ture. However, the CH_2^+ plane for structure I is displaced 2.9° upward from the C–C line toward H_8. This corresponds to a small distortion toward a staggered ethane type of geometry.

Calculation 10 refers to the symmetrically bridged structure III which is found to be 11.4 kcal/mol less stable than the most stable classical form (I). This is close to the *ab initio* value previously calculated (9.0 kcal/mol, without full optimization),[3] and in very good agreement with Pfeiffer and Jewett's value (12.1 kcal/mol, with partial minimization).[8] The CH_2 groups are bent away from the bridging hydrogen (H_8), and 2.5° from the C–C line as shown (III). The perpendicular distance of the bridging proton from the C–C bond is 1.15 Å.

To determine whether the bridged structure III is a saddle point on the potential surface (transition state) or a local minimum (intermediate) in the degenerate rearrangement of one classical ethyl cation to another, a computation was carried out in which H_8 was moved 0.05 Å parallel to the C–C bond and the planes $H_4C_2H_5$ and $H_1C_1H_2$ were rotated counterclockwise by 1°. This lead to an energy *lowering* of 40 cal/mol, indicating that III is a transition state and not a metastable species (intermediate). Thus, these calculations predict a gas-phase activation barrier of 11.4 kcal/mol for 1,2-hydride shifts in the ethyl cation.[13]

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[13] For related, recent results in strong acid media, see P. C. Myhre and E. Evans, *J. Amer. Chem. Soc.*, **91**, 5641 (1969); P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969).

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Activated Complex for Hydrogen Migration in the Ethyl Cation. *Ab Initio* Calculations

Sir:

We wish to report the results of *ab initio* LCAO–MO SCF calculations concerning the structure of the ethyl cation.[1] The results of the calculations bear on two related problems of experimental and theoretical interest. First, we are concerned with the relative stabilities of open or "classical" and hydrogen-bridged or "nonclassical" ethyl cations. Second, we wish to examine whether a hydrogen-bridged structure is best described as an activated complex or an intermediate for 1,2 hydride migration in the ethyl cation. Of course these calcuations apply only to the gas phase and solvation effects may alter the equilibrium geometry and structure of carbonium ions in solution.

Previous semiempirical calculations for $C_2H_5^+$ have given conflicting predictions concerning the structure of the ethyl cation: some reports indicate the bridged structure to be more stable[2] while other reports find the open structure as the more stable conformation.[3] *Ab initio* calculations including the present work indicate that the bridged structure is less stable than the classical conformation.[1,2b,4] In Table I we give the energies for the bridged and classical structures shown in Figure 1. The basis set for these calculations consists of gaussian lobe functions with Whitten's exponents and coefficients for each function.[5] The H(1s) function is represented by a linear combination of five gaussian functions. All of the calculations reported here were obtained with the five-term hydrogen function split into two parts which were then individually subject to linear minimization by the SCF procedure. A basis set of this quality has had excellent success in yielding molecular geometries in close agreement with experiment.[6] We have examined a large number of conformations of $C_2H_5^+$ in an effort to find relative energies and optimal geometries for the open and bridged forms. In addition we wished to understand the bonding environments in these conformations and have performed population analyses on each of the conformations studied. The details of the energy terms of the numerous conformations studied as well as population analyses for these conformations will be presented in a full paper. We describe here points of immediate interest.

Table I. Energies for Bridged and Classical Structures

Structure[a]	E^b	ΔE^c
A	−78.22466	12.43
B	−78.22519	12.10
C	−78.22920	9.58
D	−78.24446	

[a] For a description of the structures see Figure 1 and text. [b] Total energies in hartrees. [c] Energies in kcal/mol relative to structure D.

For the open or classical ethyl cation we first consider a structure with the CH_3 group tetrahedral with $r_{CH} = 1.091$ Å, the CH_2 group trigonal with $r_{CH} = 1.086$ Å, and a plane of symmetry through one of the CH_3 hydrogens and the CC bond. Energy minimization with respect to the CC bond length yields $r_{CC} = 1.51$ Å. The choice of a planar cationic center has previously been shown to yield the equilibrium confor-

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[1] J. E. Williams, Jr., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970). We express our appreciation to Professor Schleyer for providing us with the results of this work before publication.

[2] (a) T. Yonezawa, H. Nakatsuji, and H. Kato, *ibid.*, **90**, 1239 (1968); (b) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969); (c) J. J. Dannenberg and T. D. Berke, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract No. PHYS 163.

[3] R. Hoffman, *J. Chem. Phys.*, **40**, 2480 (1964); R. E. Davis and A. S. N. Murthy, *Tetrahedron*, **24**, 4595 (1968); G. Klopman, private communication, 1969.

[4] J. E. Williams, Ph.D. Thesis, Princeton University, 1969.

[5] J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

[6] For a summary of some results see L. C. Allen in "Quantum Theory of Atoms, Molecules, and the Solid State," P. O. Lowdin, Ed., Academic Press, New York, N. Y., 1966.

