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Molecular Orbital Studies of the Dipole Moments of Methyl Substituted Amines, Phosphines, and their Borane Adducts[1a]

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The magnitudes and trends of the dipole moments of $Me_xH_{3-x}E$ and $Me_xH_{3-x}EBH_3$ ($E = N, P; x = 0 \rightarrow 3; Me = CH_3$) were investigated via CNDO–MO methods. Moments evaluated by the CNDO/2D approach reproduced the experimental data better than the strict CNDO/2 formalism. Transformation of the canonical CNDO/2 MO's to localized MO's (LMO's) permitted a partitioning of the total moments into bond moments, bond polarization moments, and lone pair moments. Values of the lone pair moments of the phosphines are calculated to be greater than those of the amines. Within the framework of the CNDO/2D approximation, coordination of BH_3 to H_3N involves a charge migration primarily between the N-bound and B-bound hydrogens (0.33e) while coordination to H_3P is primarily $P \rightarrow B$ (0.27e). The covalent character of the BN and BP bonding LMO's is 46 and 61%, respectively. The CNDO molecular orbital results are in general agreement with Weaver and Parry's model for dipole moments and base strengths of amines and phosphines.

Introduction

The evaluation of the dipole moments of the title compounds from a variety of experimental and theoretical viewpoints is potentially important for obtaining a general model for the nature of the coordinate bond in phosphine- and amineboranes. Several years ago, Parry and co-workers[2] developed a useful qualitative model for these compounds which is capable of accounting for the striking contrasts in the trends in experimentally determined moments (Figure 1). They and others clearly recognized that an acceptable model for the dipole moments should be consistent with observed trends in other physical and chemical properties of these compounds such as relative base strengths of amines and phosphines.[3]

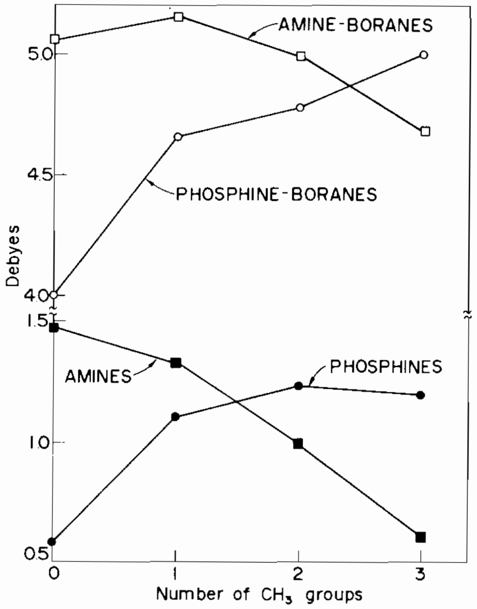

Figure 1. Experimental dipole moments (Debyes) of methylamines, phosphines, and their borane adducts.

The primary aims herein are to provide a comprehensive and quantitative interpretation of the dipole moments of the title compounds and to analyze more completely the effect of borane coordination to amines and phosphines. This is now feasible in terms of all-valence semi-empirical molecular orbital calculations whose reliability may be tested by reference to experimental dipole moments and to *ab initio* calculations which are now available for a few of the molecules.

We have chosen the CNDO–MO method[4] for obtaining our set of canonical molecular orbitals (CMO) and have calculated dipole moments within both the strict CNDO/2 formalism and the CNDO/2D approximation.[5,6] The latter involves a Löwdin deorthogonalization of the CMO's followed by calculation of dipole moments by the complete dipole moment ex-

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pression. From the localized molecular orbitals (LMO)[7] obtained from the CMO's, a clearer picture of the B–N and B–P coordinate bonds emerges than is available from analyses of delocalized CMO's[5,8–13]. The only parallel work[13] involves a LMO treatment of H_3P, Me_3P, and H_3PBH_3.

Within the CNDO/2 framework, the dipole moment expression is

$$\vec{\mu}_{\mathrm{total}} = \vec{\mu}_{\mathrm{Q}} + \vec{\mu}_{\mathrm{sp+pd}} \tag{1}$$

where μ_Q is the contribution due to the calculated equilibrium charge distribution and $\mu_{\mathrm{sp+pd}}$ is due to atomic *sp* and *pd* polarization. The latter may be partitioned

$$\vec{\mu}_{\mathrm{sp+pd}} = \sum_{i}^{\mathrm{bonds}} \vec{\mu}_i(\mathrm{AB}) + \sum_{j}^{\mathrm{n.b.p.}} \vec{\mu}_j(\mathrm{e}) \tag{2}$$

where $\mu_i(\mathrm{AB})$ represents the *sp* and/or *pd* polarizations calculated from the LMO describing the AB bond and $\mu_j(\mathrm{e})$ the lone pair moment obtained from an LMO describing a non-bonding pair of electrons. This partioning can lead to a theoretical test of the published empirical bond moment and lone pair moment estimates.

