Group Contributions to the Electrostatic Molecular Potential

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Abstract: Starting from a partition of the SCF molecular wave function in terms of localized orbitals, the electrostatic potentials of electron pairs corresponding to diatomic bonds and to lone pairs are defined. The electrostatic potential of an electron pair has a characteristic shape which does not vary strongly from molecule to molecule. On the contrary, the overall molecular potential in a given position heavily depends upon the actual geometry of the neighboring groups. A systematic construction of the electrostatic potential of larger groups and eventually of complete molecules makes it possible to rationalize some aspects of the properties of a given chemical group (or site in the molecule). It also enables one to predict variations of these properties when the molecular conformation changes or when chemical substitutions in the molecular framework take place.

In a recent review[1] by two of the present authors (E.S., J.T.) the results of a preliminary discussion on the conservation and transferability of the electrostatic molecular potential due to specific chemical groups have been reported. It turned out that the electrostatic potential V, being a physical observable defined in every point of the space outside the nuclei and sensitive to changes in the electron distribution, can be considered as a good index to assess the transferability characteristics of chemical groups. In the present paper, however, we will not search for a better quantification of the conservation degree, but, rather, we will assume a sufficient conservation with a view to rationalizing the shape of V for some groups and to analyzing the effect of the superposition of the various group contributions to give the overall potential. In other words, attention is focused on the electrostatic potential itself as a quantity worthy of consideration "in se", this quantity being an observable related to some aspects of the chemical reactivity of the molecule.[1]

Definition of the Electron Pair Potential

Starting from a set of localized molecular orbitals λ_i (in the present case, Boys's exclusive orbitals,[2] with the limitation of keeping σ and π orbitals separate), any electron pair may be characterized through its "chemically significant" portion χ in the corresponding LO.[3] For a bond between two atoms A and B, for instance, χ_{AB} will be defined as the suitably normalized contribution to the LO from all the atomic orbitals on the two atoms A and B,

$$\lambda = C_{AB}\chi_{AB} + C_R\chi_R \qquad (1)$$

where χ_R clearly represents the contribution to λ from the remainder of the atomic basis set centered at atoms other than A and B. For inner-shell or lone-pair electrons, whose LO's have essentially one-center character, one has analogously

$$\lambda = C_A\chi_A + C_R\chi_R \qquad (2)$$

In this paper we will not consider LO's spread over three or more atoms.

The contributions from the remainder are in general sufficiently small to be considered as "tails"; the exclusive orbitals are well localized, as can be appreciated from the mean-square deviation of the main component χ from λ:

$$\int(\lambda - \chi)^2\,d\tau = 2(1 - \langle\lambda/\mu\rangle) \qquad (3)$$

which is, in general, less than 0.05.[3-5]

It will be convenient, for obvious reasons, to concern ourselves with neutral subunits. To this end, we will perform a completely arbitrary partition of the nuclear charges[1,6,7] and we will associate to each electron pair two unit positive charges. For a bond pair, such charges will be placed at the positions of the relevant nuclei A and B, and for a lone pair (or an inner shell), both charges will be placed at the position of the corresponding nucleus A. The electrostatic potential of a bond pair subunit will then assume the form

$$\bar{V}_i(1) = -2\int \chi_i(2)\,\frac{1}{r_{12}}\,\chi_i(2)\,d\tau_2 + \frac{1}{R_{A1}} + \frac{1}{R_{B1}} \qquad (4)$$

while a similar expression will hold for lone pairs or inner shells. The index i will be specified as b_{AB} for a σ bond, as π_{AB} for a π bond, as l_A for a lone pair, and $1s_A$ for an inner shell.

Localization of molecular orbitals as well as partition of the nuclear charges does not change, of course, the overall value of V at any point. On the other hand, replacing in the expression of V the LO's λ with their significant portions χ (where the "tails" are discarded) affects the value of the electrostatic molecular potential. It will be seen later that the "errors" introduced by neglecting the tails do not heavily influence our results. In this paper we will show by a number of suitable examples how it is possible to use the electron pair potentials $\bar{V}_i$ as models to get a first-order interpretation of the characteristics of the electrostatic potential in given regions of space, and we will reveal the limitations of this simple approach.

