipated in methylamine borane. However, one would expect that the BH_3 group acting on this more centrally located and *more polarizable* lone pair would distort it from its position in methylamine somewhat more than was observed in ammonia. In short, the strongly directed lone pair of ammonia ($\mu_{e^2} = 1.14$) is perturbed outward by the BH_3 group; the slightly less strongly directed lone pair of methylamine ($\mu_{e^2} = 0.97$) is perturbed outward more than was the lone pair of ammonia because the lone-pair cloud is more easily deformed in CH_3NH_2. The net result is a somewhat larger value for the over-all molecular moment of $CH_3NH_2BH_3$ than for H_3NBH_3.

In dimethylamine the BH_3 group acts on a much less strongly directed lone pair ($\mu_{e^2} = 0.70$). Although the electron pair is more easily polarized than that of CH_3NH_2, the original polarization of this cloud toward the two CH_3 groups has seriously reduced the lone-pair moment, and the effect of a BH_3 group on this lone pair

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[22] As in the case of the CH_3 groups, the BH_3 group is considered as a unit in calculating the value of μ_{N-BH_3} or the moment of the N–B bond.

[23] Values quoted for μ_{e^2} in this section are taken from the middle curve of Figure 2. The absolute values are arbitrary within ±0.30, but the relative values are significant.

is not enough to bring the over-all molecular moment up to the value for $CH_3NH_2BH_3$ or H_3NBH_3. In trimethylamine the lone-pair moment of the free base is even lower ($\mu_{e^2} = 0.21$) and the moment of $(CH_3)_3NBH_3$ is lower than that of any of the other three amine boranes.

The effects of the lone pair and the general loosening effect of methyl substitution can be seen by subtracting the value of the lone-pair moment of the free amine from the measured moments of the amine boranes. The values from the middle curve in Figure 2 have been subtracted and the difference plotted in the lower curve of Figure 3. The rising curve indicates that the lone-pair contribution was indeed responsible for the rise and fall of the original curve. The rise of the difference curve reflects the fact that each methyl group tends to loosen the electron cloud so that the polarization of this cloud by the BH_3 group gets larger in the series from NH_3 to $N(CH_3)_3$. The pK data suggest that the most pronounced loosening effect is created by the first methyl group when one goes from NH_3 to NH_2CH_3. This same fact is illustrated by the fact that the difference curve is higher at methylamine than would be expected by a strictly linear relationship.

The foregoing arguments can be summarized as follows. The variation in the moments of amine boranes with alkyl substitution on the nitrogen will be determined by the effects discussed in the section on the methylamines. (1) Replacement of a hydrogen by an alkyl group loosens the electron cloud, particularly of the lone pair. (2) Alkyl groups tend to polarize this cloud toward the alkyl group itself, thus lowering the moment of the free electron pair in the amine or the over-all molecular moments of the amine boranes. A quantitative estimate of the alkyl polarization effect is provided by the variation of the moment of the uncoordinated pair of the free amine shown in Figure 2. (3) Borane groups also tend to polarize the loosened electron cloud; this borane polarization effect tends to increase the moment. A quantitative illustration of this effect is provided by the curve showing the difference between the lone-pair moment and the moments of the amine boranes (lower curve, Figure 3). Such subtraction eliminates the polarization effects due to the alkyl groups (item 2, above) and leaves only borane polarization effects. The significant "loosening effect" or increase in polarizability due to the first alkyl group is clearly apparent in this curve. Smaller effects appear for the succeeding two replacements.

Since the curves in Figure 2 are nearly parallel, the same result would be obtained, regardless of the curve selected from Figure 2. While the absolute scale would shift as one selects different curves in Figure 2, the curve shape and the significant trends would not be affected. The middle curve of Figure 2 was selected for drawing Figure 3 and for determining the size of the lone-pair moments cited since it represents values near the center of the possible range of bond moment values.

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The Structure of Phosphine Borane

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On the basis of high-resolution nmr spectra it has been shown that the compound originally reported as $B_2H_6 \cdot 2PH_3$ is the monomer, H_3BPH_3, in the liquid state. Infrared and Raman spectra show that the same structure is maintained in the solid phase.

In 1940 Gamble and Gilmont prepared "diborane diphosphine" by mixing diborane and phosphine at low temperatures.[1] On the basis of rudimentary chemical evidence an analogy was drawn to the diammoniate of diborane and a structure analogous to that accepted at that time for $B_2H_6 \cdot 2NH_3$ was proposed, $[PH_4^+][H_3BPH_2BH_3^-]$. No molecular weight data were available to support the postulated ionic dimer.

Some of the reactions of $[H_3PBH]_n$ can be interpreted best in terms of a single monomeric formulation. For example, trimethylamine displaces PH_3 quantitatively to give $H_3BN(CH_3)_3$,[2] and a kinetic study of the reaction of B_2H_6 and PH_3 by Brumberger and Marcus[3] suggested the monomeric representation.

Since the original structural postulates were presented, a new model for $B_2H_6 \cdot 2NH_3$ has been accepted[4] in place of the earlier ammonium type of solid, $[NH_4^+][H_3BNH_2BH_3^-]$, but neither the new diammoniate

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(1) E. L. Gamble and P. Gilmont, *J. Am. Chem. Soc.*, **62**, 717 (1940).

(2) See footnote 5 of ref 1.

(3) H. Brumberger and R. A. Marcus, *J. Chem. Phys.*, **24**, 741 (1956).

(4) D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958); S. G. Shore and R. W. Parry, *ibid.*, **80**, 12 (1958); R. C. Taylor, D. R. Schultz, and A. R. Emery, *ibid.*, **80**, 27 (1958); C. E. Nordman and C. R. Peters, *ibid.*, **81**, 3551 (1959).