We may define the $i^{\underline{th}}$ bond moment as

$$\vec{\mu}_i^{\mathrm{BM}}(\mathrm{AB}) = \vec{\mu}_{\mathrm{Q}_i}(\mathrm{AB}) + \vec{\mu}_i(\mathrm{AB}) \tag{3}$$

Summing over all $\mu_{\mathrm{Q}_i}(\mathrm{AB})$ gives μ_Q. For a given LMO the x-component of $\mu_{\mathrm{Q}_i}(\mathrm{AB})$ would be

$$\mu_{\mathrm{Q}_i}{}^{x}(\mathrm{AB}) = 2.5413[x_A(Z_A'-P_i^A) + x_B(Z_B'-P_i^B)]\ \mathrm{Debyes} \tag{4}$$

where P_i^A and P_i^B are the total electron densities on atoms A and B relating to the $i^{\underline{th}}$ localized bond orbital, x_A and x_B are the x coordinates of atoms A and B in a.u. and Z_A' and Z_B' are the nuclear charges. As it is necessary to divide the total atomic nuclear charge among all bonds (2 center-2 electron bonds are assumed), Z_A' and Z_B' are both set equal to 1. As will be noted later, polarization contributions, $\vec{\mu}_i(\mathrm{AB})$, are not generally calculated to lie along the bond axes and as a result values of $\vec{\mu}_i^{\mathrm{BM}}(\mathrm{AB})$ cannot be strictly regarded as bond moments. However, in a number of instances the CNDO/2 $\vec{\mu}_{\mathrm{Q}_i}(\mathrm{AB})$ values are in reasonable agreement with some of the previous empirical bond moment estimates for the molecules studied here. This analogy between $\vec{\mu}_{\mathrm{Q}_i}(\mathrm{AB})$ and the empirical bond moment is given further weight by recent *ab initio* analyses[14] of the C–H bond dipole in terms of LMO's. Rothenberg's results[14a] showed that removal of the atomic dipole bond moment contribution (*i.e.*, our $\vec{\mu}_i(\mathrm{AB})$) from the total bond moment yielded a net moment of the same order as the empirical CH bond moment, 0.3–0.4D(C^-H^+). Within this approximation the terms *bond moment* and *lone pair moment* used by Weaver, Parry and others correspond respectively to our *bond moments* ($\vec{\mu}_{\mathrm{Q}_i}$) and the sum of all *polarization moments* ($\vec{\mu}_{\mathrm{sp+pd}}$). It is important to recognize that the polarization moment arising from non bonding electrons is only one component in the total molecular polarization moment.

Recently, there has been renewed interest in electronegativity equilization procedures for the calculation of charge distributions in molecules.[15,16] Therefore, we have applied one of these procedures[16] to the present set of molecules. As currently formulated, this electronegativity equalization technique does not allow for the calculation of lone pair moments; however, it is possible to compare the calculated trends in atom charge densities with those calculated via population analyses of CNDO wave functions.

Calculations

The CNDO calculations were performed using program CINDOM,[17] and parameters developed by Santry[18] were used for phosphorous. Calculations on each molecule containing phosphorus were performed with both 3*s*, 3*p* (*sp*) and 3*s*, 3*p*, 3*d* (*spd*) atomic orbital basis sets. LMO's were obtained by incorporating the subroutine ORLOC[19] into CINDOM.

Atomic coordinates were obtained with program PROXYZ[20] using the bond distances and angles given in Table I. A standard staggered geometry for the borane adducts was assumed. Professor J. E. Bloor kindly provided us with a listing of his deorthogonalization subroutine which was also incorporated into the CINDOM program. The complete dipole moment calculations were performed using a molecular properties program of the Quantum Theory Project, University of Florida.

Polarization moments ($\mu_j(\mathrm{e})$ and $\mu_i(\mathrm{AB})$) were calculated according to

$$\mu_{\mathrm{sp}}{}^{x}(\mathrm{Y}) = -14.6722\,\alpha_{\mathrm{Y}}^{-1}(c_s c_x)\mathrm{Debyes} \tag{5}$$

for Y a first row atom and

$$\mu_{\mathrm{sp+pd}}{}^{x}(\mathrm{Y}') = -15.91105\,\alpha_{\mathrm{Y}'}^{-1}(\sqrt{5/3}\,c_s c_x + c_z c_{xz} + c_y c_{xy} + c_x c_{x^2-y^2} - 1/\sqrt{3}\,c_x c_{z^2}) \tag{6a}$$

$$\mu_{\mathrm{sp+pd}}{}^{y}(\mathrm{Y}') = -15.91105\,\alpha_{\mathrm{Y}'}^{-1}(\sqrt{5/3}\,c_s c_y + c_z c_{yz} + c_x c_{xy} - c_y c_{x^2-y^2} - 1/\sqrt{3}\,c_y c_{z^2}) \tag{6b}$$

$$\mu_{\mathrm{sp+pd}}{}^{z}(\mathrm{Y}') = -15.91105\,\alpha_{\mathrm{Y}'}^{-1}(\sqrt{5/3}\,c_s c_z + 2/\sqrt{3}\,c_z c_{z^2} + c_x c_{xz} + c_y c_{yz})\ \mathrm{Debyes} \tag{6c}$$

for Y′ a second row atom. Further,

$$\vec{\mu}_j(\mathrm{e}) = \vec{\mu}_{\mathrm{sp}}(\mathrm{Y})\ \mathrm{or}\ \vec{\mu}_{\mathrm{sp+pd}}(\mathrm{Y}')$$

for a non-bonding pair on Y or Y′.

