Table I. Bond Orbital Overlap Integrals in Diaminoethane

$\langle n_1 \vert \sigma(N(1)-H) \rangle$	+0.0892
$\langle n_1 \vert \sigma(N(1)-C(2)) \rangle$	+0.0812
$\langle n_1 \vert \sigma(C(2)-H) \rangle$	+0.0718
$\langle n_1 \vert \sigma(C(2)-C(3)) \rangle$	−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]

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.

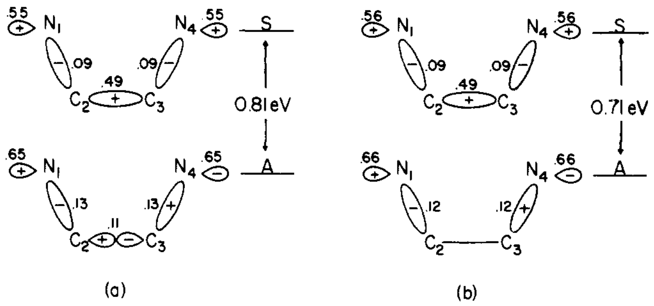

Figure 1. Highest occupied molecular orbitals of diaminoethane, as calculated (a) in the full BO basis, (b) with omission of all antibonds from the basis. Only the contributions of heavy-atom orbitals to each MO are depicted.

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

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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-

Table I. Heats of Vaporization (ΔH_{vap}) and Heats of Solution in Water (ΔH_{soln}) of Haloacetic Acids at 25° (in kcal/mol)

Acid	$\Delta H_{vap}{}^{a,b}$	$\Delta H_{soln}{}^{b,c}$	$\Delta H_{solv}{}^{RCO_2H\,d}$
Fluoroacetic	20.05	3.01	−17.04
Chloroacetic	18.92	3.76	−15.16
Bromoacetic	18.81	3.47	−15.34
Difluoroacetic	16.21	−1.68	−17.89
Dichloroacetic	14.45	−1.71	−16.16

[a] Enthalpy difference between pure liquid or solid and monomer vapor. $\Delta H_{vap} = \Delta H_{vap}(\text{exptl}) + (1 - \alpha)7.41$, where α is the degree of dissociation of dimer vapor, dimer $\rightleftarrows$ 2monomer, and 7.41 is the best value for the heat of dissociation taken from A. D. H. Clauge and H. J. Bernstein, *Spectrochim. Acta, Part A*, **25**, 593 (1969). [b] All measurements carried out on an LKB-8700 vaporization and solution calorimeter. $\Delta H_{vap}(\text{exptl})$ values have standard deviations ranging from 0.03 to 0.06 kcal/mol. $\Delta H_{soln}(\text{exptl})$ values are better than ±0.1 kcal/mol. [c] Enthalpy difference between pure liquid or solid and dilute aqueous solution of undissociated acid, $\Delta H_{soln} = \Delta H_{soln}(\text{exptl}) - \alpha\Delta H_{ioniz}$, where α is the degree of dissociation in water, $RCO_2H \rightleftarrows RCO_2^- + H^+$, and ΔH_{ioniz} is the heat of ionization in water (see Table II). [d] $\Delta H_{solv}{}^{RCO_2H} = \Delta H_{soln} - \Delta H_{vap}$.

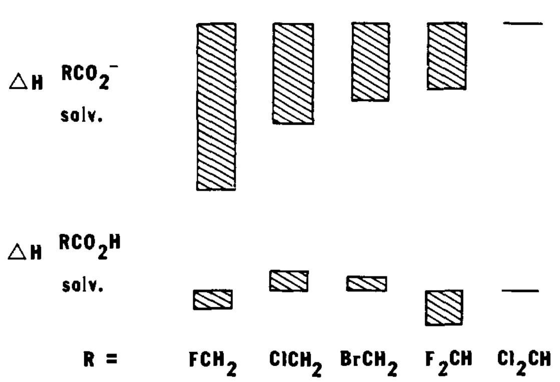

Figure 1. Hydration energies of haloacetic acids and haloacetic anions relative to dichloroacetic acid and dichloroacetate ion.

Table II. Heats of Hydration of Haloacetic Acids ($\Delta H_{solv}{}^{RCO_2H}$) and of Haloacetate Ions ($\Delta H_{solv}{}^{RCO_2^-}$) at 25° (in kcal/mol)

Acid	$\Delta H_{solv}{}^{RCO_2H}$	ΔH_{ioniz},[a] gas	ΔH_{ioniz},[b] aq	$\Delta H_{solv}{}^{RCO_2^-\,c}$
Fluoroacetic	−17.04	334.6	−1.67[d]	−92.6
Chloroacetic	−15.16	332.6	−1.14[e]	−88.2
Bromoacetic	−15.34	331.5	−1.00[f]	−87.1
Difluoroacetic	−17.89	327.4	−1.99[g]	−86.6
Dichloroacetic	−16.16	325.6	−2.04[h]	−83.1

