calculation on methylsilane, the agreement with experiment is generally rather poor. Qualitatively, all calculations do predict the silicon to be at the negative end of the methylsilane moment, in agreement with recent experimental results[15] even though we find negative (positive) point charges on the carbon (silicon). In fact, all CNDO calculations also predict negative (positive) charges on carbon (phosphorus) in methylphosphine.

With the limited number of molecules treated in this paper, little can be concluded concerning the general effect of including d orbitals on CNDO calculated dipole moments. For this reason we are presently carrying out an extensive survey of the ability of these and other CNDO approaches to predict such properties as dipole moments, geometries, and rotation and inversion barriers.

The Gauche Effect. "Isolation" of Lone Pair–Lone Pair Interactions[1]

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Abstract: Repulsive potentials (two-electron interactions) among lone pairs situated on adjacent atoms in sp^3 hybrid orbitals have been calculated as a function of the dihedral angle. Systems containing two, three, and four lone pairs arranged 1–1, 1–2, and 2–2, respectively, on adjacent centers have been studied. A minimum-overlap criterion has been employed to (1) ascertain the preferred dihedral angle based on direct, one-electron interactions and (2) the optimal angle for stabilizing interaction with an adjacent bond (back-donation). The results permit a simple interpretation of the equilibrium conformations of systems containing adjacent lone pairs and also may be extended to systems containing lone pairs adjacent to polar bonds, in particular, the case where fluorine is the polar group. The model is felt to be inapplicable for the situation where there are adjacent polar bonds.

In studies of molecular structure, an important point of focus has been those molecules in which there are unshared electron pairs and/or polar bonds associated with adjacent central atoms. The unusual feature of such species is the difficulty in rationalizing their equilibrium conformations in terms of valence-shell electron-pair repulsion theory (VSEPR),[2] a highly successful approach in predicting central atom geometries. As a consequence, *ab initio* SCF-MO studies of such systems (*e.g.*, N_2H_4, H_2O_2, NH_2OH, and CH_2FOH) have been carried out in several groups.[3-9] The essence of these results is that, given an adequate basis set (at least double ζ in quality), *ab initio* calculations will reproduce the principal features of the rotational profiles for these molecules, including the rather troublesome trans barrier in H_2O_2.[4a,5b,5c,7]

The *ab initio* results, in one sense, have disposed of the problem as they obviously "contain the required information"[8b] regarding rotational profiles. On the other hand, it is not uncommon to encounter rationalizations of the equilibrium conformations of such species as those minimizing lone pair–lone pair repulsions.[10] Wolfe, *et al.*, however, have stated that such interactions "behave as though they are invariant with dihedral angle."[8] Intuitively we would expect such interactions to be important (if not dominant) in determining the equilibrium conformation, but satisfactory decomposition of total energy profiles in terms of such simple chemical ideas has not yet been accomplished. Two decomposition procedures are currently in use and merit some comment. The first examines each component of the total energy, *i.e.*, kinetic energy (T), electron-nuclear attraction (V_{ne}), electron–electron repulsion (V_{ee}), and nuclear–nuclear repulsion (V_{nn}), as a function of dihedral angle. A second approach, introduced by Allen,[11] focuses on the changes in overall attractive ($E_{att} = V_{ne}$) and repulsive ($E_{rep} = T + V_{ee} + V_{nn}$) contributions to the total energy as the dihedral angle is varied. While both approaches are generally useful from an MO point of view, neither will permit a clear view of the role of lone pair–lone pair interactions (if

(1) Presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., August 26–31, 1973, Abstract No. ORGN 38.

(2) (a) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970); (b) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 389 (1957); (c) this theory was developed to deal with the arrangement of ligands about a central atom; it does *not* address itself to the situation of adjacent lone pairs and bonding pairs.

(3) L. Pedersen and K. Morokuma, *J. Chem. Phys.*, **46**, 3941 (1967).

(4) (a) W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967); (b) W. H. Fink and L. C. Allen, *ibid.*, **46**, 2276 (1967).

(5) (a) A. Veillard, *Theor. Chim. Acta*, **5**, 413 (1969); (b) A. Veillard, *Chem. Phys. Lett.*, **4**, 51 (1969); (c) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

(6) E. L. Wagner, *Theor. Chim. Acta*, **23**, 115 (1971).

(7) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 2371 (1972).

(8) (a) S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972); (b) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971); (c) S. Wolfe, L. M. Tel, J. H. Liang and I. G. Csizmadia *J. Amer. Chem. Soc.*, **94**, 1361 (1972).

(9) See ref 8a for a compilation of the experimental data.

(10) For example, D. B. Boyd, *Theor. Chim. Acta*, **30**, 137 (1973).

(11) (a) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968); (b) for a criticism of this type of analysis, see I. R. Epstein and W. M. Lipscomb, *J. Amer. Chem. Soc.*, **92**, 6094 (1970).

any) in determining the minimum energy conformation. Consider the interaction between two adjacent H–N bonds as depicted in I, where some form of localization

I
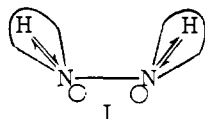
is presumed for convenience. The potential energy contributions that vary with dihedral angle will be the electron–electron repulsion, $4V_{ee}$ (V_{ee} is the repulsion between two electrons, one in each bond), the electron–proton attraction, $4V_{ne}$ (V_{ne} is the attraction between a proton and an electron of the adjacent bond), and the proton–proton repulsion, V_{nn}. Both decomposition procedures would require the incorporation of the terms $4V_{ee}$ and $4V_{ne}$ into *different* energy components while, in actual fact, the variation in the sum ($4V_{ee}$ + $4V_{ne}$ + V_{nn}) best describes these bond–bond interactions. Hence, lone pair–lone pair contributions to both $V_{ne}(E_{att})$ and V_{ee} (or E_{rep}) will be masked by the inclusion of the components of bond–bond (and bond–lone pair) interactions.