Shape of the Pair Potentials

In this section, we will show graphically the features of the electrostatic potential for a few characteristic two-electron groups, namely the C–C, C–N, C–H, and N–H σ bonds, the N lone pair, and the C–C π bond. According to the usual convention,[1] the potential is presented, for selected planes, as isoenergetic curves giving directly in kilocalories per mole the interaction energy of $\bar{V}_i$ with a positive unit point charge (i.e., the electrostatic energy of the two-electron group, kept rigid, with the unit point charge). All the examples given in this paper are drawn from SCF molecular wave functions constructed from Clementi's Gaussian basis set.[8]

Figures 1a and 1b refer respectively to examples of C–C and C–N bonds. In both cases the occurrence of a predominant quadrupole component is evident.[9] For the examples reported in Figure 1, the symmetry of the molecular framework for the C–C bond makes the nodal surfaces of $\bar{V}_{CC}$ almost exactly coincident with the zeros of a pure quadrupolar distribution, while in the C–N bond the difference in electronegativity between the two atoms gives rise to a shift of the electron density toward N, with a consequent increase of the positive lobe of $\bar{V}$ lying near the C nucleus.

Polarization effects are even more evident in the potentials of the C–H and N–H bonds (Figures 1c and 1d). It is possible to interpret this effect as being due to the vector summation

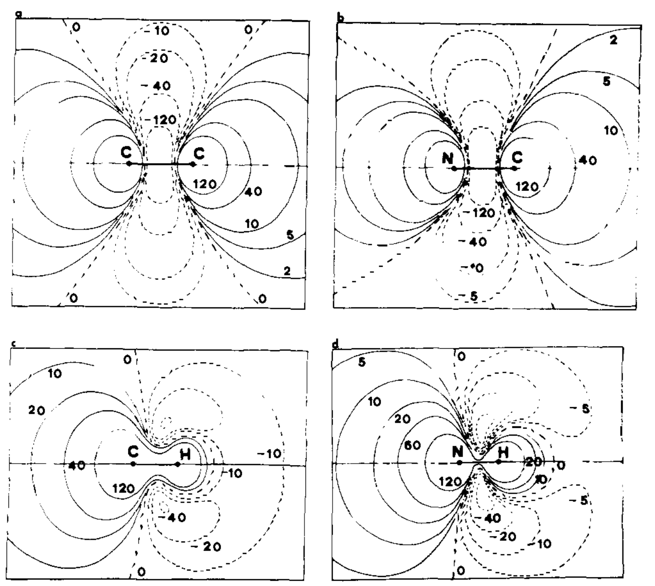


Figure 1. The shape of the electrostatic potential for some two-electron subunits: (a) a C-C bond, (b) a C-N bond, (c) a C-H bond, (d) a N-H bond. Isopotential curves are given in kcal/mol.

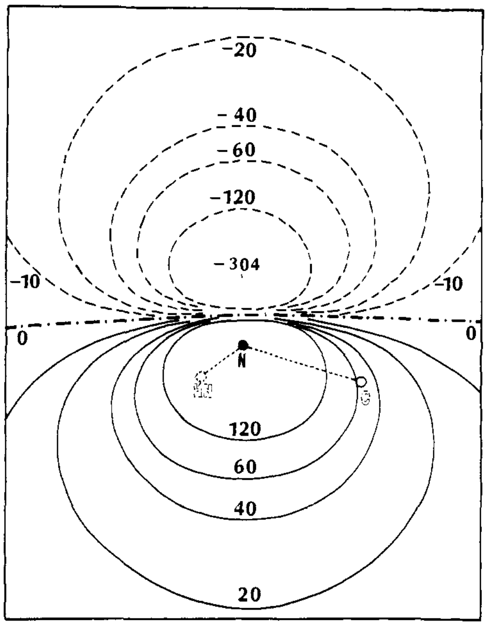


Figure 2. The shape of the electrostatic potential for a N lone pair (sp^3 hybridization).

of the atomic hybrid moment[10] of the heavier atom M with the charge transfer moment produced by the electronegativity difference between H and M. The charge transfer moments are smaller in the CH than in the NH bond as is shown by the net charges on H, 0.561 and 0.654 e, respectively, for the actual cases reported in the figure. The calculated total dipole moments are of 2.04 and 1.23 D (M^+H^-) for the two cases.

