Conceptual Model of "Through-Bonds" Interactions

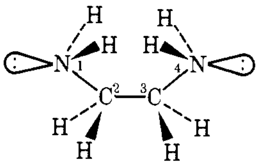
T. K. Brunck and F. Weinhold*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received September 29, 1975*

Abstract: Characteristic patterns of "through-bonds" interactions are interpreted by means of a natural extension of Huckel-like concepts to the mixing of localized bonds and lone pairs, taking due account of overlap and the special nodal demands of the highest occupied molecular orbital. Direct molecular orbital calculations in a "linear-combination-of-bond-orbitals" formulation show that this point of view is to be preferred over that based on possible cancellations due to orbital symmetry.

Hoffmann[1] has drawn attention to the necessity of amending the traditional view of σ electrons tightly localized around individual chemical bonds. When orbitals interact in a saturated molecule, the assumption that the interaction proceeds "through space," e.g., without mediation of a σ chain, is often inconsistent with the evidence of experimental techniques (notably photoelectron spectroscopy) which directly probe molecular orbital (MO) symmetries and splittings. All-electron or all-valence-electron MO calculations often give a reasonable account of photoelectron splittings, but leave open the question of a suitable conceptual model for the "through-bonds" interactions. What is sought is that minimal modification of the operationally useful valence concepts, which is necessary for a general pattern of thinking about σ delocalization effects.

The observations to be accounted for are typified by 1,2-diaminoethane,[2] whose highest filled orbitals consist primarily of the symmetric (S) and antisymmetric (A) combinations of the two nitrogen lone-pair orbitals. The splitting of these orbitals is calculated (e.g., in the INDO-SCF-MO method of Pople et al.[3]) to be 0.8 eV, with the ordering A below S, contrary to what is expected if the interaction occurs "through space". To account for this ordering, Hoffmann employed a *four*-orbital system comprised of two localized lone-pair orbitals and the localized C-C bond and antibond. A puzzling feature of this picture is the selection of the 2-3 C-C orbitals, while the corresponding C-N bond orbitals (the 1-2 and 3-4 bonds), as well as all C-H and N-H bond orbitals, were excluded from consideration. The rationalization given by Hoffmann, a type of symmetry argument, is that "while the 2-3 bond is uniquely located on the axis, the other bonds . . . always enter in symmetry related pairs"; in particular, the S combination of bonds 1-2 and 3-4 and the S combination of *anti*bonds 1-2 and 3-4 would in the first approximation have mutually cancelling effects when allowed to interact with the S combination of lone pairs, and lead to no net perturbation. Similarly, the antisymmetric combinations of bonds and antibonds are supposed to have mutually cancelling effects on the A level of lone pairs.



These suppositions can be tested in a fairly direct manner. It is feasible to implement the numerical calculation of MO's in a "linear-combination-of-bond-orbitals" (LCBO) framework which corresponds to the general picture under discussion. The basis set for the self-consistent-field MO calculations then consists not of the usual unhybridized, undirected atomic orbitals (AO's), but of "bond" (σ), "antibond" (σ^*), and "lone pair" (n) orbitals constructed, in the manner suggested by elementary valence theory, from directed hybrid orbitals properly oriented to reflect the local bonding requirements. The unitary matrix corresponding to this overall change of basis was employed to transform the Hamiltonian matrix into the bond orbital (BO) representation. Complete details of the computational procedure will be described elsewhere. Our implementation of this procedure was carried out with the INDO-SCF-MO method,[3] and idealized geometries were adopted, but the qualitative conclusions to be drawn here are expected to be insensitive to the particular version of MO theory employed, and to minor geometrical variations.