The polarization moment $\vec{\mu}_i(\mathrm{AB})$ for a pair of bonded atoms, where, for example, Y = A and Y′ = B, is

$$\vec{\mu}_i(YY') = \vec{\mu}_{sp}(Y) + \vec{\mu}_{sp+pd}(Y'). \qquad (7)$$

α_Y and $\alpha_{Y'}$ are the Slater exponents for Y and Y′. The c_ν are the atomic orbital (ν = s, p_x, ..., d_{xy}, ...) coefficients for the LMO's. Equations 5 and 6 are appropriately reduced forms of those given by Santry[18] for μ_{sp} and μ_{pd} and have been corrected for typographical errors in the original work.

TABLE I. Structural Parameters for Calculation of Atomic Coordinates.[a]

	H_3N[b]	MeH_2N[c]	Me_2HN[d]	Me_3N[e]
r(N–H)	1.01	1.011	1.011	–
r(N–C)	–	1.474	1.474	1.472
<HNH	107.3	–	–	–
<HCN	–	f	f	f
<HNC	–	f	112.0	–
<CNC	–	–	109.0	108.7

	$Me_xH_{3-x}NBH_3$[a,g]	$Me_xH_{3-x}P$[a,h]	$Me_xH_{3-x}PBH_3$[a,i]
r(E–B)	1.56	–	1.90
r(H–B)	1.19	–	1.22
r(E–H)	1.01	1.43	1.40
r(E–C)	1.53	1.85	1.81
<EBH	f	–	f
<HEB	f	–	116.3
<HEH	f, j	93.5	100.0[j]
<CEB	f	–	114.67
<HCE	f	f	f
<CPH	–	97.0	–
<CPC	–	99.0	99.0[j]

[a] r(C–H) and <HCH were assumed to be 1.09 Å and 109.47125°, respectively, unless otherwise noted. [b] D. K. Coles, W. E. Good, J. K. Bragg and A. H. Sharbaugh, *Phys. Rev., 82,* 877 (1951). [c] D. R. Lide, *J. Chem. Phys., 27,* 343 (1957); *ibid., 20,* 1812 (1952). [d] J. E. Wollrab and V. W. Laurie, *ibid., 48,* 5058 (1968). [e] D. R. Lide and D. E. Mann, *ibid., 28,* 572 (1958); J. E. Wollrab and V. W. Laurie, *ibid., 51,* 1580 (1969). [f] 109.47125°. [g] E = N. We have chosen to use the same parameters as Shillady (reference 5) for consistency with his work. These values were originally used by Veillard *et al.* (reference 12b). Armstrong and Perkins (reference 10a) have noted that this distance may be too short; they calculated r(N–B) to be 1.665 Å at the energy minimum. Durig *et al.* (footnote o, Table II) report an experimental value of 1.609 Å for the B–N bond in Me_3NBH_3; their data were also consistent with a bond length as long as 1.637 Å but the shorter length was favored. Our calculation of H_3BNH_3 was repeated with r(N–B) equal to 1.62 Å; no significant alterations from our results with an r of 1.56 Å were obtained. [h] E = P. We have chosen to standardize our parameters. See D. E. C. Corbridge, in *Topics in Phosphorus Chemistry,* vol. 3, E. J. Griffith and M. Grayson, eds., Wiley–Interscience, New York, 1966. [i] E = P. Standard values were selected on the basis of the data of reference[26]. r(C–H) = 1.08 Å. [j] These angles were not used in the computation of the atomic coordinates.

Calculations of the bond and polarization moments from the LMO's were performed with the exclusion of the atomic orbital contamination coefficients (0.1 and less in BH bonds with the majority less than 0.03) due to the non-participating atoms. As an indication of the error introduced by this MO truncation we may compare the total μ_Q obtained from the CMO's with the total μ_Q obtained by summing all μ_{Q_i} (AB) from the LMO's. For ammonia and phosphine there is the desired perfect agreement (contamination coefficients less than 0.002). For phosphineborane the difference is only 0.08 D; this may be regarded as fortuitous as coefficients as high as 0.1 are neglected. Overall, the disparities increase with increasing methyl substitution to 0.29, 0.46, 0.97 and 1.01 D for trimethylphosphine, -amine, -amineborane, and -phosphineborane. These discrepancies should be kept in mind during the subsequent discussion of the individual bond and polarization moments. However, most likely the differences are fairly well distributed over the entire molecular framework such that the error *per bond* is probably not significant.