In lone pairs the dipolar component of the atomic hybrid is dominant. Such a feature appears clearly in Figure 2 where the $\bar{V}$ map for a lone pair is reported. One would think that the large differences in hybridization, which lone pairs in different molecular frameworks can have, should produce large changes in the value of the dipolar component. By confining ourselves to the cases of N and O lone pairs of more general occurrence, one can realize that such changes are actually sufficiently limited. A control could be performed, for instance, by examining the values of the group dipole moments; the reader is referred to preceding papers[3-5] where such values are reported for a set of molecules all calculated with the same basis set. Another test can be done through the values of the minimum of $\bar{V}$. The minimum of Figure 2 (−304 kcal/mol) is typical of sp^3 hybridized N lone pairs; for N lone pairs in sp^2 hybridization one has minima ranging over the interval −305 to −315 kcal/mol (five- and six-membered heterocycles) and −300 to −310 kcal/mol (azo compounds); for lone pairs in sp hybridization (XCN compounds) one has values around −290 kcal/mol. In conclusion the maximum deviations among the $\bar{V}_{l_N}$ minima are within 10% of the total mean value. Also, because the total shape of $\bar{V}_{l_N}$ maintains the same features in all the cases we have examined, the map of Figure 2 can be considered as representative of a large number of N lone pairs. The situation is completely different when the N lone pair is described by a pure $2p_\pi$ orbital. In this case $\bar{V}_{l_N}$ assumes a quadrupolelike aspect with a couple of minima about −82 kcal/mol deep.

For the O lone pairs, the situation is the same; typical values are the following ones: sp^3 hybridization, −360 kcal/mol; sp^2 hybridization in heterocycles, −350 kcal/mol, and in carbonyls, −370 kcal/mol; while for a pure $2p_\pi$ orbital one has a couple of minima around −91 kcal/mol. It may be interesting to note that the minima for the oxygen lone pairs are lower than those for nitrogen, despite the larger proton affinity of N with respect to O. The contributions of the electrostatic potentials of the nearby groups in actual molecules are sufficient however to reverse such a trend.[1] In actual molecules the contributions of the other groups have a direct practical implication which it is convenient to emphasize. The ordering of the proton affinities of atoms having lone pairs can be predicted with some success[11-13] by examining the value of the minima of the overall molecular potential placed near such atoms. As a general rule the actual ordering of such minima is given by the contributions of the nearby groups, although numerically the main contribution is due to the lone pair itself.

As a last example, in Figure 3 we report the potential for a π_{C-C} homonuclear bond. The lower portion of the figure refers to the nodal plane of the bond and the upper portion to the perpendicular plane. The shape of the potential is ruled by the D_{2h} symmetry of the charge distribution, and in this case the positive portion of V in the nodal plane is again due to the deshielding of the nuclear charges.

In order to assess the relevance and usefulness of the few examples of electrostatic potentials for the simple groups which we have reported above, some comments are needed.

We have intentionally not specified from which molecule the examples have been drawn. They are to be considered only as general models, the emphasis being placed on the general shape rather than on numerical values or on quantitative relationships. Such general features, though, have been found to be reasonably constant in a fairly large set of molecules and we think that they may be profitably used as a basis for semiquantitative considerations about the influence each group has in defining the electrostatic potential of the overall molecule.

On the other hand, changes in the group geometry, in the molecular conformation, and, chiefly, in the molecular framework will induce variations in the pair potential. In some cases, in spite of their seemingly lesser weight, these variations can be essential to account for some specific features of the overall molecular potential.

Other words of caution must be spent about the comparison of potentials deriving from different sources. The numerical values of the potentials $\bar{V}$ depend upon the basis set of atomic orbitals employed in the calculation and also upon the localization process adopted. By using always the same basis set and the same localization process, as in the present paper, we think

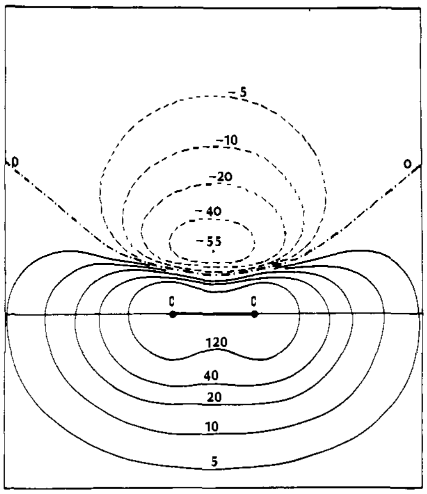


Figure 3. The shape of the electrostatic potential for a π C–C bond. The upper portion refers to the maximum electronic density plane, the lower portion to the nodal plane.

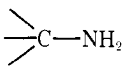
that such inconveniences are minimized and comparisons can be made more safely.

Electrostatic Potential of Larger Groups

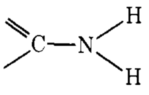
According to the present approximation, the electrostatic potential of the usual chemical groups can be obtained simply by a summation over the electrostatic potentials of the appropriate two-electron groups arranged in the convenient spatial disposition. The results of such summations, with overlapping positive and negative lobes, are not, in general, of immediate visualization and consequently we will show with a few examples how the interplay of different contributions gives rise eventually to the electrostatic potential of the group.