In order to assess the importance of lone pair–lone pair interactions in shaping rotational profiles, therefore, it is essential to somehow isolate them and attempt to relate their profiles to that for the total energy for the molecule in question. We report herein the results of calculations in which we have attempted to do this with, we believe, some success. We will examine model systems of the type AB where atoms A and B are directly bonded. The lone pair arrangement will be designated as the *m–n case*, meaning that m lone pairs are on atom A and n lone pairs on atom B; the total number of orbitals considered in each case being (m + n). The structures II–IV summarize the models to be

1-1 case	1-2 case	2-2 case
AB = CC,NN	AB = CC,NO	AB = CC,OO
II	III	IV
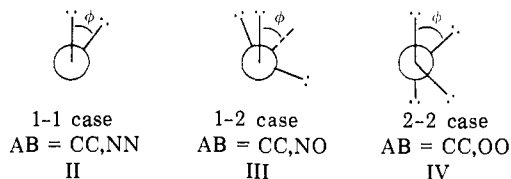
examined. Clearly, II corresponds to N_2H_4, III to NH_2OH, and IV to H_2O_2.
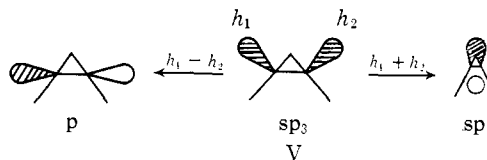
Calculations

Two-Electron Interactions. We have employed as the starting orbitals for the calculation sp[3] hybrids in all cases for all atoms. The assumption of hybrid orbitals for the lone pairs is, we feel, justified on the following grounds. (a) It is well known that the transformation from an AO basis to a hybrid basis is a unitary one and the total energy is invariant to such a transformation.[12] (b) VSERP theory is used to deduce molecular geometries from which hybridization is commonly inferred. (c) Plots of the function $\delta\rho(r)$ for various molecular wave functions calculated in AO basis exhibit regions of positive density difference that are consistent with the notion of hybrid orbitals occupied by unshared electron pairs.[13] (d) Localized molecular orbitals for represen-

tative molecules show directed lone pairs in orbitals strongly resembling hybridized functions.[14]

Where two lone pairs are on one center, SCF–MO calculations suggest two nonequivalent orbitals, one containing significant s character and the other primarily p in character. This is accommodated by our orthogonalization procedure which, in effect, takes the in-phase and out-of-phase combinations of the sp[3] hybrids (V). As hybrids on adjacent atoms are not

V

orthogonal, we have generated maximum-overlap molecular orbitals (MOMO's)[15] for the calculations of electron–electron repulsions. These are delocalized orbitals which correspond to the *orthonormal, symmetry-adapted functions* of the parent molecule in hybrid basis. (This correspondence prevails throughout the rotational cycle for II and IV but only at 0 and 180° for III.) The calculation, then, identifies the molecular lone pair orbitals $\{\psi_i\}$ with the symmetry adapted functions $\{\sigma_i\}$ constructed from the hybrid basis set $\{h_p\}$. While this identification can be only be

$$\psi_i \approx \sigma_i = \sum_{p=1}^{n} C_{pi}h_p \qquad (1)$$

approximately true, it will permit us to evaluate, to first order, the role of lone pair–lone pair repulsions in determining the rotational profile. (Bond angle variations with changes of dihedral angle found in theoretical studies[5b,c] indicate that the assumption of sp[3] hybridization throughout is probably an oversimplification. The sp[3] hybrids differ from the "actual" hybrids only by a unitary transformation. Our "hidden" assumption is that under such a transformation the change in s–p character of the lone pair orbitals will be small.) Using the MOMO's, therefore, the total of two-electron interactions is designated V_{ee}' and calculated assuming two electrons per MO as

$$V_{ee}' = \sum_{i,j=1}^{n} 2J_{ij} - K_{ij} \qquad (2)$$

where J_{ij} and K_{ij} have their customary meanings.

It should be emphasized at this time that the amplitudes calculated for V_{ee}' will *not* be those for the total energy profile. This is a consequence of omission of bond–lone pair and bond–bond interactions in our calculations. These will "damp" the amplitudes, as will be seen in the 1–2 case. The amplitudes of rotation potentials for E_{total} in typical molecules are smaller than those calculated for V_{ee}' by factors of 3–5.

One-Electron Interactions. As has been pointed out,[8] repulsions are not the only significant vicinal interactions. We should like to examine also the consequences of variations in the dihedral angle on the interactions arising from one-electron interactions. Let us define our lone pair MO's as symmetry orbitals for which the following is true.

(12) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 5129 (1965).

(13) P. K. Smith and J. W. Richardson, *J. Phys. Chem.*, **71**, 924 (1967), for example.

(14) M. A. Robb, W. J. Haines, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **95**, 42 (1973).

(15) R. J. Bartlett and Y. Ohrn, *Theor. Chim. Acta*, **21**, 215 (1971).

$$\psi_i = N_i \sum_p C_{pi} h_p \qquad (3a)$$

$$\sum_p |C_{pi}|^2 = 1 \qquad (3b)$$

$$N_i^{-2} = \sum_p \sum_q C_{pi}^* C_{qi} S_{pq} \qquad S_{pq} = \langle h_p | h_q \rangle \qquad (3c)$$

The direct, one-electron interactions are associated with selected components of the operator $\hat{H}_{core}$, which we will collect into the operator $\hat{H}'$. Hence, it follows that

$$H_{ii}' = N_i^2 \sum_p \sum_q C_{pi}^* C_{qi} H_{pq}' \qquad H_{pq}' = \langle h_p | \hat{H}' | h_q \rangle \qquad (4)$$

For lone pairs all relevant orbitals have equal occupation numbers ($\nu_i = \nu = 2$) and their contribution to the total energy may be taken as the sum of the H_{ii}''s. In order to obtain and measure the variation of this sum with dihedral angle, it is more useful to use the expansion

$$\sum_i H_{ii}' = \sum_{i=1}^n [(\sum_p \sum_q C_{pi}^* C_{qi} H_{pq}') \times \\ \prod_{j \neq i}^n (\sum_r \sum_s C_{rj}^* C_{sj} S_{rs})] \prod_{k=1}^n N_k^2 \qquad (5)$$

The rotational profile will depend on the behavior of the sum in (5) which is $(n-1)$th order in overlap and first order in H_{pq}'. Both of these correspond to one-electron integrals between hybrids constructed from AO's of σ and π symmetry. Thus the two-center H_{pq}''s and S_{pq}'s will be of the form, at fixed internuclear distance[16]

$$A + B \cos \phi \qquad (6)$$

A preliminary examination of H_{pq}' and S_{pq} using STO's shows that the ratio of A to B is approximately ± 0.1, corresponding to zero values at $\phi = 90 \mp 6°$. In other words, H_{pq}' and S_{pq} have the same functional dependence upon ϕ with their minima being fairly close in value. The principal distinction is that they are generally of opposite algebraic sign throughout the rotational cycle.