Calculation of atomic charges also was carried out using the electronegativity equilization program, CHELEQ, of Jolly and Perry.[16] This empirical method has been calibrated with x-ray photoelectron spectroscopic core binding energies. In contrast with most schemes, electronegativity equilization extends over the whole molecule.

Results and Discussion

Comparison of the CNDO/2 and CNDO/2D methods as to their ability to predict dipole moments for a wide variety of molecules has led to the conclusion[5,21] that in general CNDO/2D is only marginally better in reproducing experimental values; however, there is evidence that CNDO/2D produces more reasonable electron density maps. As will be seen below, CNDO/2D does significantly better in reproducing experimental trends in the particular series of related molecules treated here and, with one exception, provides better numerical agreement with experiment for the individual molecules.

A particular problem of CNDO/2 is its failure to account properly for the effect of replacing nitrogen-bound hydrogen atoms with methyl groups.[5,12c,d] In addition, Shillady *et al.*[5] have observed that for the special case of boron coordination complexes, *i.e.*, H_3NBH_3, CNDO/2 calculated charge distributions are in rather poor agreement with those from *ab initio* calculations;[9–12a,b] apparently, CNDO/2 over-estimates charge transfer between boron and nitrogen (the major charge redistribution according to *ab initio* studies appears to involve primarily the hydrogens). CNDO/2D charge distributions obtained from Mulliken population analyses are in closer harmony with *ab initio* results. This might have been expected in view of the basic CNDO prescription,[22] which necessitates a deorthogonalization of CNDO molecular orbitals for a valid comparison with *ab initio* wave functions.

Total Dipole Moments

The calculated CNDO/2 and CNDO/2D dipole moments are compared with experiment in Table II. Also, the contributions to the CNDO/2 moment arising from the equilibrium charge distribution (μ_Q) and from atomic polarizations (μ_{sp} and μ_{pd}) are presented. The most significant result is the good agreement between the experimental trends and the CNDO/2D moments for all four series of molecules. This may be appreciated by comparing Figure 1 with Figure 2. For the phosphines and their adducts the CNDO/2D *spd* basis calculations are definitely in better agreement with experiment than the *sp* results; only the former are presented in Figure 2.[23]

TABLE II. Comparison of CNDO/2 and CNDO/2D Dipole Moments (Debyes) of Methyl Substituted Amines, Phosphines, and their Borane Adducts.

	μ_Q[a]	μ_{sp}[b]	μ_{pd}[c]	$\mu_{CNDO/2}$[d]	$\mu_{CNDO/2D}$[e]	μ_{exp}	Ref.
Amines							
H_3N	0.42	1.65		2.08	1.57	1.47	f
MeH_2N	0.36	1.61		1.97	1.49	1.33	g
Me_2HN	0.23	1.50		1.74	1.47	1.01	h
Me_3N	0.24	1.51		1.75	1.25	0.612	i
Amineboranes							
H_3NBH_3	4.99	1.46		6.45	6.22	5.05	2c
MeH_2NBH_3	5.25	1.44		6.59	6.33	5.15	2c
Me_2HNBH_3	5.34	1.37		6.63	6.31	4.99	2c
Me_3NBH_3	5.34	1.25		6.60	6.23	4.69[r]	2c, n, o
Phosphines (sp)							
H_3P	–0.75	3.36		2.61	1.26	0.579	j
MeH_2P	–0.75	3.49		2.76	1.74	1.10	k
Me_2HP	–0.75	3.56		2.83	1.98	1.23	l
Me_3P	–0.70	3.57		2.87	2.10	1.19	m
Phosphines (spd)							
H_3P	–0.91	3.35	–1.95	0.49	0.01	0.579	f
MeH_2P	–0.83	3.53	–1.59	1.98	1.52	1.10	g
Me_2HP	–0.69	3.64	–1.16	2.46	1.81	1.23	h
Me_3P	–0.49	3.69	–0.58	2.62	1.81	1.19	i
Phosphineboranes (sp)							
H_3PBH_3	4.60	2.18		6.78	5.31	4.00	p
MeH_2PBH_3	4.92	2.21		7.12	5.86	4.66[s]	2f, q
Me_2HPBH_3	5.14	2.21		7.34	6.21	4.78	2f
Me_3PBH_3	5.29	2.19		7.48	6.44	4.99[s]	2f, q
Phosphineboranes (spd)							
H_3PBH_3	3.48	1.92	–0.77	4.63	3.97	4.00	p
MeH_2PBH_3	4.16	2.01	–0.69	5.70	5.01	4.66[s]	2f, q
Me_2HPBH_3	4.51	2.07	–0.54	6.39	5.62	4.78	2f
Me_3PBH_3	4.81	2.08	–0.03	6.86	6.02	4.99[s]	2f, q

