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Dipole Moment Derivatives, Polar Tensors, and Effective Charges of Ammonia and Phosphine

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Preferred signs for the dipole moment derivatives of phosphine are selected on the basis of comparison of CNDO calculated values with the experimental alternatives. The atomic polar tensors, effective charges, mean dipole moment derivatives, and anisotropies for the preferred experimental values of this molecule and of ammonia are presented. A recently suggested criterion for the selection of preferred signs based on effective charge values is found to be valid for phosphine but not for ammonia.

Introduction

Preferred sets of signs for the dipole moment derivatives with respect to the normal coordinates, $\partial p/\partial Q_i$, have been determined for almost all of the molecules for which complete experimental intensity data are available. However phosphine is an exception even though its infrared fundamental gas phase intensities have been known for some time.[1] In a localized molecular orbital study of ammonia[2] CNDO estimates of the derivatives with respect to the symmetry coordinates, $\partial p/\partial S_j$, were compared with the experimental alternative sets of derivatives determined using the intensity data and normal coordinates of ref 1. Preferred signs for $\partial p/\partial Q_i$ are clearly indicated in both the A_1 and E symmetry species. In this report we compare these CNDO values of $\partial p/\partial S_j$ for NH_3 and previously unreported CNDO values for PH_3 with the various experimental alternative sets of derivatives calculated using the normal coordinates corresponding to the refined force fields of Duncan and Mills.[3] Their general harmonic force fields, determined using centrifugal distortion and Coriolis constants in addition to the harmonic frequencies of the parent and full deuterated molecules, are very similar to the ones recently obtained by Schlegel et al.[4] by means of ab initio quantum mechanical calculations. The selection of preferred signs for $\partial p/\partial Q_i$, besides allowing us to perform a comparative study of the dipole moment derivatives of these molecules, permits us to test the hypothesis of Prasad and Singh[5] that the correct signs correspond to values of the atomic effective charges which show a maximum difference for the central and terminal atoms.

Calculations

The $\partial p/\partial S_j$ values determined from the intensity data of ref 1 and the normal coordinate transformations of ref 3 are presented in Table I. The symmetry coordinates are identical with those of McKean and Schatz[1] (see Table I) except that the bending coordinates are weighted by the equilibrium NH and PH bond lengths so that all of the derivatives have common units of e. Interatomic distances and angles of 1.014 Å and 106° 47′ for ammonia and 1.419 Å and 93° 30′ for phosphine were used.[1] The molecular orientation relative to a space-fixed Cartesian coordinate system is given in Figure 1. The CNDO[6] calculations were performed as described previously.[7] As the theoretical results refer to rotation-free distortions in a space-fixed coordinate system whereas the experimental values imply that the Eckart conditions are sat-

isfied, rotational corrections of +0.014 and −0.048e for NH_3 and +0.002 and −0.021e for PH_3 were applied to the experimental values of $\partial p_x/\partial S_3$ and $\partial p_x/\partial S_4$, respectively. These values correspond to S_4 distortions of the internal coordinates such that the angles between the NH and PH bonds and the z axis in Figure 1 remain constant.

The experimental derivatives were transformed to atomic polar tensors, $\mathbf{P}_X{}^{(\alpha)}$, and effective charges, ξ_α, using the relations[8]

$$\mathbf{P}_X = \mathbf{P}_S \mathbf{U} \mathbf{B} + \mathbf{P}_\rho \beta \tag{1}$$

and

$$\xi_\alpha{}^2 = \mathrm{TR}\,[\mathbf{P}_X{}^{(\alpha)}\mathbf{P}_X{}^{(\alpha)\prime}] \tag{2}$$

Atomic mean dipole moment derivatives, $\bar{p}^\alpha$, and anisotropies, $\beta_\alpha{}^2$, which are related to the effective charge by

$$\xi_\alpha{}^2 = 3(\bar{p}^\alpha)^2 + \tfrac{2}{3}\beta_\alpha{}^2 \tag{3}$$

were calculated using[9]

$$\bar{p}^\alpha = \frac{1}{3}\mathrm{TR}\,[\mathbf{P}_X{}^{(\alpha)}] = \frac{1}{3}\,(p_{xx} + p_{yy} + p_{zz}) \tag{4}$$

and

$$\beta_\alpha{}^2 = \frac{1}{2}\,[(p_{xx} - p_{yy})^2 + (p_{yy} - p_{zz})^2$$
$$+ (p_{zz} - p_{xx})^2 + 3(p_{xy}{}^2 + p_{yz}{}^2$$
$$+ p_{xz}{}^2 + p_{yx}{}^2 + p_{zy}{}^2 + p_{zx}{}^2)] \tag{5}$$

Results

The CNDO values of $\partial p/\partial S_j$ for NH_3 and PH_3 are compared with the experimental alternatives in Table I. The experimental values for NH_3 are quite similar to those obtained using the normal coordinates of McKean and Schatz.[1] The choice of $\partial p/\partial Q_{3a}$ with a negative sign and $\partial p/\partial Q_1$, $\partial p/\partial Q_2$, and $\partial p/\partial Q_{4a}$ with positive signs, as reported previously[2] are to be preferred for the values in Table I also.