As might have been expected, the transformation from AO's to BO's effects a partial prediagonalization of the Hamiltonian matrix, the off-diagonal elements generally being substantially reduced in value. The new diagonal elements represent roughly the orbital energies of localized bonds, antibonds, and lone pairs, while the off-diagonal elements represent their rather weak interactions which lead to the final delocalization. Solution of the eigenvalue problem in the BO basis leads to a set of MO's in the LCBO form,

$$\varphi_i = \sum_j c_{ij} b_j$$

where c_{ij} is a measure of the contribution of bond orbital b_j (which might be of σ, σ^*, or n type) to the final delocalized molecular orbital φ_i.

In 1,2-diaminoethane, as Hoffmann had noted, the MO which is principally $n_1 + n_4$ has a rather large contribution from the trans σ bond σ_{23}, but rather little from the "nearest neighbor" σ_{12} (or from σ_{34}, or any C-H or N-H bond), the LCBO coefficients being of magnitude 0.49 and 0.09, respectively (see Figure 1a). However, detailed inspection of the Hamiltonian matrix shows that the element $\langle n_1|\mathcal{H}|\sigma_{12}\rangle$ between the nitrogen lone pair and the adjoining σ bond is more than ten times larger than that with the adjoining antibond ($\langle n_1|\mathcal{H}|\sigma_{12}\rangle = -0.1471$ au, $\langle n_1|\mathcal{H}|\sigma_{12}^*\rangle = -0.0136$ au), suggesting that no significant cancellation can occur when the $n_1 + n_4$ combination is simultaneously perturbed by $\sigma_{12} + \sigma_{34}$ and $\sigma_{12}^* + \sigma_{34}^*$. But a more direct test of the "cancellation by symmetry" hypothesis can be made by simply *omitting* all the antibonds from the basis set, and calculating the delocalized MO's in the truncated basis. Neither the (fully occupied) MO's nor their energy splittings are significantly altered by this truncation, as shown for the two highest MO's in Figure 1b. The contribution of σ_{12} (and σ_{34}) remains small for the S combination, despite the fact that no potential cancellation is available from any σ^* orbitals. This result is hardly surprising, for the antibonds lie much higher in energy than do the bonds or lone pairs, so there is little tendency for the Hamiltonian operator to mix these orbitals with lower-lying orbitals, and the shape of the final occupied MO's (as well as their general splitting pattern) is relatively unaffected if these antibonds are ignored entirely.

---

* Address correspondence to this author at Department of Chemistry, University of Wisconsin, Madison, Wis. 53706.

Table I. Bond Orbital Overlap Integrals in Diaminoethane

$\langle n_1\|\sigma(\mathrm{N(1)\text{-}H})\rangle$	+0.0892
$\langle n_1\|\sigma(\mathrm{N(1)\text{-}C(2)})\rangle$	+0.0812
$\langle n_1\|\sigma(\mathrm{C(2)\text{-}H})\rangle$	+0.0718
$\langle n_1\|\sigma(\mathrm{C(2)\text{-}C(3)})\rangle$	−0.0915

What then *is* the proper explanation for the observed pattern of delocalization and energy splitting? We believe this pattern is best understood by a simple extension of Huckel-like ideas to the interactions of localized bonds and lone pairs, making use of the idea that the interaction of two such units will be in some measure proportional to their *overlap.* Table I gives numerical values of such overlaps in diaminoethane. In general, one expects that the lowest lying MO's will be the in-phase combinations of these basis obitals, with the largest contributions arising from orbitals having the largest positive overlap with the dominant ("parent") orbital(s). The *highest* filled orbitals, however, should be the most *out*-of-phase combinations of orbitals, with the orbitals of most *negative* overlap predominating.[4] As in the elementary Huckel theory of conjugated polyenes, the phase with which some b_i enters the highest MO is generally an alternating function of its position. The magnitude of the contribution of a particular orbital in the highest occupied MO is determined by the "principle of most negative overlap", the counterpart of the "principle of maximum overlap" for the lowest-lying orbitals. Table I shows that the trans bond σ_{23} is strongly singled out by overlap considerations alone to interact most effectively with the nitrogen lone pair in the highest-energy (most noded) linear combination of occupied bond orbitals. Such considerations suggest further that unusually large splittings of the lone pair S and A orbitals will occur whenever a σ bond lies trans to each lone pair, or when a succession of such "trans bridges" is available to carry the interaction from one orbital to the other.[5]

