

THE INFLUENCE OF INCREASING SOLVATION ON THE RELATIVE
ENERGIES OF BISECTED AND BRIDGED ETHYL CATIONS¹

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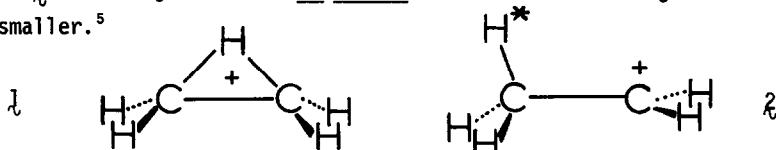
In a recent communication,² we reported molecular orbital and perturbation theory calculations which revealed that specific solvation at positively charged carbons in carbocations becomes less favorable with increasing charge delocalization. Although this notion is consistent with simple arguments from perturbation theory² and electrostatics,³ the results also led to the proposal that the relative energies of isomeric carbonium ions can vary from the gas phase to solution. The necessary conditions are significantly different charge delocalization for the cations and the presence of counter ions or solvent molecules that are good electron donors. More specifically, this implies that delocalized carbocations, such as nonclassical species, may be relatively less viable in solution than in the gas phase when compared with isomeric classical species.

Since our preliminary report² considered explicitly only interactions with one solvent molecule, the idea that additional solvation could eliminate the initial discrepancy in the solvation energy of delocalized versus localized isomers was not fully addressed. This possibility seemed unlikely, however, based on the similarity of hydrogen bond energies that was found for a variety of carbonium ions with varying delocalization. Thus, the weaker interaction between solvent and carbons in the delocalized ions was not expected to be compensated by increased hydrogen bonding. To probe this issue more thoroughly, calculations are presented here which reveal that the solvation energy difference for bisected and bridged ethyl cations shows no sign of being reduced even after addition of up to five solvent molecules. The origin of the weaker solvation of the bridged ion is also analyzed in terms of simple molecular orbital concepts.

Results

As previously discussed,² HCl is a good choice of solvent for our studies since it provides relatively weak solvation and minimizes steric concerns. The molecular orbital approach that has been employed is MINDO/3⁴ with complete geometry optimization in the stated symmetries. For the ethyl cation itself, the MINDO/3 results predict the bridged form (1) to be the only minimum. A bisected structure with a fixed CCH* angle of 100° (2) is calculated to be 7 kcal/mole

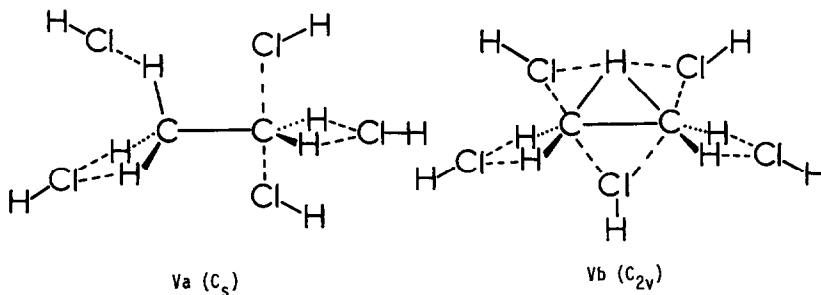
less stable than λ . Although the best ab initio studies favor a bridged structure, the energy difference is smaller.⁵



The calculated relative energies for the most stable structures of the ethyl cations in the presence of one (Ia-e) and two (IIa-f) HCl molecules are shown in the figure!¹ In both cases classical structures (Ia and IIa) are now preferred to the lowest energy bridged ones (Ic and IIb) by roughly 14 kcal/mole. The calculated stabilization energies for several of the species relative to separated λ and hydrogen chlorides are given in the table below.

n	Bisected $C_2H_5(ClH)_n^+$	ΔE_S (kcal/mole)	Bridged $C_2H_5(ClH)_n^+$	ΔE_S (kcal/mole)	E(Bisected)- E(Bridged)
0	λ	-7.2	λ	0	7.2
1	Ia	25.8	Ic	12.2	-13.6
2	IIa	36.6	IIb	21.8	-14.8
5	Va	56.9	Vb	40.8	-16.1

The next reasonable step is to add enough solvent so that each atom in the ethyl cations could be coordinated with at least one HCl. An adequate number of solvent molecules that is still computationally manageable is five. The most stable classical and bridged structures that are found in this case are Va and Vb⁶ with Vb 16 kcal/mole less stable than Va. Thus, the



MINDO/3 results show no indication of a trend towards selective stabilization of the bridged ion by increasing solvation. Naturally, it could be argued that more solvent is still needed.

Discussion

Frontier orbital theory claims that interactions between electron donating solvent molecules and a carbocation should be strongest at the sites with the largest coefficients in the LUMO of the cation.² As can be seen from the drawings of their LUMO's⁷, this prediction is borne out for λ and ζ by structures Ic and Ia, respectively. The origin of the difference in the stabili-