(a) The Aminic Group. Let us consider the NH_2 group as being constructed from the localized orbitals $1s_N$, b_{NHa}, and b_{NHb} and from the six corresponding nuclear charges. The shape of $\bar{V}$ for such a group in the plane defined by the nuclei is displayed in Figure 4. Notice the negative region along the symmetry axis. In such a portion of space the negative lobes of both NH groups strengthen each other, while in the other regions the interference gives a positive potential as a net result. The example in the figure refers to a group having an angle $\angle$HNH = 120°, but the results are similar when the group has a tetrahedral arrangement. In every case the contribution of $\bar{V}_{1s}$ is spherically symmetrical and could be discarded at distances larger than 1 Å from the relevant nucleus.

Some differences between an aminic group tetrahedrically arranged, as



in aliphatic amines, and a planar aminic group, like



with trigonal hybridization, begin to show up when the potential of b_{CN} and l_N in the convenient spatial arrangement are added to $\bar{V}_{NH_2}$ already defined.

Of particular significance are the values of the electrostatic potential in the plane perpendicular to NH_2 and bisecting the HNH angle; the maps are reported in Figure 5. The differences in the minimum arise essentially from two sources: the difference between an sp^3 lone pair and a $2p_\pi$ pair potential (see the preceding section), and the different orientation of the quadrupolelike potential of b_{CN}. Notice how the negative minimum of the N lone pair changes when such a group is included into a larger group.

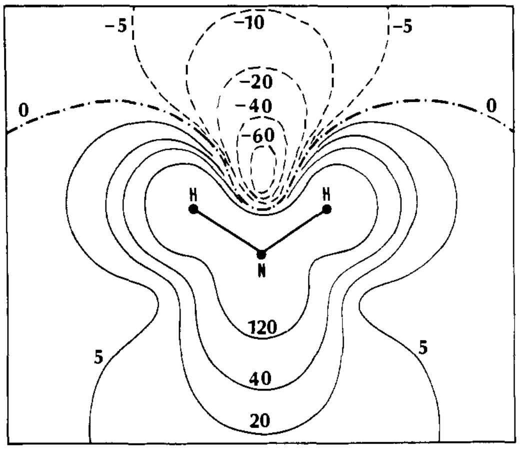


Figure 4. Electrostatic potential map for the NH_2 group with trigonal arrangement.

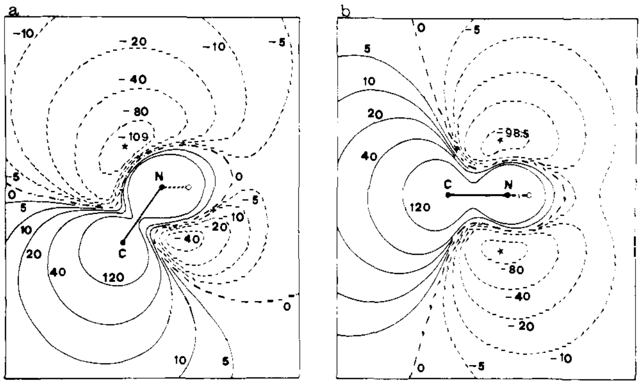
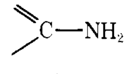


Figure 5. Electrostatic potential map for the group (C)-NH_2 in the plane perpendicular to the NH_2 group: (a) tetrahedral hybridization of N, (b) trigonal hybridization.

For sp^3 hybridization, the minimum passes from −304 (see the preceding section) to −109 kcal/mol in the actual case (see Figure 5a), while for a pure $2p_\pi$ electron pair the value of $\bar{V}_{min}$ increases from −82 to −98.5 kcal/mol (Figure 5b). A rationalization of such effects is immediate if one thinks of the shapes of $\bar{V}$ for b_{CN} and b_{NH}, as already displayed.

In the planar group



the addition of a pure $2p_\pi$ pair on the nitrogen evidently represents a very poor approximation, because in this way one completely neglects the conjugation which is the actual origin of the planar arrangement of the group. When conjugation is introduced, the resulting lowering of the population of the $2p_\pi$ orbital will produce a reduction of the negative region near N. In actual cases, however, the effect is not the most relevant; for example, its inclusion in the pertinent group of formamide reduces the minimum from −98.5 to −91 kcal/mol.