The comparison of theoretical values with the experimental alternatives for PH_3 is also straight forward. Only the $+ - - -$ choice of signs ($\partial p/\partial Q_1$ being positive and the others negative) leads to signs of the experimental $\partial p/\partial S_j$ in agreement with the CNDO signs.

A comparison of the signs of the experimental derivatives for NH_3 and PH_3 is indeed interesting. For both molecules $\partial p_z/\partial S_1$ is positive and $\partial p_z/\partial S_{3a}$ is negative. If intramolecular

TABLE I: Comparison of the Experimental and CNDO Calculated Dipole Moment Derivatives for NH₃ and PH₃ (e)^{a,b}

	NH₃	
A₁	$\partial p_z/\partial S_1$	$\partial p_z/\partial S_2$
+ +^{c}	+0.057	+0.321
+ −	+0.106	−0.302
CNDO	+0.011	+0.303
E	$\partial p_x/\partial S_{3a}$	$\partial p_x/\partial S_{4a}$
+ +	+0.018	+0.118
− −	−0.046	−0.022
+ −	+0.028	−0.023
− +	−0.056	+0.119
CNDO	−0.180	+0.109
	PH₃	
A₁	$\partial p_z/\partial S_1$	$\partial p_z/\partial S_2$
+ +	+0.259	+0.078
+ −	+0.218	−0.115
CNDO (spd)	+0.248	−0.453
E	$\partial p_x/\partial S_{3a}$	$\partial p_x/\partial S_{4a}$
+ +	+0.167	+0.094
− −	−0.171	−0.052
+ −	+0.169	−0.056
− +	−0.173	+0.097
CNDO (spd)	−0.402	−0.252

^{a} Units of electrons, e. 1 D Å^{-1} = 0.2082e = 3.335 × 10^{-20} C. ^{b} The symmetry coordinates are given by: $S_1 = 3^{-1/2}(d_1 + d_2 + d_3)$, $S_2 = 3^{-1/2}r_0(\alpha_{12} + \alpha_{23} + \alpha_{13})$, $S_{3a} = 6^{-1/2}(2d_1 - d_2 - d_3)$, and $S_4 = 6^{-1/2}r_0(2\alpha_{23} - \alpha_{12} - \alpha_{13})$ where d_i and α_{ij} represent the bond and angle coordinates as they are numbered in Figure 1. ^{c} The different sign possibilities for $\partial p/\partial Q_i$. For example, (+ −) in the A₁ species means that $\partial p_z/\partial Q_1$ is positive and $\partial p_z/\partial Q_2$ is negative. Correspondingly in the E species, those signs indicate that $\partial p_x/\partial Q_3$ and $\partial p_x/\partial Q_4$ are positive and negative, respectively.
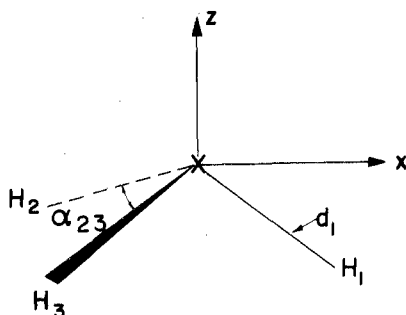
Figure 1.

charge transfer provided the only significant contributions to the values of these derivatives, their signs imply that electronic charge is transferred in the direction of the moving hydrogens as the NH or PH bond lengths increase. However the localized molecular orbital study of ammonia[2] indicates that contributions from equilibrium charge movements and distortions of the electronic charge densities described by means of sp polarizations about the central atom are also significant. The net result of all these contributions is considerably larger for PH₃ than for NH₃ as reflected in the larger absolute magnitudes of the experimental phosphine derivatives.

The bending symmetry coordinates for the two molecules show opposite signs for the derivatives, however. In the case of NH₃, the positive signs of $\partial p/\partial S_2$ and $\partial p/\partial S_{4a}$ indicate that electronic charge moves in a direction opposite to that of the hydrogen atoms as S_2 and S_{4a} increase. A bond moment model

description would imply bond moments of the sense $^-$NH$^+$. The signs of these two derivatives are negative for phosphine implying an opposite flow of charge and a $^+$PH$^-$ sense for the bond moments. Contrary to the situation for the stretching coordinates, the bending derivatives of NH₃ correspond to larger dipole moment changes than do those of PH₃.

In Table II we present values for the atomic polar tensors calculated using eq 1 and the preferred experimental values of $\partial p/\partial S_j$ in Table I. The atomic polar tensors for P and N are of diagonal form with $\partial p_x/\partial x_\alpha = \partial p_y/\partial y_\alpha$ as dictated by symmetry. The polar tensors for the hydrogen atoms in the xz plane of Figure 1 show off-diagonal elements as large or larger than the diagonal elements. Polar tensors for the other two hydrogen atoms, which are not presented here, have nonzero values for all their elements using this coordinate system. These tensors can be simplified by a rotation of the Cartesian coordinate axes such that one axis is coincident with a bond and the other two are perpendicular to it. However molecular symmetry does not allow the polar tensors of hydrogen a simpler form than the one given in Table II.