Let us examine (5) more closely to develop a qualitative probe for the rotational behavior of one-electron interactions. For the two-orbital case (II) we obtain

$$H_{11}' + H_{22}' = (H_{pp}' - S_{pq} H_{pq}')/(1 - S_{pq}^2) \qquad (7)$$

Clearly, the rotational profile will depend upon the behavior of $S_{pq} H_{pq}'$. The basic effect is *destabilization* unless this term is zero (S_{pq} or $H_{pq}' = 0$). This effect has been described as exclusion[17] repulsion. Near the minimum S_{pq} is small, if not actually zero, giving a denominator close to unity. This leads to

$$H_{11}' + H_{22}' \approx H_{pp}' - S_{pq} H_{pq}' \qquad (8)$$

If we now introduce the assumption $H_{pq}' \propto -S_{pq}$, eq 8 becomes

$$H_{11}' + H_{22}' \propto f(S) \qquad f(S) = -1 + S_{pq}^2 \qquad (9)$$

As we move away from the minimum S_{pq} becomes significantly different from zero but never exceeds ∼0.2 for the orbitals employed in this study. Thus the denominator of (7) is in the range 0.94–1.00 throughout the

range of ϕ. On this basis we take the behavior of (9) to be a reasonable measure of the variation of one-electron interactions with dihedral angle. (It should be noted that simple overlap considerations are remarkably successful in predicting the equilibrium conformations of hydrazines, etc.[18,19] This obviously derives from the similar behavior of H_{pq}' and S_{pq} as indicated in discussing (6).)

This analysis, when applied to the three-orbital (III) and four-orbital (IV) cases yields similar results regarding the denominators analogous to that in (7); i.e., the variation over the range of ϕ is small. Further, examination of the right-hand side of (9) shows it to be the negative product of the eigenvalues of the overlap matrix, obtainable from generation of the MOMO's. We extend our treatment, therefore, to all cases (II–IV), taking

$$\sum_{i=1}^n H_{ii}' \propto f(S) \qquad f(S) = -\prod_{i=1}^n N_i^{-2} \qquad (10)$$

We presume that (a) this destabilization effect is characteristic of equal orbital population for $n > 2$, (b) one-electron interactions are most favorable when (5) is at a minimum, and (c) this behavior of (5) may be conveniently approximated by (10). We shall base our discussions of the conformational dependence of one-electron interactions, therefore, on considerations of the function $f(S)$. Supplementary calculations approximating H_{pq}' with extended Hückel-type terms suggest that no significant errors are introduced by the use of (10) (*vide poste*).

Fourier Analysis. Pople, et al.,[7] have recently exploited Fourier analysis of theoretical rotational profiles. The potential constants V_1, V_2, and V_3 were respectively interpreted as reflecting dipole–dipole interaction, back-donation, and bond–bond repulsion. In molecules such as N_2H_4 and H_2O_2 we prefer to think of V_1 as reflecting lone pair–lone pair repulsion, but the distinction is not a clear one, to be sure. The crucial feature of this analysis is that V_1 and V_2 become the dominant potential terms in the cases we are considering. To aid our study we have employed such an analysis retaining a leading constant, i.e.

$$V(\phi) = V_0 + \frac{1}{2} \sum_{k=1}^3 V_k [1 - \cos k\phi] \qquad (11)$$

from which we will attempt to establish the role of lone pair–lone pair interactions in determining the rotational profiles in the parent molecules.

In our preliminary studies the results were found to be qualitatively the same for hybrids constructed from best-atom Slater-type orbitals,[20] double-ζ atomic orbitals,[21] and Hartree–Fock limit atomic orbitals.[21] We will confine this report to results obtained using the Hartree–Fock limit AO's for carbon (^3P state), nitrogen (^4S state), and oxygen (^3P state). The required integrals were calculated using DIATOM,[22] most of the values having converged to 10^{-7} au. The quantities V_{ee}' and

(16) The AO contributions to H_{pq}' may be expressed in terms of overlap functions. See C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951), for example.
(17) S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *J. Amer. Chem. Soc.*, **95**, 3806 (1973).
(18) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).
(19) S. F. Nelsen, J. M. Buschek, and P. J. Hintz, *J. Amer. Chem. Soc.*, **95**, 2014 (1973).
(20) D. W. Boerth, unpublished results.
(21) E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).
(22) J. Jesuitis, Quantum Chemistry Program Exchange (QCPE), program No. 138 entitled DIATOM. This program is a modification of QCPE program No. 29 by F. J. Corbato and A. C. Swittendick entitled DIAT.

Table I. Potential Constants for Lone Pair–Lone Pair Interactions (The 1–1 Case)

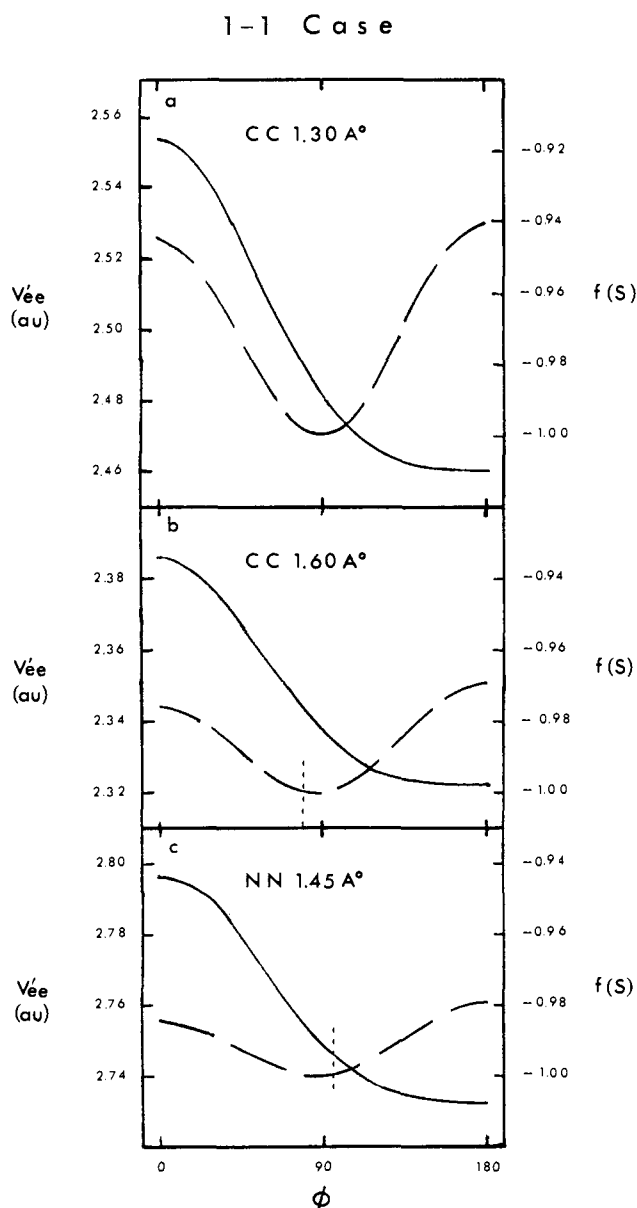| Atom pair AB, r_{AB}	V_0	$V_1 \times 10^2$	$V_2 \times 10^2$	$V_3 \times 10^2$	ϕ_{min}, deg	ϕ_{max}, deg
CC, 1.30 Å						
V_{ee}', au	2.55332	-9.092	-2.486	-0.212	180	0
f(S)	-0.94380	0.379	-5.808	0	89	180
CC, 1.60 Å						
V_{ee}', au	2.38614	-6.337	-1.666	-0.063	180	0
f(S)	-0.97584	0.639	-2.727	0	87	180
NN, 1.45 Å						
V_{ee}', au	2.79728	-6.455	-1.565	-0.042	180	0
f(S)	-0.98432	0.460	-1.790	0	86	180