More relevant are the effects due to the neighboring groups. In alkylic amines the introduction of $\bar{V}_{CH_3}$ reduces the minimum from −109 to −73.8 kcal/mol. As will be shown later, for a CH_3 group the electrostatic potential is negative only in the region outside the three hydrogen atoms and positive at the opposite site. The contribution of the alkylic group does not strongly depend upon its dimension. For instance, the introduction of a C_2H_5 group (with trans arrangement of the methyl with respect to the N lone pair) brings the minimum to −73.7 kcal/mol. Also, the substitution of NH bonds with alkylic

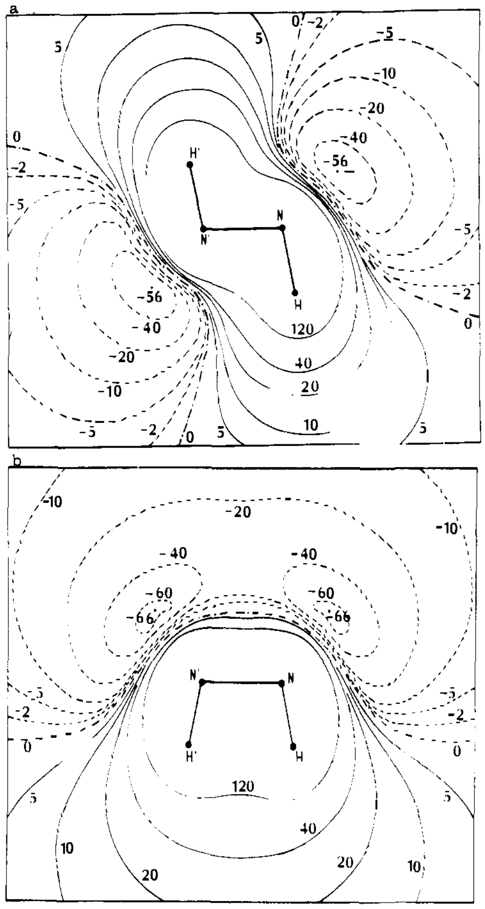


Figure 6. Electrostatic potential maps of diimide: (a) trans form, (b) cis form. The position of the point P is indicated by an arrow.

groups does not alter noticeably the position and the value of the minimum. We find for the minima of $(CH_3)_2NH$ and $(CH_3)_3N$ −73.4 and −75.9 kcal/mol,[14] respectively.

In the planar conjugated amines, the introduction of other groups in the molecule reduces even more drastically the minimum of the potential (for instance to −14.0 kcal/mol in formamide[16]); a good portion (larger than ¼) of the positive contributions in the region of the minimum is due to the π bonds present in the molecular remainder. The lesser proton affinity of planar amines with respect to the alkylic ones cannot be attributed only to electrostatic effects. However, these effects seem to be quite important and related, as the preceding analysis suggests, to different sources.

(b) The Alkyl Groups. By adding the electrostatic potentials of three CH bonds in tetrahedral arrangement (plus $\bar{V}_{1s_C}$) one obtains a group potential ($\bar{V}_{CH_3}$) characterized by a negative region centered on the ternary axis. The minimum in this region has values of the order of −50 kcal/mol and lies outside the plane of the three hydrogens.

If one also includes the C–C bond in the group, the minimum is lowered to values around −19 kcal/mol. When the CH_3 group is attached to heteroatoms, like in methylamines or methyl ethers, the positive contribution of the C–X bond in the region outside the three hydrogens is larger than that of b_{CC}, but not sufficient to delete the negative region (about −16 kcal/mol for $N\text{-}CH_3$ and −13.5 for $O\text{-}CH_3$).

Similarly, the inclusion of the two nearby C–C bonds in the methylenic group is not sufficient to delete completely the negative region arising from the superposition of two $\bar{V}_{CH}$ along the bisector of the HCH angle.

It is convenient to remark that such minima are smaller than those related to lone pairs. The effect of the other groups present in the molecule can delete such negative regions completely,[18,19] and even when they are conserved in the complete molecule (for instance in hydrocarbons or in molecules having large hydrocarbon substituents) they are not sufficient to give a predominant electrostatic contribution to the interaction energy with incoming positively charged reactants,[21] though in some cases the occurrence of negative regions offers some hints in defining the location of the channels for the approach of a reagent, for instance in the case of protonation processes.[22]

Table I. Geometry and Characterization of the Minima of V for the Two Forms of Diimide

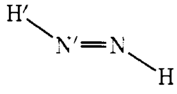
	Location of H′	Location of V_{min}	V_{min}[a]
		I, trans	
r, Å	0.99	1.19	−56.1
ϑ, deg	100	132.8	
		II, cis	
r, Å	0.99	1.21	−65.9
ϑ, deg	100	125.0	
	R(N–N) = 1.25 Å		

[a] kcal/mol.