The values of the atomic effective charge, mean dipole moment derivative, and anisotropy presented in Table III were calculated by applying eq 2, 4, and 5 to the values in Table II. It is somewhat surprising that the effective charge of nitrogen is smaller than that of phosphorus. For the X_2CY[10] (X = F, Cl; Y = O, S), BX_3[11] (X = F, Cl), and CH_3X[9] (X = F, Cl, Br, I), the effective charge values of the terminal atoms increase as the electronegativity of those atoms increase. These results indicate the opposite trend for a central atom. A relatively small value for the mean dipole moment derivative of the nitrogen atom, which results from a cancellation of positive and negative diagonal elements of $\mathbf{P}_X{}^{(N)}$, leads to a small value of ξ_N in spite of the fact that its anisotropy value is quite large. That the effective charges of central atoms may indeed show different behaviors with respect to atomic properties than the terminal atoms can be seen upon inspection of these values for other molecules. The effective charge of nitrogen in NF₃ is smaller than that of phosphorus in PF₃.[5,12] Also ξ_C is reported to be smaller than ξ_{Si} for both the XH₄ and XF₄ (X = C, Si) groups.[5] It should be noted here that Prasad and Singh[5] state that NH₃ and PH₃ are exceptions to this behavior for central atoms. However they based their observation on ξ_α values corresponding to an apparently incorrect sign choice for $\partial p/\partial Q_i$ of ammonia, which we discuss later. The effective charge values of hydrogen increase with the electronegativity of the central atom in these molecules. This is not a completely general phenomenon, however, as ξ_F in PF₃ is larger than in NF₃.[12]

Recently Prasad and Singh[5] have suggested that a comparison of the effective charge values for the central and terminal atoms can be used to indicate the correct set of signs for $\partial p/\partial Q_i$. They found that the difference in $\xi_\alpha{}^2$ values for the central atom and the sum of these values for the terminal atoms is maximum for the preferred sign combinations for several groups of molecules. The preferred sign choice for PH₃ (+ − − −) gives $\xi_P{}^2 - 3\xi_H{}^2 = 0.250e^2$ which corresponds to the maximum difference found by Prasad and Singh considering all the possible sign alternatives. For the preferred (+ + − +) choice of NH₃ this difference is 0.036e^2 whereas several other alternative sign combinations yield larger values. In ref 5 a difference of 0.091e^2 is reported for the (+ − + +) set of signs. This choice, as indicated by the signs of $\partial p/\partial S_j$ in Table I, necessitates the acceptance of electronic charge flows and distortions in opposite directions for the NH bending motions (i.e., NH bond moments of opposite senses).

TABLE II: Atomic Polar Tensors for NH$_3$ and PH$_3$ (e)^a

	$\mathbf{P}_X^{(N)}$			$\mathbf{P}_X^{H_1)\,b}$		
NH$_3$ (+ + − +)	+0.110	0	0	−0.101	0	−0.187
	0	+0.110	0	0	+0.027	0
	0	0	−0.524	+0.106	0	+0.175

	$\mathbf{P}_X^{(P)}$			$\mathbf{P}_X^{(H_1)\,b}$		
PH$_3$ (+ − − −)	+0.318	0	0	−0.115	0	0.072
	0	+0.318	0	0	−0.097	0
	0	0	+0.434	+0.057	0	−0.145

^{a} Units of electrons, e. ^{b} The atomic polar tensors of hydrogen atom number 1 in Figure 1. The atomic polar tensors for the other hydrogen atoms can be generated by rotations as described in ref 9.

TABLE III: Mean Dipole Moment Derivatives, Anisotropies, and Effective Charges of NH$_3$ and PH$_3$ (e)^a

XH$_3$	$\bar{p}^x$	$\beta_X{}^2$	ξ_X	$\bar{p}^{H\,b}$	$\beta_H{}^{2\,b}$	$\xi_H{}^b$
NH$_3$ (+ + − +)	−0.101	0.402	0.547	0.034	0.127	0.296
PH$_3$ (+ − − −)	0.357	0.013	0.625	−0.119	0.014	0.228

^{a} Units of electrons, e, and electrons squared, e^2 (for $\beta_\alpha{}^2$). ^{b} As these three quantities are invariant to rotations of the Cartesian coordinate axes subscripts for hydrogen are not necessary.

Furthermore the positive value of $\partial p/\partial S_{3a}$ for this set of signs implies that electronic charge moves in a direction opposite to that of the hydrogen atoms. This is contrary to what has been found for *all* the other molecules for which preferred sign combinations have been chosen. Independent of the types of central and terminal atoms, electronic charge has always been found to move in the same direction as the terminal atoms when the bond lengths are increased. A maximum difference of $0.305e^2$ is reported for the (+ − − −) sign choice contrary to the sign choice indicated by the theory. As CNDO calculated values are considered to be more accurate for first row atoms than for those of the second row, ammonia appears to present one exception to the rule proposed by Prasad and Singh.

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