[a] Contribution to $\mu_{CNDO/2}$ arising from the equilibrium charge distribution. [b] Contribution to $\mu_{CNDO/2}$ arising from *sp* polarization of the orbitals about the nuclei. [c] Contribution to $\mu_{CNDO/2}$ arising from *pd* polarization of the phosphorus atomic orbitals. [d] $\mu_{CNDO/2} = \mu_Q + \mu_{sp} + \mu_{pd}$. [e] Obtained from the rigorous expression for the dipole moment using the deorthogonalized eigenvectors. [f] Table I, footnote b. [g] Table I, footnote c. [h] Table I, footnote d. [i] Table I, footnote e. [j] C. A. Burrus, *J. Chem. Phys., 28,* 427 (1958); M. H. Sirvetz and R. E. Weston, *ibid., 21,* 898 (1953). [k] T. Kojima, E. Breig and C. C. Lin, *ibid., 35,* 2139 (1961). [l] R. Nelson, *ibid., 39,* 2382 (1963). [m] D. R. Lide and D. E. Mann, *ibid., 29,* 914 (1958). [n] R. S. Armstrong, G. J. Peacock and K. R. Stamp, *J. C. S. Dalton,* 1132 (1973). [o] J. R. Durig, Y. S. Li and J. Odom., *J. Molec. Struct., 16,* 443 (1973). [p] J. R. Durig, Y. S. Li, L. A. Carreira and J. Odom, *J. Am. Chem. Soc., 95,* 2491 (1973). [q] Ref. 26. [r] Ref. 2c. [s] Ref. 2f.

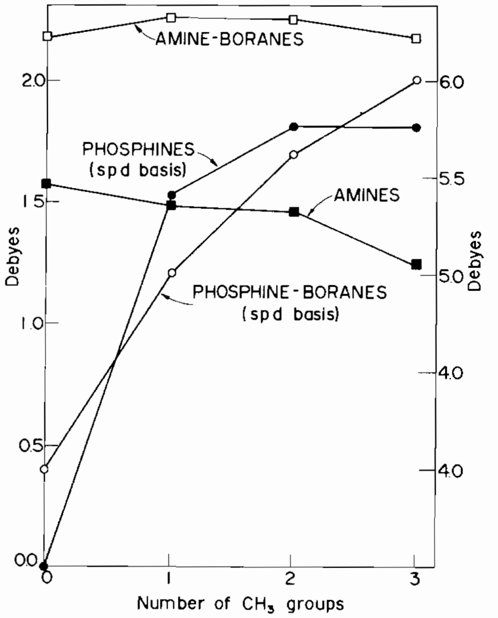

Figure 2. CNDO/2D dipole moments (Debyes) of methylamines, phosphines (left ordinate) and their borane adducts (right ordinate).

Several outstanding features are apparent from the data in Table II. For the amines the major contributions to the total CNDO/2 moments (and presumably to the CNDO/2D moments) are due to the atomic polarizations (μ_{sp}) on nitrogen. For the phosphines the values of μ_{sp} are calculated to be more than twice as great as for the amines (this is probably exaggerated) but we note that they are moderately compensated, except for trimethylphosphine, by inclusion of *d* orbitals in the basis set. This admits the possibility of *pd* polarization which contributes to the moment in the opposite sense of the *sp* plarization. This is not a new observation. Santry and Segal[24] previously noted that inclusion of *d* orbitals is essential to the CNDO/2 estimation of reasonable static moments for molecules containing second row atoms. Our results for phosphine and trimethylphosphine with regard to the importance of *pd* back-polarization are consistent with those obtained *ab initio.*[25] For the borane adducts, the dominant feature is the large moment due to the equilibrium charge distribution. These values and μ_{sp} are tempered for the phosphineboranes (*spd* basis) by a partial cancellation due to *pd* back-polarization (only for Me_3PBH_3 is μ_{pd} negligible). Inclusion of *d* orbitals also appears to lower the value of μ_Q, in effect, by allowing the phosphorus atom to sustain an environment of higher electron density.

Bond Moments

In Table III we give the CNDO/2 bond moments μ_{Q_i} (AB) calculated according to equation 4. For the HN moment in the free amines an essentially constant value of 0.39D is obtained, in good agreement with 0.30D selected by Weaver and Parry (WP).[2d] The reasonable constancy of this moment with increasing methyl substitution is carried over to the adducts although borane coordination more or less doubles its value in accord with WP's prediction.[2d] Similar trends are noted for the CN and CH bond moments, Table III.

The HP and CP moments in Table III are calculated to have the opposite sense of the HN and CN moments, clearly reflecting the equilibrium charge distributions (Table IV). The influence of increasing methyl substitution on the magnitudes of HP moments is slightly greater than on the HN moments; however, CP moments are unaffected. In contrast with the HN moments, there is negligible calculated effect of borane coordination on the HP moment. According to the WP model[2d], however, we would have expected a decrease in the computed absolute magnitudes of both the HP and CP moments. Only for the latter is their expectation fulfilled.