Changes in the Electrostatic Potential Due to Conformational Effects

In the preceding section we reported some data to demonstrate the importance of the contributions of the neighboring groups to the shape of the electrostatic potential near a given chemical group. The examination of the interplay of group potentials in different conformations of a single molecule may lead however to a clearer appreciation of such effects.

Let us consider the simple example of the two forms (trans and cis) of diimide: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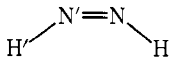
II

The overall electrostatic potential maps show that both isomers have, in the molecular plane, a couple of symmetric minima corresponding to the N lone pair regions. In Figure 6, the in-plane maps for I and II are reported. The value of the minimum differs by 10 kcal/mol (values of the minima and their positions as well as geometry of both species are reported in Table I).

Such a difference may be interpreted, in a first-order approximation, as being due to the different interplay in the two isomers of two groups: (i) a fixed group N′NH composed of the pairs b_{NH}, l_N, $b_{NN'}$, $\pi_{NN'}$, $1s_N$ and (ii) a mobile second group :N′H′ composed of $1s_{N'}$, $l_{N'}$ and $b_{N'H'}$ which assumes in the two cases a different orientation. The map of $\bar{V}_{N'H'}$ is reported in Figure 7.

In order to get a quantitative basis for our analysis let us consider what happens at a single point, for instance the point P corresponding to the position of the minimum of V for conformation I (such a point is indicated by an arrow in Figure 6a). It is evident that at such a point there will be a different contribution from the :N′H′ group in the two cases (the position of P relative to :N′H′ is indicated by stars in Figure 7). Numerically, the contribution of the fixed group N′NH is −89.6 kcal/mol and the :N′H′ group gives a contribution of 39.6 kcal/mol to the trans conformer and of 29.3 kcal/mol to the cis one. This difference of 10.3 kcal/mol should be compared with the difference of 9.8 kcal/mol[23] quoted above between the minima found directly with the two independently determined wave functions.

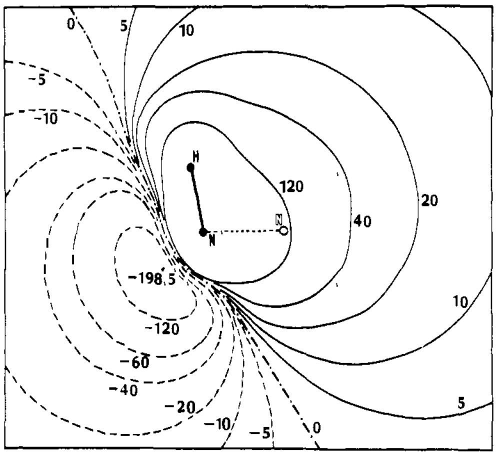

Figure 7. Electrostatic potential map of the :NH group in the diimide molecule. From the location of the stars one can appreciate the value of the V_{NH} contribution to the electrostatic potential at P in the two conformations of diimide.

Polarization-Induced Modifications of the Pair Potentials

In actual molecules, the presence of other groups will produce, on a given group A, electric fields which will obviously modify the charge distribution of A and consequently V_A. The overall mutual polarization effects are not, in general, only of classical origin, and moreover their treatment lies decidedly outside the approximation stated at the beginning of this paper.[24] It may turn out to be convenient, however, to give for a simple case a rough idea of the magnitude of these effects.

To this end, we will consider again the formamide molecule. A partition into two groups, CHO (composed by $1s_C$, b_{CO}, π_{CO}, l_O, l_O') and C-NH$_2$ (b_{CN}, $1s_N$, b_{NHa}, b_{NHb}), will be considered here.

The in-plane map of V_{CHO} is reported in Figure 8. [Incidentally, it may be remarked that this map offers an example of the composition of pair potentials which is similar to those formerly discussed. A C=O group has C_{2v} symmetry, with two minima symmetrically placed (minima around −370 kcal/mol). The inclusion of a CH bond (see Figure 1c) destroys such symmetry, leading to the situation depicted in Figure 8. A further addition of the C-NH$_2$ group partially restores the local symmetry leading to a description very near to that of the exact SCF potential map (see Figure 4 of ref 11); a rather uniform and deep valley encircles the oxygen and the minimum (−75 kcal/mol) represents only a small depression inside the valley.]