Figure 1. The variation in repulsion energy, V_{ee}' (—), and the one-electron energy function, f(S) (- - -), for two electron pairs in sp³ hybrid orbitals on adjacent atoms AB (II) as a function of the dihedral angle ϕ: (a) AB = carbon–carbon, r_{CC} = 1.30 Å; (b) AB = carbon–carbon, r_{CC} = 1.60 Å; (c) AB = nitrogen–nitrogen, r_{NN} = 1.45 Å.
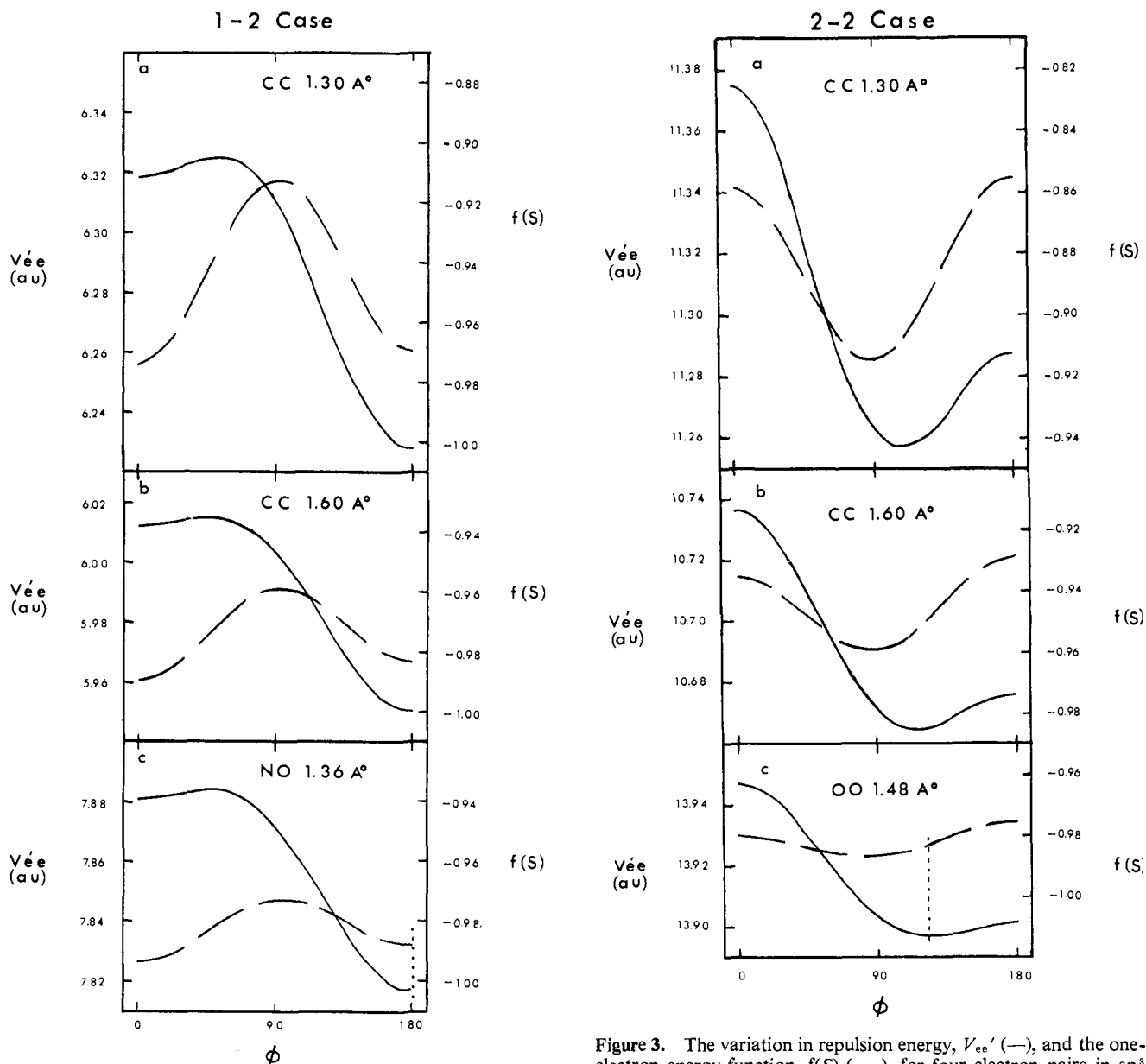
f(S) were calculated at 10° intervals over the range 0–180°.

Results

The models considered for the 1–1 case (II) were carbon–carbon (CC) with internuclear distances of 1.30

and 1.60 Å and nitrogen–nitrogen (NN) with r_{NN} = 1.45 Å. The CC results should be compared to full calculations on ethylene dicarbanion ($C_2H_4{}^{2-}$), where the equilibrium dihedral angle was found to be 79° at either distance.[8c] Barrier heights, however, decreased with increasing internuclear distance. Our model calculations indicate that this trend in barrier height is reflected in both one- and two-electron interactions (see Figures 1a and 1b) for isolated lone pairs. The results for NN (Figure 1c) are qualitatively the same as for CC, indicating that variations in the size of the orbitals are not likely to change the manner in which V_{ee}' and f(S) vary with ϕ. The several calculations on the parent molecule, N_2H_4,[4b,5b,6,7,8b] predict ϕ_{min} to lie in the range 90–100°. The noteworthy feature of all 1–1 cases is that the minimum dihedral angles for the parent molecules do *not* reflect the most favorable arrangements from considerations of electron–electron repulsions alone; rather, these minima seem to correspond fairly closely to the minima for f(S). The results of Fourier analysis for these model systems are presented in Table I. As one would anticipate, $V_{ee}'(\phi)$ is strongly cos ϕ dependent, but, nontrivial dependence on cos 2ϕ is evident. For f(S) the converse is true, as expected. An interesting consequence of the sign and magnitude of the V_2 term in V_{ee}' is the fact that at ϕ = 90°, V_{ee}' is significantly less than $\frac{1}{2}$ ($V(0°)$ + $V(180°)$). Fourier analysis of the several calculations for N_2H_4[4b,5b,6,7] shows that, for the total energy rotational profile, the ratio (V_2/V_1) is unity or slightly larger ($\sim$1.0–1.4).