Both N+→B and P+→B moments are large, notably constant (4.09 and 3.55D, respectively), and the prime contributors to the overall moment in both series of adducts in accord with Weaver and Parry's model[2d,e]. Using the CNDO P–B and B–H moments and <HBH 109.5° (exptl.[26a] ~113°) we calculate an average P–BH_3 moment of 4.05D to be compared with 3.97D for trimethylphosphineborane obtained by Bryan and Kuczkowski from microwave data[26]. However, there is a large difference in the way the individual moments are partitioned, the sum of WP's three P–CH_3 moments being fortuitously equal to the sum of the three CNDO P–CH_3 moments *plus* all the atomic polarization contributions. Our calculated average P+→CH_3 moments are 0.50D for the phosphines and 0.06–0.22D in their adducts.

Polarization Moments

Those corresponding to the lone pair moments were calculated from the non-bonding LMO's using equations 5 and 6, and are given in parenthesis in Table III. Their extremely large values, 3.39–3.63D for the amines[27] and 6.18–6.77D for the phosphines, might have been anticipated in light of Coulson's discussion[28]. The greater magnitude for the phosphines runs counter to the zero lone pair moment assumed by Weaver and Parry, and the intuitive estimates of others[2,3]. However, our result deserves serious consideration because of the greater radial extension of the phosphorus valence orbitals than those of nitrogen and because atomic polarization moments are neglected in empirical analyses. The atomic *pd* polarization contribution (0.05, 0.20, 0.33, 0.43 D for PH_3 through PMe_3) to μ(e) of phosphorus is calculated to be negligible. This is consistent with results from the *ab initio* LMO study[13] showing that 3*d* functions contribute only to

TABLE III. Bond Moments and Lone Pair Moments from Localized CNDO/2 Molecular Orbitals.[a]

Molecule	H+⟶ E[b]	C+⟶E[b]	E+⟶ B(E:)[b]	H+⟶C	B+⟶H
H_3N	0.38	–	(3.63)	–	–
MeH_2N	0.39	0.54	(3.55)	0.03	–
Me_2HN	0.42	0.59	(3.39)	0.04	–
Me_3N	–	0.63	(3.43)	0.04	–
H_3P	–0.56	–	(6.18)	–	–
MeH_2P	–0.64	–0.70	(6.43)	0.28	–
Me_2HP	–0.69	–0.73	(6.64)	0.20	–
Me_3P	–	–0.74	(6.77)	0.20	–
H_3NBH_3	0.79	–	4.09	–	0.61
MeH_2NBH_3	0.73	1.40	4.08	0.22	0.68
Me_2HNBH_3	0.68	1.31	4.09	0.19	0.72
Me_3NBH_3	–	1.25	4.12	0.17	0.77
H_3PBH_3	–0.51	–	3.54	–	0.57
MeH_2PBH_3	–0.60	–0.47	3.54	0.41	0.49
Me_2HPBH_3	–0.68	–0.51	3.56	0.36	0.50
Me_3PBH_3	–	–0.54	3.57	0.32	0.49

[a] Moments in Debyes. Numbers in parenthesis are lone pair moments. A negative sign signifies the moment has the opposite sense to that indicated in the column heading. Structural parameters given in Table I and the LMO's were used for the calculations. See the Calculations section for qualitative error estimates. For phosphorus compounds only *spd* results are presented. [b] E = N,P.

TABLE IV. Net Atomic Charges for the Amines, Phosphines and their Borane Adducts.[a]

	E = N			E = P		
	CNDO/2	CNDO/2D	CHELEQ	CNDO/2	CNDO/2D	CHELEQ
H_3E						
E	–0.237	–0.371	–0.211	0.245	0.420	–0.096
H	0.079	0.124	0.070	–0.082	–0.140	0.032
Me_3E						
E	–0.140	–0.192	–0.186	0.157	0.616	–0.060
C	0.083	0.017	0.004	–0.085	–0.312	–0.031
H_C	–0.012	0.016	0.019	0.012	0.035	0.017
H_3EBH_3						
E	0.003	–0.330	–0.145	0.672	0.719	0.161
H_E	0.158	0.220	0.225	–0.081	–0.148	0.149
B	–0.136	0.081	–0.064	–0.285	–0.086	–0.132
H_B	–0.114	–0.137	–0.155	–0.049	–0.063	–0.159
Me_3EBH_3						
E	0.074	–0.140	–0.153	0.555	0.879	0.170
B	–0.086	0.145	–0.065	–0.260	–0.041	–0.131
H_B	–0.141	–0.171	–0.155	–0.078	–0.096	–0.158
C	0.069	–0.020	0.141	–0.131	–0.392	0.074
H_C	0.025	0.063	0.029	0.037	0.070	0.024

[a] CNDO/2 and CNDO/2D charges for H_C, H_B, and C are average values. A tabulation of charges for all the molecules studied here may be obtained from the authors.

the PH and PC bond orbitals. Thus the main role of *pd* polarization, now clearly seen, is the cancellation of the large lone pair moment through back-polarization of the phosphorus *bonding* electrons.