For the present discussion, the relevant fact is the difference in the values of V_{CHO} experienced by the two NH bonds. The formamide atoms not included in the CHO group are indicated in Figure 8 by open circles. V_{CHO} produces asymmetric electric fields ($E(r) = -\text{grad}V(r)$) on these bonds. In the middle of the NH bonds the parallel components are 0.093 au for NH$_a$ and 0.083 au for NH$_b$, both pointing toward the H atoms. One could thus anticipate that the electrons of b_{NHa} (in cis arrangement with respect to C=O) should have a larger shift toward N in comparison with those of b_{NHb}. Actually, the two charge distributions show differences in the correct direction. The net electronic population is 0.318 e for H$_a$ and 0.336 e for H$_b$. The bond dipole moments are 1.16 D for b_{NHa} and 1.23 D for b_{NHb} (N^+-H^- dipole orientation), etc. These variations in the charge distribution produce, in turn, changes in the electrostatic N-H pair potentials. For instance, the nodal plane along the NH axis (see the model of Figure 1d) lies at 1.43 Å from H$_a$ and 1.33 Å from H$_b$. At a distance of 1.2 Å the values are: $V_{NHa} = +5$ and $V_{NHb} = +3$ kcal/mol.

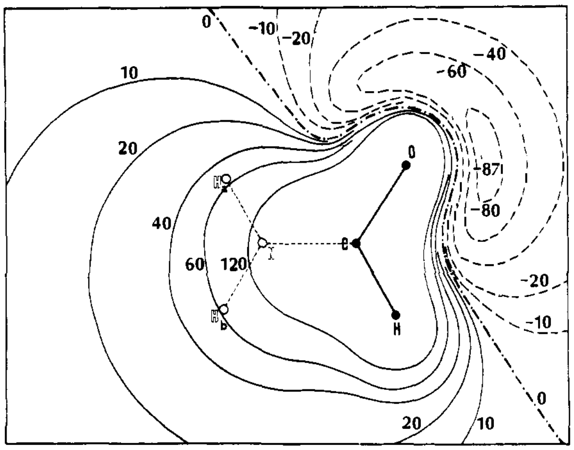

Figure 8. Electrostatic potential map of the CHO group. The position of the other atoms of formamide is indicated by open circles.

Differences in the physicochemical behavior of similar groups placed in an asymmetric environment are well known and it is not necessary to put more emphasis on this topic.[25] In the formamide molecule too, differences between NH$_a$ and NH$_b$ can be detected, at least, by means of theoretical calculations (see, for instance, the trend of the interaction energy with a neutral molecule (H_2O)[27] or with an ion (OH^-)[28]).

From the preceding discussion it should clearly turn out that it is possible to decompose the cause of such differential effects into two parts: first the direct effect through space of the asymmetries of the electrostatic field produced by the other groups of the molecule and second the effects due to the different polarization of the groups under examination.

The juxtaposition of the model group potentials, as we have attempted here, evidences only the first effect and may give only an indirect hint of the second. As it was said above, only a more refined treatment which corrects to a higher level of approximation the first-order picture here presented could quantify the overall differential effect.

Concluding Remarks

Models of pair contributions to the electrostatic molecular potential have been employed in this paper chiefly to show to what extent the local characteristic of the electrostatic potential depends upon the topography of the molecule.

The expression of V as a sum of model pair contributions is of course approximate because the corresponding electron pair distributions are not strictly orthogonal and consequently the expression of a physical observable like V as a simple summation of such contributions is not formally correct. The entity of such errors turns out however to be relatively small for all the cases we have examined (only a selection of which has been here reported) and thus it is possible to obtain an essentially correct description of the main features of V.

In particular, as has been shown in this paper, the pair models give a rationale of the actual shape of V and of its variations when molecular conformation changes or when some groups in the molecule are substituted by others. It is potentially interesting to obtain, via transferable pair models, reasonable approximations to the electrostatic potential of large molecules, widening in such a way the field of utilization of V as an index related to the chemical behavior of substrates with respect to ionic or dipolar reagents.