The calculations for the 1–2 case (III) include the CC models and consider nitrogen–oxygen (NO) with r_{NO} = 1.36 Å. These results are of particular interest as the symmetry orbital argument is valid only at the extrema of the rotational cycle. No full calculations are available on the rather esoteric parent system $C_2H_3{}^{3-}$, but results are available for NH_2OH.[3,7] The calculated minimum energy conformation[3,7] corresponds to ϕ = 180° for our choice of origin. As for II, the apparent trend is toward decreased barrier heights when internuclear distance is increased or orbital size is decreased (see Figure 2). For V_{ee}' two interesting features emerge. First, consideration of the range 0° $\leq \phi \leq$ 60° shows how the amplitude may be damped for interaction of a lone pair on A with the several lone pairs (and/or bonds) on B. This "interference" reduces the amplitude by roughly an order of magnitude in this region, though the overall amplitude is not significantly different from that obtained in the 1–1 case (II). Second, the maxima in V_{ee}' do not correspond precisely to lone pair–lone pair eclipsing, as VSEPR theory might predict. The minima in V_{ee}' are, however, consistent with VSEPR predictions. The quantity f(S) is characterized by

1-2 Case

a
CC 1.30 A°

V_{ee}' (au)

f(S)

b
CC 1.60 A°

V_{ee}' (au)

f(S)

c
NO 1.36 A°

V_{ee}' (au)

f(S)

ϕ

2-2 Case

a
CC 1.30 A°

V_{ee}' (au)

f(S)

b
CC 1.60 A°

V_{ee}' (au)

f(S)

c
OO 1.48 A°

V_{ee}' (au)

f(S)

ϕ

Figure 2. The variation in repulsion energy, V_{ee}' (—), and the one-electron energy function, $f(S)$ (- - -), for three electron pairs in sp^3 hybrids arranged 1-2 on adjacent atoms AB (III) as a function of the dihedral angle ϕ: (a) AB = carbon–carbon, r_{CC} = 1.30 Å; (b) AB = carbon–carbon, r_{CC} = 1.60 Å; (c) AB = nitrogen–oxygen, r_{NO} = 1.36 Å.

Figure 3. The variation in repulsion energy, V_{ee}' (—), and the one-electron energy function, $f(S)$ (- - -), for four electron pairs in sp^3 hybrids arranged 2-2 on adjacent atoms AB (IV) as a function of the dihedral angle ϕ: (a) AB = carbon–carbon, r_{CC} = 1.20 Å; (b) AB = carbon–carbon, r_{CC} = 1.60 Å; (c) AB = oxygen–oxygen, r_{OO} = 1.48 Å.

minima at 0 and 180°. The former is the lower, but the difference between the two is small compared to the amplitude over the full range. This is indicated in Table II (footnote a) where the results of Fourier analysis of V_{ee}' and $f(S)$ are recorded. The previous observations regarding the relative amplitudes of V_1 and V_2 still hold, except that V_2 is increasing in importance for V_{ee}'. Also included in Table II are the potential constants for V_{ee}' (CC, r_{CC} = 1.60 Å) that arise from superposition of two 1-1 potentials. While the V_1 thus derived is very nearly correct, V_2 and V_3 are rather unsatisfactory, being, respectively, too small and too large. Further, ϕ_{max} is at too small an angle and the difference $V(max) - V(0°) \approx 3.5$ kcal is too small by a factor of 4-5. Nonetheless, the curve thus derived is qualitatively correct. Fourier analysis of the

total energy rotational profile for NH_2OH^7 shows that (V_2/V_1) is now less than unity (~ 0.8).

Calculations for the 2-2 case (IV) include the CC models as well as oxygen–oxygen (OO) with r_{OO} = 1.48 Å. The aforementioned dependence of amplitude on internuclear distance and orbital size is again evident (Figure 3). While, again, no full calculations are available pertaining to the CC models, the OO model may be related to calculations for the parent molecule, H_2O_2.[4b,5b,7,8b] In those calculations producing a trans barrier,[5b,7,8b] the dihedral angle for minimum energy is in the range 120–125°. For all models a trans barrier is evident in V_{ee}', with minima in the range 105–125°. This result for the CC models is reflected in the increasing importance of V_2 relative to V_1 (Table III). A 2-2 V_{ee}' curve might be considered to arise either from the superposition of four 1-1 potentials or two 1-2 potentials. The resultant potential constants for both

Table II. Potential Constants for Lone Pair–Lone Pair Interaction (The 1–2 Case)

Atom pair AB, r_{AB}	V_0	$V_1 \times 10^2$	$V_2 \times 10^2$	$V_3 \times 10^2$	ϕ_{min}, deg	ϕ_{max}, deg
CC, 1.30 Å						
V_{ee}, au	6.31888	−9.272	3.625	0.215	180	52
f(S)	−0.97282	0.379	5.808	0	0[a]	91
CC, 1.60 Å						
V_{ee}', au[b]	6.01250	−6.278	2.254	0.062	180	47
V_{ee}', au[c]		−6.337	1.666	0.126	180	32
f(S)	−0.98937	0.639	2.727	0	0[a]	93
NO, 1.36 Å						
V_{ee}', au	7.88089	−6.433	2.364	0.040	180	48
f(S)	−0.99363	0.549	1.781	0	0[a]	94

[a] The minima at 180° are only slightly higher, $V(180°) − V(0°)$ being 0.00379 (CC, r = 1.30Å), 0.00638 (CC, 1.60 Å), and 0.00549 (NO). [b] These potential constants come from direct calculations of V_{ee}'. $V(max) − V(0°)$ = 0.00262 au. [c] These potential constants were derived from the superposition of two 1–1 potentials. $V(max) − V(0°)$ = 0.00056 au.