[a] See ref 2 and 3. [b] Measured using an LKB-8700 solution calorimeter; all values better than ±0.1 kcal/mol. [c] $\Delta H_{solv}{}^{RCO_2^-} = \Delta H_{ioniz,aq} - \Delta H_{ioniz,gas} + \Delta H_{solv}{}^{RCO_2H} - \Delta H_{solv}{}^{H^+}$, where the hydration enthalpy of the proton, $\Delta H_{solv}{}^{H^+}$, is taken as −260.7 kcal/mol [H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963)]. [d] Lit. value − 1.39: D. J. G. Ives and J. H. Pryor, *J. Chem. Soc.*, 2104 (1955). [e] Lit. value −1.14; footnote *d.* [f] Lit. value −1.24; footnote *d.* [g] Lit. value −2.00: J. L. Kurz and J. M. Farrar, *J. Am. Chem. Soc.*, **91**, 6057 (1969). [h] Lit. value −1.9: footnote *g*.

acetic acids in the order F < Cl < Br or an increase in the hydration energies of the haloacetate ions in the order Br < Cl < F, or by some combination of such effects.

These possibilities can be distinguished by measurement of the hydration energies ($\Delta H_{solv}{}^{RCO_2H}$) of the haloacetic acids. The hydration energies of the haloacetate ions ($\Delta H_{solv}{}^{RCO_2^-}$) can then be deduced using the appropriate thermodynamic cycle (Scheme I).

Scheme I

$$\begin{tikzcd}
RCO_2H\ (\text{gas}) \arrow[r, "\Delta H_{ioniz,\ gas}"] & RCO_2^-\ (\text{gas}) \arrow[dd, "\Delta H_{solv}{}^{RCO_2^-}"] & + & H^+\ (\text{gas}) \arrow[dd, "\Delta H_{solv}{}^{H^+}"] \\
RCO_2H\ (\text{solid or liquid}) \arrow[u, "\Delta H_{vap}"'] \arrow[d, "\Delta H_{soln}"'] & & & \\
RCO_2H\ (\text{aq}) \arrow[r, "\Delta H_{ioniz,\ aq}"] & RCO_2^-\ (\text{aq}) & + & H^+\ (\text{aq})
\end{tikzcd}$$

Table I contains measurements of the heats of vaporization and heats of solution in water required to obtain the heats of solvation ($\Delta H_{solv}{}^{RCO_2H}$) of several haloacetic acids. In Table II the heats of hydration of these haloacetic acids are combined with the heats of ionization in water and the heats of ionization in the gas phase[2,3] to obtain the heats of hydration of the haloacetate anions. From these data it can be seen that the reversal of the order of the gas phase and aqueous ionization energies is caused entirely by an increasing hydration energy of the haloacetate anions in the order Br < Cl < F. This effect is large enough to overcome a similar, but smaller, trend in the hydration energies of the haloacetic acids which, by itself, would tend to reinforce the gas phase acidity order. The behavior of the difluoroacetic and dichloroacetic acids and their anions relative to one another is analogous to that of the monohalo acids. The overall order (Figure 1) of the hydration enthalpies of the anions parallels the order of gas phase acidities. As the *gas-phase acidity decreases, the hydration energy of the haloacetate ions increases.* There is no discernible relationship between acidity (or any other property) and the hydration energy of the acids themselves.

Experimental Section

Materials. Commercial samples of the haloacetic acids were sublimed or distilled. Purity was established by melting point for the three solid acids and by equivalent weight determination via titration for all the acids. The materials were transferred into ampules and into the vaporization calorimeter cell inside a drybox to avoid contamination by moisture.

Calorimetry. The heats of solution and ionization in water were measured using an LKB 8721-1 reaction and solution calorimeter. The quantities of solute ranged from 0.015 to 0.15 g, the amount of solvent being 100 ml in all cases. Heats of solution in water were determined by measuring the heat of solution in water and correcting for the heat of ionization (a substantial correction), and also by measuring the heat of solution in 0.10 N HCl, where ionization is considerably suppressed and the correction is therefore much smaller. Both methods gave the same results. Heats of ionization in water were calculated from the corresponding heats of neutralization. These were measured in the same way as the heats of solution, but using 0.10 N NaOH as solvent. The heats of vaporization at 25.0 °C were measured with an LKB 8721-3 vaporization calorimeter using the method of Wadso.[4] Samples evaporated in each run ranged from 3 to 30 mg, about a dozen runs being performed for each compound.

References and Notes

(1) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 4050 (1973).
(2) K. Hiraoka, R. Yamdagni, and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 6833 (1973).
(3) The gas-phase ionization energies[1,2] come from equilibrium data and are therefore $\Delta G°$ values. Measurement of the $\Delta S°$ for difluoroacetic acid gave a value of ~2.5 eu.[2] This corresponds to a difference of 0.7 kcal/mol between $\Delta H°_{ioniz}$ and $\Delta G°_{ioniz}$ at 25°. Since the *variation* in this value along a series of haloacetic acids can be expected to be an order of magnitude less than the value itself, the error introduced by our use of these gas-phase ionization free energies as enthalpies is below the threshold of the effects being discussed.
(4) I. Wadso, *Acta Chem. Scand.*, **20**, 536 (1966); **22**, 2438 (1968).