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(9) Such a shape of the pair electrostatic potential, which was obtained without any particular stipulation on the form of the bond orbital, is in accordance with the intuitive description of a σ bond. If such a bond is thought to be described by two atomic hybrids pointing each one toward the other, there will be a larger electron density in the region between the two atoms for two reasons: (a) each atomic hybrid is projected into the internuclear region and consequently the unit positive charge placed on the nucleus becomes relatively more deshielded on the outer region around the bond axis; (b) the formation of the bond produces a further piling up of electrons in the overlap region and consequently the outer regions of the bond become even more depleted of electrons with respect to the simple summation of the two atomic hybrid distributions.
(10) For the definition of the atomic hybrid moments and for the corresponding decomposition of the molecular dipole moment into partial contributions, see, for example, C. A. Coulson "Valence", Oxford University Press, London, 1961.
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(14) The values above reported refer obviously to the summation of model pair potentials. Actual SCF calculations give the following set of minima: CH_3NH_2, −75.9; $C_2H_5NH_2$, −79.7; $(CH_3)_2NH$, −70.0; $(CH_3)_3N$, −64.3. A comparison with the experimental[15] gas phase proton affinities of these amines (in the same order), 218.4, 221.1, 224.9, 229.1 kcal/mol, shows the limits of the electrostatic approximation. Such differences between the trend of experimental PA's and V values can be explained by means of a finer description of the protonation process, including the increasing polarization energies along the set of molecules, the effects due to changes in geometry and the charge transfer contributions.
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(23) One could object that such comparison is not valid because V_{min} does not have the same coordinates in the two isomers. Actually the effect due to such small difference in position is completely negligible for the present discussion: in fact at the P point, V is equal to 9.7 kcal/mol.
(24) For instance a rationalization of the mutual polarization effects could be obtained by means of a geminal description of the interacting groups.
(25) Differential electrostatic polarization can be usefully introduced, for example, in the interpretation of NMR spectra. Hydrogen exchange is too fast in formamide to permit direct application to this molecule, but in *N*-dimethylformamide there is good evidence that polarization effects due to the CHO group give a noticeable contribution to the difference of chemical shifts and of ^{13}C–H coupling constants between *cis*- and *trans*-methyl hydrogens.[26]
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Orbital Mixing Rule[1]

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Abstract: The interaction among more than two molecular orbitals is considered. An orbital (ψ_{Ai}) of a system, say A, mixes into itself the other orbital (ψ_{Aj}) of A, which is originally orthogonal to ψ_{Ai}, through the interaction with ψ_{Bk} of the other system, B. The sign relation of ψ_{Ai}, ψ_{Aj}, and ψ_{Bk} in the perturbed orbital ψ_{Ai}' is definitely given by molecular orbital perturbation theory (orbital mixing rule). The rule gives rise to an important view, origin, and direction of nonequivalent orbital extension. The importance of the nonequivalency in frontier orbital extension is exemplified by electrophilic exo additions to norbornenes and related compounds, and by the syn–anti stereoselectivity in Diels–Alder reactions of 5-monosubstituted cyclopentadienes. It is also suggested that a vacant d orbital of sulfur plays a significant role in determining the stereochemical courses of the reactions where thiocarbonyl compounds and thioalkoxy derivatives of ethylene and acetylene accept nucleophilic reagents. A transannular cross σ-bond formation between proximal double bonds caused by electrophiles was explained by the rule. Furthermore, the strength and the direction of π-orbital polarization were predicted and used in interpreting the chemical behavior of π bonds.

The concept of orbital interaction has played a predominant role in the theoretical investigation of the mechanisms of chemical reactions and the electronic structures of molecules. Attention has been paid almost exclusively to interaction between a pair of orbitals. The interaction of an orbital with a second orbital necessarily involves others (orbital mixing), appreciably in some cases. The orbital mixing analyses have been employed by Libit and Hoffmann,[2a] Inagaki and Fukui,[1b] Fujimoto and Hoffmann,[2b] and Imamura and Hirano[2c] to elucidate different chemical phenomena. The purpose of this paper is to clarify, in our own way, the orbital mixing rule on the basis of perturbation theory, and to shed light on the chemical phenomena of which the reasoning remains uncertain or unchallenged.

Theoretical Background

Let us concern ourselves with two orthonormal sets of orbitals between which interaction is allowed. Orbitals of one set are represented by ψ_{Ai} and ψ_{Aj}, those of the other set being represented by ψ_{Bk}. The orbital energy is denoted by ϵ, with the subscript standing for the orbital. One obtains a theoretical formulation for mixing among nondegenerate orbitals in the second-order perturbed orbital as follows (see Appendix):

$$\psi_{Ai}' = \psi_{Ai} + \frac{h_{ik}h_{jk}}{(\epsilon_{Ai} - \epsilon_{Aj})(\epsilon_{Ai} - \epsilon_{Bk})}\psi_{Aj} + \frac{h_{ik}}{\epsilon_{Ai} - \epsilon_{Bk}}\psi_{Bk} \tag{1}$$

in which the prime stands for the perturbed orbital.