Table III. Potential Constants for Lone Pair–Lone Pair Interaction (The 2–2 Case)

Atom pair AB, r_{AB}	V_0	$V_1 \times 10^2$	$V_2 \times 10^2$	$V_3 \times 10^2$	ϕ_{min}, deg	ϕ_{max}, deg
CC, 1.30 Å						
V_{ee}', au	11.37474	−8.578	−6.792	−0.209	108	0
f(S)	−0.85829	0.330	−5.807	0	89	180
CC, 1.60 Å						
V_{ee}', au[a]	10.73658	−6.000	−3.469	−0.059	115	0
V_{ee}', au[b]		−6.337	−1.666	−0.252	180	0
V_{ee}', au[c]		−6.278	−2.254	−0.124	138	0
f(S)	−0.93490	0.600	−2.724	0	87	180
OO, 1.48 Å						
V_{ee}', au	13.94729	−4.578	−2.084	−0.013	123	0
f(S)	−0.98019	0.437	−0.858	0	83	180

[a] These potential constants come from direct calculation of V_{ee}'. $V(180°) − V(min)$ = 0.01005 au. [b] These potential constants arise from the superposition of four 1–1 potentials. [c] These potential constants arise from the superposition of two 1–2 potentials. $V(180°) − V(min)$ = 0.00104 au.

possibilities have been included in Table III for CC, r = 1.60 Å. The former will not produce a trans barrier, but the latter gives a potential correct in form, the trans barrier being too small by an order of magnitude. This suggests that the "interference" effect previously described plays an important role in determining the shape of the potential, a fact reflected in the relative magnitude of V_2 for the superposition potentials. The function f(S) continues to exhibit predominately cos 2ϕ dependence. For the OO model, however, V_1 and V_2 are more nearly equal in magnitude than in any previous instance. This results in a rather small variation in f(S) as compared to the CC models. The qualitative behavior, however, is consistent for all models considered. Fourier analysis of the total energy profiles for H_2O_2[5b,7] gives the ratio V_2/V_1 as $\sim$0.5.

Discussion

The most significant outcome of these model calculations is, to our minds, the close correspondence ($\pm 10°$) between the equilibrium dihedral angles calculated for the parent molecules[3–8] and those we find in our considerations of isolated lone pair–lone pair interactions. That is to say, either V_{ee}' or f(S) (or both) has a minimum fairly close to the angle calculated for the parent species. This may be pure happenstance, but we are of the opinion that it indicates a substantial role for these interactions in determining the minimum energy conformation. We also note that there are ranges of the coordinate ϕ significantly removed from the minima in f(S) and V_{ee}', namely, 0–50° for II and IV and 50–100° for III. There appears to be no experimental or theoretical evidence for *simple* molecules representing

the cases considered here in which these ranges for the dihedral angles are preferred. (We exclude systems containing ligands other than H.) This essentially negative evidence may be rationalized in several ways, one of which constitutes the rules for the "gauche effect."[8] It would appear to be simpler, however, for these systems, to interpret the observed equilibrium conformations as being dictated primarily by lone pair–lone pair *interactions* (*not repulsions*).

1–1 Case. The most troublesome systems to rationalize are those corresponding to II, where the dihedral angles found are far from those one would predict based on repulsions alone. It seems clear (Figure 1) that, while f(S) spans its entire amplitude in the range 80–180°, V_{ee}' changes only moderately in this range. If we tentatively select the midpoint between the two minima ($\sim$135°), this corresponds to near eclipsing of the lone pairs with bonds (as well as one such bond–bond interaction). These interactions should amount to net repulsion (see the discussion of I), though not as large in magnitude as lone pair–lone pair repulsion. The alternatives are (a) rotation to 180° where one-electron effects are most unfavorable or (b) relieving the eclipsing by rotation to a smaller dihedral angle for which the cost in terms of electron–electron repulsion is moderate. This interpretation is consistent with the relative magnitude of the potential constants we have derived from the various wave functions for N_2H_4.[4b,5b,6,7,8b] Lone pair–lone pair repulsions (V_1) and minimum destabilization (V_2) are of about equal importance. Bond eclipsing (V_3), while of diminished importance relative to ethane, is still significant ($V_3/V_1 \approx 0.14 − 0.23$). The algebraic signs of V_1 and V_2

(both negative) are consistent with this interpretation. Pople, *et al.*,[1] have related V_2 to back-donation in these systems. It is our belief that such is the case only when electronegative atoms rather than hydrogen are ligands. For reasons we shall outline below we prefer to consider the one-electron effects, as we have described them, to be the principal component of the V_2 terms for the simple parent molecules.

1–2 Case. The 1–2 case III shows itself to be the simplest to interpret. We had anticipated some problems, as the symmetry orbital argument is valid only at 0 and 180°. Yet, for all models, there are no obvious aberrations in either V_{ee}' or f(S). A possible source of error in f(S) arises for the NO model since, as indicated, this function was obtained by replacing H_{pq}' by $-S_{pq}$ in (9). While this is an acceptable approximation for the homonuclear models where $H_{pp}' = H_{qq}'$, the disappearance of this equality for NO could lead to significant misrepresentation of the conformational behavior of the one-electron interactions. We have tested this by representing H' with extended Hückel-type matrix elements and found no significant changes in the relative signs and magnitudes of the Fourier coefficients ($\phi_{min} = 95°$). In this model the best arrangement in terms of one-electron interactions is $\phi = 0°$, but the second minimum at $\phi = 180°$ is only slightly higher. Two-electron interactions, however, preclude the former arrangement. Hence, the equilibrium dihedral angle should be 180°, as is found in the full calculations.[3,7] Based on these considerations, one would anticipate that for the parent molecule V_1 and V_2 should again be the dominant terms in the Fourier decomposition. This is indeed true for NH_2OH, but V_2 is now positive, reflecting the preference for 0 or 180° with regard to one-electron effects. Clearly, these results are consistent with ideas from VSEPR theory[2] in that the lone pairs tend to be as far apart as possible. Finally, it is of interest to note that general shape of the calculated rotational profiles for NH_2-OH[3,7] is quite reminiscent of that which we find for V_{ee}'.

2–2 Case. As we have seen with the systems upon which II is modeled, one-electron interactions preclude the simple extension of VSEPR theory[2] to lone pairs on adjacent atoms. The other difficulty is exemplified by the models for the 2–2 case, IV. For all models considered, the minimum in V_{ee}' corresponds to approximate eclipsing of two lone pairs on adjacent centers (in hybrid representation). This arrangement would appear objectionable within the framework of the simple theory; it is best understood *via* the symmetry adaptation inherent in our generation of MOMO's. Recalling the results in V, this $\sim$120° conformation corresponds to VI. When viewed in this manner, the
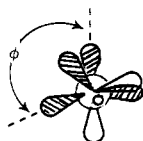
VI

preference for this arrangement becomes obvious, as no severe eclipsing is necessary. Indeed, only in this region can such be avoided. The precise value of ϕ_{min} is quite sensitive to internuclear separation on orbital

size (Figure 3, Table III). Since adjacent (1–1) sp hybrids, like sp[3] hybrids, should prefer a 180° arrangement, we reason that increasing the internuclear distance (CC) or decreasing the orbital size (OO) permits the p-type lone pair orbitals to approach each other more closely. This follows from the fact that, taking the symmetry axis of the orbital as the z axis, $\langle x^2 \rangle / \langle z^2 \rangle$ is larger for an sp hybrid than for a pure p orbital.