The total atomic dipole polarization moments calculated using the bonding LMO's, only, for the amines and phosphines have the opposite sense to the lone pair moments of these molecules. This is readily inferred by noting the smaller values of the total polarization moments given in Table II. Thus, in ammonia there is a total "bond" polarization moment of 3.63–1.65 = 1.98D opposing μ(e) compared with 4.78D for phosphine (*spd* basis). Atomic polarization vectors, obtained from the bonding LMO's, do not lie along bond axes. For example, the NH vector in ammonia lies slightly within the NH_3 pyramid. Choosing, however, for purposes of discussion to consider these quantities as "bond" polarization moments leads to several illuminating observations.

HN and HC bond polarization moments calculated from the LMO's are ~1.6 and 2.0D, respectively. These large values are expected since, obviously, for hydrogen no *sp* polarization moment is allowed which might cancel with another moment. Where neither bonding atom is hydrogen, significant cancellations are possible, *e.g.*, for an NC bond the value is ~0.14D. Thus, from the relative constancy of μ_{sp} (Table II) we might infer that the polarization moment from an NH bond is quite similar to that of a N–CH_3 group, and similarly for the PH and P–CH_3 moieties. In contrast, the effect of methyl substitution for hydrogen on μ_{pd} is much more pronounced, especially if we remember that its contribution to the phosphorus lone pair moment is negligible.

Accepting, at least for the amines, that the computed bond moments (μ_{Q_i}) are reasonable, we must conclude that some, if not all, bond polarization moments are exaggerated. As a check, we refer to the *ab initio* work[14] on the CH bond for a series of hydrocarbons in which the total CH moment (C^+H^-) is calculated in the range 1.7 to 2.0D (depending on the C hybridization). Our total CH moments (C^+H^-, note the opposite sense to the empirical moment), calculated using equation 3, fall exactly in this range for all our methylated compounds. While dipole moment values obtained from minimal basis set *ab initio* calculations (*e.g.* ref. 14b) may be questioned[29], Rothenburg's analyses[14a] were carried out with extended basis sets and double zeta quality atomic SCF orbitals thus giving extra weight to the *ab initio* CH bond polarization moments. Should the CNDO/2 result for the CH bond dipole not be fortuitous, we may attribute our over-estimates of the total μ_{sp} to poorly calculated NH and NC contributions.

CNDO/2 "corrected" polarization moments may be evaluated on the assumption that the μ_Q values of Table II are reasonable. Thus, subtraction of μ_Q from the experimental value for the total moment gives the corrected polarization moments for the amines of 1.05, 0.97, 0.77, and 0.37D (H_3N through Me_3N). Comparison with WP's[2d] polarization moments, 1.14, 0.96, 0.70 and 0.20D, supports the amine μ_Q values which are also in good agreement with values obtainable from the CHELEQ charges (*vide infra*, Table IV).

"Corrected" polarization moments for the phosphines, however, are large (1.5–2.0D, assuming the total dipole moment vector is $R_3 \longrightarrow P$). It is instructive to calculate the "corrected" moments using μ_Q evaluated from the CHELEQ charges and geometrical parameters of Table I. Dipole moments (μ_Q) are calculated as 0.36 and 0.38D for phosphine and trimethylphosphine, respectively, giving CHELEQ total polarization moments of 0.20D for H_3P and approximately 0.75–0.85 for the three methylphosphines. These small polarization moments are more in line with Weaver and Parry's lone pair moment estimates.

Equilibrium Charge Distributions

CNDO/2D results for H_3N, H_3NBH_3, and H_3PBH_3 compare most favorably with population analyses from *ab initio* studies[5a,8(b,c),9a,10,11b]. Coordination of borane to ammonia involves a charge redistribution (0.33e, CNDO/2D) primarily between the N-bound and B-bound hydrogens. This contrasts sharply with the H_3PBH_3 results in which the electron transfer (0.27e, CNDO/2D) is primarily $P \rightarrow B$, in excellent agreement with that calculated *ab initio*[8b] using correct experimental geometry[30] (0.30e, $P \rightarrow B$); CNDO/2 transfers 0.47e and CHELEQ, 0.61e. The CNDO/2D calculated polarity for the B–N bond (N^-B^+) gives the best agreement with the *ab initio* results[10,11b]. However, all three of our calculations predict P^+B^- for the phosphineboranes in comparison with the apolar nature derived from Sabin's detailed *ab initio* study[8b].

The overall effects of increasing methyl substitution may be summarized as follows. For the amines and phosphines all sets (Table IV) predict a decrease in N or P electron density with the exception of CNDO/2 for the phosphines. Owing to chemical shift trends[31] and the generally good CNDO/2D results we favor the calculated –I effect of methyl groups.

The amount of charge residing in the 3*d* orbitals of phosphorus is relevant to a description of the bonding in the phosphines and phosphineboranes. The general effect of borane coordination to a phosphine is to increase the 3*d* phosphorus electron density. Increasing substitution of methyl groups for hydrogen in the phosphines and phosphineboranes diminishes the 3*d* orbital population. This latter trend is manifested in a systematic reduction of the *pd* polarization contributions to their dipole moments. It also suggests that methyl–phosphorus hyperconjugation is not of major importance in determining chemical and physical properties of these compounds.