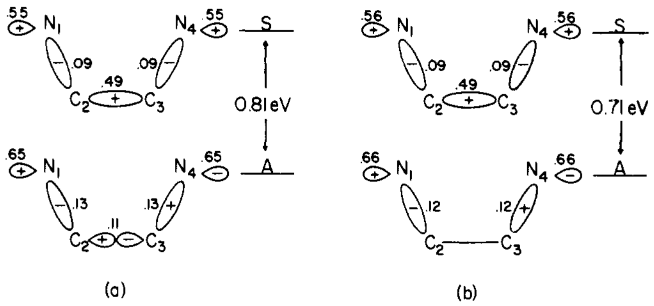


Figure 1. Highest occupied molecular orbitals of diaminoethane, as calculated (a) in the full BO basis, (b) with omission of all antibonds from the basis. Only the contributions of heavy-atom orbitals to each MO are depicted.

This simple theory applies most readily to molecules having a particular orbital of interest (such as an isolated π orbital or lone pair orbital) lying above the occupied manifold of σ bonding levels. It predicts that the influence of such an orbital propagates preferentially through trans arrangements of bonds, since these offer the most negative overlaps as befit the uppermost occupied level. We are currently using such ideas to analyze the optical activity of substituted carbonyl compounds, which exhibit another type of evidence for the existence of "through-bonds" interactions over surprisingly long distances.

Acknowledgment. We thank Professor J. I. Brauman for discussions. The financial support of the National Science Foundation and the Camille and Henry Dreyfus Foundation is gratefully acknowledged.

References and Notes

(1) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1–9 (1971).

(2) The indicated conformation is chosen in order to make contact with the related 1,4-diazabicyclo[2.2.2]octane, for which experimental photoelectron data are available; see ref 1.

(3) See, e.g., J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.

(4) A more formal justification of such a "principle of most negative overlap" is described elsewhere: F. Weinhold and T. K. Brunck, *J. Am. Chem. Soc.*, in press.

(5) Experimental evidence for such patterns also appears to be available from NMR coupling constants, trans-elimination reactions, Grob fragmentation reactions, and elsewhere.

Aqueous vs. Gas-Phase Acidities of the Haloacetic Acids. Enthalpies of Hydration of Haloacetic Acids and Haloacetate Ions

Paul Haberfield* and Animesh K. Rakshit

Contribution from the Department of Chemistry, Brooklyn College of the City University of New York, Brooklyn, New York 11210. Received November 10, 1975

Abstract: The hydration enthalpies of fluoroacetic, chloroacetic, bromoacetic, difluoroacetic, and dichloroacetic acids were determined. These values, combined with the aqueous and gas-phase ionization energies of these acids, were used to calculate the hydration enthalpies of the corresponding haloacetate anions. The differences between the gas-phase and aqueous acidities of these acids are seen to rise mainly from differences in the hydration enthalpies of the anions. *As the gas-phase acidity decreases, the hydration enthalpy of the haloacetate ions increases.*

It has recently been discovered[1,2] by Kebarle and co-workers that the gas-phase acidity order of the haloacetic acids is Br > Cl > F, or the reverse of the aqueous order. The well-known aqueous order is therefore caused not by the increasing inductive effect in the order Br < Cl < F, as is generally supposed, but rather by a solvation effect.[2]

One can envision two such solvation effects: one operating on the haloacetic acids and one operating on the haloacetate ions, and, possibly, a combination of these, working either in concert or in opposition to one another.

Thus the reversal of the aqueous acidity order could be caused by an increase in the hydration energies of the halo-