The most noteworthy feature among these models is the V_{ee}' profile for OO which appears to dominate completely the molecular potential, in terms of determining ϕ_{min}. This model is perhaps unique in that the one-electron probe, f(S), shows only slight variation over the range of ϕ. The ratio V_2/V_1 for f(S) is approximately 2 for OO, while it ranges from 4 to 17 for the CC models. This large variation in V_2/V_1 is not evident for the V_{ee}' profiles. (This is not unreasonable given the basic difference in behavior of the quantities as r increases. One-electron integrals tend to vary as exp $(-r)$, while repulsions vary as $1/r$.) Based on these results, we predict that a study of $C_2H_2^{4-}$ will show a stronger influence of one-electron interactions in determining ϕ_{min}.

Our approach has presumed directed hybrids, evaluated their interactions as a function of dihedral angle, and attempted to relate the results to the molecular profiles. Our evaluation depends on the persistence of the directional character within the framework of a nonempirical SCF calculation carried out in hybrid basis. We have no direct evidence for such persistence. On the other hand, INDO calculations, which will not admit to variation of hybrid repulsion with dihedral angle, predict dihedral angles for N_2H_4 (69.0°) and H_2O_2 (83.5°) which are too small.[23] Other integral approximations cannot be ruled out as contributing to this systematic error, but we consider these results to be at least consistent with our analysis.

Back-Donation and Polar Bonds. We have ascribed a relatively minor role to back-donation[7] of the lone pairs into adjacent bonds. Direct lone pair–lone pair interactions appear to account for the form of the molecular rotational profile reasonably well, given that the ligands are hydrogen atoms. Substitution of a polar group for hydrogen on an atom adjacent to one bearing a lone pair alters the situation significantly.[7] The simplest description presumes an adjacent bond to have been formed from a ligand orbital χ_L and a central-atom hybrid orbital χ_h. Bonding is associated with the in-phase combination ($\chi_L + \chi_h$), but the antibonding combination ($\chi_L - \chi_h$) may act as an acceptor for an adjacent unshared electron pair. Perhaps a more convenient visualization is presented in Figure 4. There are two cases of practical interest. The ligand A may be of about the same electronegativity as the central atom ($\alpha_A \simeq \alpha_h$) or, as for a polar bond, the ligand X may be more electronegative than the central atom ($\alpha_X < \alpha_h$). In the former case the energy difference between the lone pair orbital and the bonding orbital is roughly the same as that for the lone pair–antibonding interaction, leading to minimal overall stabilization. On the other hand, when the ligand is more electronegative, as with polar bonds, the antibonding orbital is closer in energy to the lone pair orbital than is the bond-

(23) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 197, pp 104–106.
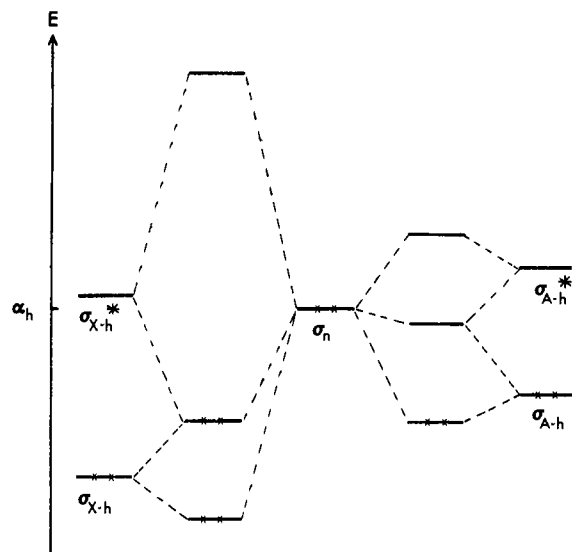
Figure 4. Schematic representation of the interaction of a lone pair orbital (χ_n) with the bonding and antibonding orbitals associated with an adjacent polar bond (left-hand side) and an adjacent nonpolar bond (right-hand side).

ing orbital. In this instance orbital interaction may lead to appreciable stabilization of the arrangement. Such interactions depend primarily upon coupling between the hybrid containing the lone pair and the adjacent hybrid used in bond formation. This coupling is most favorable when interaction between the two hybrids is greatest. Recalling the development of the function $f(S)$, where maximum interaction corresponds to maximum destabilization, the maxima in these curves should correspond to those arrangements in which introduction of the additional orbital (χ_A) can make the greatest stabilizing contribution. Let us analyze the situation in terms of one bond and one lone pair. If the hybrid orientation corresponds to the minimum in $f(S)$ for II, one electron pair is isolated as a lone pair while the other is isolated in the bond orbital ($\chi_L + \chi_h$). When the strongest hybrid coupling occurs, the four electrons may be delocalized over three atoms, resulting in net stabilization relative to the 1-1 case. Such considerations indicate that either the syn or anti arrangement is suitable (Figure 1). One would anticipate, however, a strong preference for the anti arrangement as the groups usually associated with polar bonds (X, O, N, etc.) inevitably bear unshared electron pairs thereby introducing 1,3-lone pair–lone pair repulson (see VIIa and VIIb). The ab initio results for FCH₂-

syn
VIIa

anti
VIIb
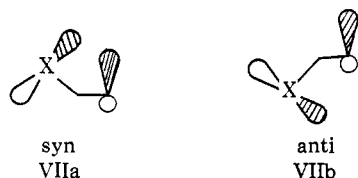
NH₂[7] are consistent with this analysis.

Another system in which lone pair–lone pair interactions have been replaced by lone pair–polar bond interactions is FCH₂OH (VIII). If the fluorine is merely substituted for the single lone pair in the 1–2 case, as repulsion factors might suggest, two destabilizing effects are evident. Bond eclipsing results, which is well known to be unfavorable. Also this conformation is

1,3 repulsions
VIIIa

back-donation
VIIIb

ab initio
VIIIc
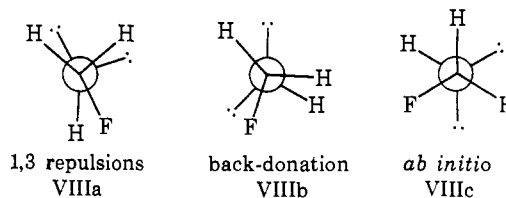
rather poor for back-donation, which is optimal at ∼90° (Figure 2). The calculated equilibrium conformation[7,8b] indicates a bias toward more facile back-donation. It is noteworthy that arguments similar to the ones we advance here have been recently employed[17b] to rationalize the anomeric effect.[24] (This has also been called the Edward-Lemieux effect.[8b])

Pople, et al.,[7] have also studied several molecules containing lone pair–lone pair interactions in which one hydrogen atom has been replaced by fluorine, thereby introducing lone pair–polar bond interactions. The results provide insight into the interplay of back-donation and lone pair–lone pair interactions in determining the equilibrium conformation. We will not detail these results, but, when H is replaced by F in NH₂OH, N₂H₄, and H₂O₂, the new equilibrium dihedral angle reflects significant, if not dominant, contributions from back-donation.