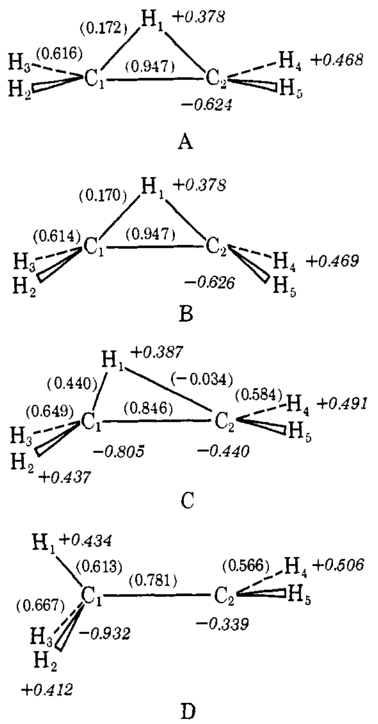

Figure 1. Conformations, charge densities (italicized), and overlap populations (in parentheses) for various bridged and open ethyl cations. See text for details of geometry of each structure.

mation for CH_3^+.[7] As observed by others, when this structure is distorted from strict tetrahedral and trigonal bonding we find that a lower energy is obtained for structure D shown in Figure 1. No attempt has been made to minimize the energy of this structure with respect to bond lengths and bond angles. Instead we have bent the $C_2H_4H_5$ group 3° counterclockwise out of the trigonal plane and bent the $C_1H_1H_2H_3$ group 6° clockwise with respect to the trigonal plane. We find this structure to be approximately 0.5 kcal/mol more stable than the open structure with tetrahedral and trigonal bonding.

For the bridged or nonclassical ethyl cation the "protonated ethylene" structure shown as structure A in Figure 1 was first examined. This structure was optimized with respect to the CC and CH bonds, the HCH angle, and the height of the bridging hydrogen. We find $r_{CC} = 1.483$ Å, $r_{CH} = 1.11$ Å, HCH angle = 120°, and the bridging hydrogen 1.2 Å above the CC bond. The $C_1H_1C_2$ plane is a plane of symmetry for this structure. Additional structures were then examined in which a plane of symmetry bisects the CC bond and passes through H_1. The lowest energy was found for the conformation indicated as structure B in Figure 1. The CC and CH bond lengths and the HCH angle were fixed and the planes of the CH_2 groups were bent away from the bridging hydrogen such that these planes are 3° below an extension of the CC line. Structure B is approximately 0.3 kcal/mol more stable than structure A. The breakdown of the total energy into its components for structures A and B reveals that the stability of the latter is due solely to a decrease in nuclear-nuclear repulsion terms upon bending. The kinetic energy, nuclear-electron attraction, and electron-electron repulsion terms all favor structure A. The population analyses indicate that the overlap populations increase in the C_1C_2 bond and decrease in the C_1H_1 bond of B in comparison to A. The charge densities of Figure 1 also indicate that protonated ethylene is an inappropriate description for the bridged structure. In actuality all of the hydrogens have some deficiency in electronic charge, but the bridging hydrogen is considerably less deficient than the terminal hydrogens H_2,H_3,H_4,H_5. Comparing the charge densities for structures A, B, and D we see that the charge density associated with H_1 increases in going from the open to the bridged form while the charge density associated with H_2 and H_3 decreases from D to B. The charge densities shown in Figure 1 support the conventional viewpoint of describing the open structure as "charge localized" and the bridged structure as "charge delocalized."

In order to determine whether structure B is an activated complex or an intermediate for 1,2 hydride migration we examined many conformations in which the structural parameters of B were slightly altered. The bridging hydrogen, H_1, was first allowed to move a short distance (0.026 Å) toward C_1 while maintaining its 1.2-Å distance above the C_1C_2 bond. No significant change in the energy was observed. The charge density on C_1 was found to increase as does the C_1–H_1 overlap population. Two other structural changes in B were considered: (1) increase in the angle of the $C_1H_2H_3$ plane to 5° below the C_1C_2 bond; (2) restoration of the trigonal conformation of the $C_2H_4H_5$ group. Both of these changes (separately and jointly) led to conformations of higher energy than structure B. We found that lower energy structures could be found if the bridging hydrogen was allowed to migrate to a position 0.26 Å from C_1 (maintaining a height of 1.2 Å above the C_1C_2 bond). If the additional structural changes mentioned above are then carried out the energy is further lowered and we arrive at structure C of Figure 1. The population analysis for structure C shows a large increase in the charge on C_1 compared to structure B. A large decrease in charge is also observed on C_2 in structure C, and our results indicate that the major orbital change is in the $C(2p_y)$ orbitals on both centers. We believe that structure C is a reasonable representation of a point on the reaction path leading from B to D. Our calculations on other structures also indicate that the points on such a reaction path will all be lower in energy than structure B and hence that B represents an activated complex for 1,2-hydride migration in ethyl cation.

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Extensive Cyclopropyl Participation at a Remote Carbonium Ion Site

Sir:

The efficacy of cyclopropane as a neighboring group in solvolytic reactions has been probed on a number of

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(7) J. E. Williams, Jr., R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 1037 (1969).