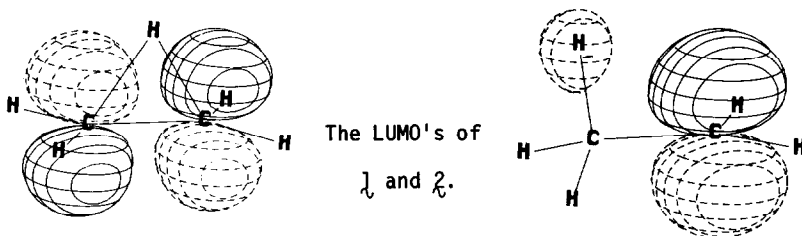
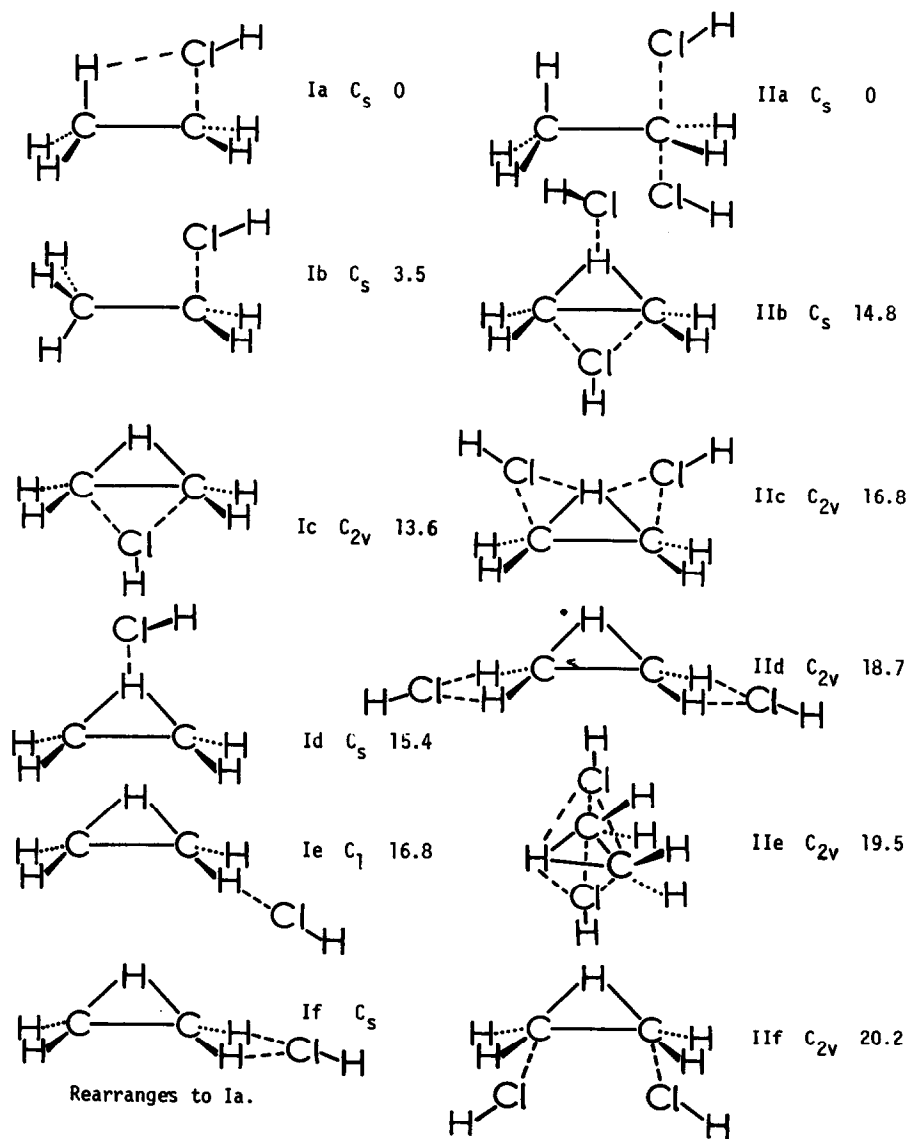


Figure. Structures, symmetries and relative energies (kcal/mole) for $C_2H_5ClH^+$ and $C_2H_5(ClH)_2^+$ species.



zation energies for Ia and Ic may be sought in the second-order perturbation theory expression (eq. 1) that was previously shown to yield good estimates of carbocation-HCl interactions.²

$$\Delta E_s = a Q / (\epsilon_L - \epsilon_H) \quad (1)$$

In the equation, the stabilization energy, ΔE_s , is a function of the electron density (Q) on the solvated carbonium carbon in the cation's LUMO if it were occupied by one electron, the energies of the cation's LUMO (ϵ_L) and the solvent molecule's HOMO (ϵ_H), and a proportionality constant, a.

To a first approximation, Q may be assumed to be the same for Ia and Ic. However, a major difference occurs in the denominator of eq 1. In λ , the LUMO is essentially nonbonding while in μ it is analogous to a π^* antibonding MO. The higher energy of the LUMO of μ (-6.0 eV versus -7.8 eV for λ via MINDO/3) makes the stabilization of Ic roughly 30% or 8 kcal/mole less than in Ia: $\Delta E_s(\text{Ic})/\Delta E_s(\text{Ia}) \approx (-7.8 + 12.1)/(-6.0 + 12.1) = .70$. The remaining difference in stabilization, 5-6 kcal/mole, is probably due to several factors including interelectron and internuclear repulsions as well as the Q values. Of course, the high LUMO energy for μ also plagues its interaction with additional solvent molecules.⁹ Furthermore, the similarity of hydrogen bond energies for localized and delocalized ions² is consistent with the observation that the total charge on hydrogens remains almost constant in isomeric cations like λ and μ . The shift of charge occurs chiefly between the carbons. Thus, in λ the total charge on hydrogens is +.62 according to MINDO/3, while it is +.58 for μ . Ab initio charge distributions also support this conclusion.¹⁰

Finally, it should be noted that the choice of solvent undoubtedly effects the bisected/bridged preference.² In a more inert solvent than HCl, e.g. Ne or CH₄ in the extreme or perhaps super acid, the gas phase preference could reassert itself. Also, at this time, the influences of entropy and outer solvent layers on the viability of aggregates such as Va and Vb remain to be assessed.

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References and Notes

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- (6) Structures in which the HCl's are coordinated with each other were not considered.
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