Our results do not give insight into the third aspect of the gauche effect, namely, polar bond–polar bond interactions. These systems require consideration of the lone pairs on the ligands and are, therefore, beyond the scope of these model studies. Epiotis has recently analyzed representative systems and accounted successfully for the observed conformational preferences.[25]

Conclusion

Examination of models for "isolated" lone pair–lone pair interactions permits a simple interpretation of the observed equilibrium conformations of various species, e.g., C₂H₄²⁻, N₂H₄, NH₂OH, and H₂O₂. The model employed also affords qualitative insight into the interaction between adjacent lone pairs and polar bonds. The model is inappropriate, however, for an understanding of the effects of π-acceptor ligands. (Experimental studies of such systems have recently been reported by Dewar and Jennings.[26]) The merits of the model are (a) its consistency with a combination of MO and VSEPR considerations and (b) retention of the notion that stereochemistry is associated with unshared electron pairs. In this latter sense, our results imply support for the notion of a "rabbit ear" effect.[27] The original experimental results which formed the basis for this idea have since been rationalized in terms of steric congestion.[28] Our point here, however, is that the original basis (total energy component analysis) for discounting such an effect was inappropriate. It is, to our minds, possible that such an effect may exist. More extensive experimental and theoretical studies are required before it may be completely discounted.

(24) (a) A. C. West and C. Schuerch, J. Amer. Chem. Soc., 95, 1333 (1973); (b) E. L. Eliel, Angew. Chem., Inter. Ed. Engl., 11, 739 (1972); (c) R. U. Lemieux in "Molecular Rearrangements," Vol. II, P. de Mayo, Ed., Interscience, New York, N. Y., 1964, p 709, and the references cited therein.

(25) N. D. Epiotis, J. Amer. Chem. Soc., 95, 3087 (1973).

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Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes

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Abstract: An equation has been developed with the guidance of recent statistical theories of electrolytes which is designed for convenient and accurate representation and prediction of the thermodynamic properties of aqueous electrolytes including mixtures with any number of components. The three previous papers have given the theoretical background and the evaluation of parameters for pure electrolytes of various charge types. The equation is here applied to a wide variety of mixed aqueous electrolytes at room temperature and at ionic strengths up to 6 M in many cases and occasionally even higher. The first objective is the prediction of properties of mixed electrolytes using only the parameters for pure electrolytes; on this basis standard deviations in ln γ or ϕ for 69 sets of mixtures are less than 0.01 in 36 cases and above 0.05 in only seven cases all involving Cs^+ or OH^-. A second objective is the determination of parameters giving the differences in short-range interaction of ions of the same sign where these differ significantly from zero. As expected, these difference terms, while always small, are relatively most important for singly charged ions (and especially for OH^- and Cs^+) and less important for ions of higher charge. The equations, including difference terms where known from binary mixtures with a common ion, were finally tested on 17 sets of mixtures involving four or more ions without any further adjustment of parameters. The standard deviation is less than 0.01 in all cases and is 0.003 or less in 11 cases. Thus these equations appear to yield accurate predictions of properties of mixed aqueous electrolytes.

Many systems of practical, biological or geological as well as chemical, interest involve mixed aqueous electrolytes. One of the primary objectives of the present series of papers is the prediction of the thermodynamic properties of such mixed electrolytes at concentrations of practical interest by equations no more complex than necessary. The three preceding papers in this series, cited hereafter as I,[1] II,[2] and III,[3] respectively, have prepared the basis for the treatment of mixed electrolytes in this paper. The first paper gave the theoretical and empirical bases for the choice of form of equations and some preliminary applications to mixed electrolytes. The evaluation of parameters for the activity and osmotic coefficients of pure electrolytes at room temperature is given in II for 1–1, 2–1, 3–1, and 4–1 types[2] and in III for 2–2 electrolytes[3] where a slightly different but compatible form of equation was required. In II and III the measured osmotic or activity coefficients were fitted substantially within experimental error up to ionic strength about 6 M in most cases.

Since the activity or osmotic coefficients of most pure electrolytes of interest have been measured at room temperature, the equations provide primarily greater convenience of interpolation for pure electrolytes. But for mixed electrolytes there are experimental data for only a very limited number of cases in contrast to the enormous range of compositions of potential interest. Hence reasonably accurate and reliable equations covering this enormous range should be of great value in making relatively accurate predictions of these properties.

The form of equation used throughout the series is defined initially for the excess Gibbs energy

$$\frac{G^{ex}}{RT} = n_w f + \frac{1}{n_w}\sum_{ij}\lambda_{ij}n_i n_j + \frac{1}{n_w^2}\sum_{ijk}\mu_{ijk}n_i n_j n_k \quad (1)$$

Here n_w is the number of kilograms of solvent and n_i, n_j, etc., are the numbers of moles of the ionic species i, j, etc. The function f depends only on the ionic strength, I, and represents in essentially the Debye–Hückel manner the long-range effects of Coulomb forces. In I it was shown that an alternate mathematical form arose from a different but equally sound statistical derivation from the Debye–Hückel distribution and that this form was slightly preferable empirically to the conventional one. Our form yields exactly the same limiting law as the familiar Debye–Hückel form and a similar but somewhat smaller effect of ionic size. Since we want to use a single function f regardless of ionic size, we must accept an approximate expression in any case.

The λ_{ij} and μ_{ijk} are, in effect, second and third virial coefficients which represent, respectively, the effects of short-range forces between ions considered two and three at a time. The second virial coefficients, λ_{ij}, depend somewhat on ionic strength; this dependence is implicit in the work of Mayer[4] and is shown simply in the derivation in I. We assume that the third virial

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(2) K. S. Pitzer and G. Mayorga, *J. Phys. Chem.*, **77**, 2300 (1973). Sign errors should be corrected by reversing the sign of E in eq 12, the signs of the last two terms in eq 13, and the sign preceding $2m$ in eq 15.

(3) K. S. Pitzer and G. Mayorga, *J. Solution Chem.*, in press.

(4) J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1959).