The Coordinate Bond

A fruitful approach to the analysis of the NB and PB bonds lies in the examination of the LMO's. A compilation may be obtained from the Authors upon request. Throughout the entire series of amineboranes the character of the BN bonding MO is essentially constant: nitrogen employs an atomic orbital of 26% *s* and 74% *p* character (hybridization $sp^{2.8}$) for bonding with one of 23% *s* and 77% *p* character ($sp^{3.4}$) on boron. The bond has a covalent character[32] of 46%.

In marked contrast, the BP LMO's are influenced by methyl substitution. Thus, for H_3PBH_3 through Me_3PBH_3, the phosphorus hybridization for the BP bond ranges from $sp^{1.3}$ to $sp^{1.7}$. The contributing boron orbital is notably insensitive. The BP covalent character is 61%. Phosphorus *d* orbital populations are insignificant in agreement with Hillier *et al.*[13]. Therefore, it appears that borane hyperconjugation does not play a significant role in strengthening the coordinate bond. The greater *s* character on phosphorus in the PB bond compared to that on nitrogen in the NB bond may, in part, be due to the HPH, HPC, and CPC bond angles being smaller than their N counterparts.

Examining the extent of rehybridization of the phosphine and amine lone pair orbitals upon borane coordination, we find that the phosphine non-bonding LMO's undergo increases in *p* character of 57, 46, 36, and 29% for H_3P through Me_3P, respectively, whereas for the amines only small changes are calculated: 16, 14, 6, and 12% increases for H_3N through Me_3N, respectively. The implication here, at least for the phosphines, is that distortion of the lone pair electrons by borane is most favorable energetically for Me_3P and least for H_3P. In other words, augmenting the number of methyl groups on phosphorus makes the lone pair more available for coordination to an acid.

The NH, NC, and CH bonding LMO's of the amines are little affected by BH_3 coordination. This is consistent with Peyerimhoff and Bunker's detailed *ab initio* analysis[11b] for H_3NBH_3. On the other hand, phosphine adduct formation provokes considerable change in the free phosphine PH bond orbitals. Inspection shows an increase in *d* character in these bonds (the total *d* contribution remains small, however, at ~3%) along with a doubling of percentage *s* character.

Basicities

The intrinsic gas phase basicities of the amines and phosphines (the proton as the reference acid) increase with increasing methyl substitution[33,34]. In addition, the basicity of ammonia is greater than that of phosphine[35]. Beauchamp has pointed out[36] that gas phase basicities are determined by the changes in orbital ionization potential and base–proton bond dissociation energies. Considering, for the moment, that the latter are essentially constant within the series of amines or phosphines, the correlation between basicity and the energy of the highest occupied molecular orbitals is borne out by the CNDO calculations. The highest occupied MO energies for the two series of compounds parallel the trends in their experimental ionization potentials[37].

The changes in ionization potential with increasing methyl substitution could be the quantitative analog of WP's notion[2d] of "loosening" of the lone pair charge cloud. This "loosening" or increase in polarizability of the nitrogen non-bonding electrons should make them more capable of strong interaction with a strong polarizing positive center such as a proton. CNDO/2D and CHELEQ also predict loss of electron density on nitrogen and on phosphorus with increasing methyl substitution (Table IV). The CNDO results are also consistent with the idea[33] that an increase in basicity may be due to extra stabilization of the quaternary ammonium or phosphonium ion through charge-induced dipole interactions with the more polarizable methyl groups. So a reasonable picture of the basicity trends based on earlier qualitative ideas appears to be quite consistent with CNDO–MO theory.

Conclusions

The CNDO calculations indicate that both BN and BP bonds are highly polar in the amineboranes and phosphineboranes. The effects of coordinate bond formation are quite marked for H_3NBH_3, where the net charge flow is from H_N to H_B, but for H_3PBH_3 the net charge flow is primarily P-to-B. The increase in basicity of amines and phosphines upon methyl substitution arises not from a single inductive effect (the methyl groups are calculated to be weakly electron withdrawing) but rather from two other factors: (1) a decrease in ionization potential for the highest filled MO for the amines, and (2) significant charge flow from CH_3 upon donor–acceptor bond formation in the phosphines.

Bond moments calculated from localized CNDO/2 orbitals correspond well to those which were empirically derived from dipole moment data by Weaver and Parry. However, the theoretical lone pair moments are much higher than Weaver and Parry's, particularly for phosphines where the CNDO "lone pair" moments are larger than in the amines. Part of this disparity originates from the neglect of atom polarization moments in the partitioning of empirical bond moment data. In addition, it appears likely that the CNDO/2 procedure used here exaggerates the polarization moments and lone pair moments. However, we do believe that the possibility of large lone pair moments in phosphines deserves consideration.

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Note added in proof (May 1, 1975):
Program ORLOC is available from QCPE (No. 267).