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John W. Peters, Christopher S. Foote*
Department of Chemistry, University of California
Los Angeles, California 90024

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Classical and Nonclassical Structures of the Vinyl Cation. An Accurate Computational Determination of Their Relative Stabilities and Optimum Rearrangement Path

Sir:

Vinyl cations are known[1] to play an important role as highly reactive intermediates in many organic reactions. Since they can have two possible structures, a classical linear one (Figure 1a) and a nonclassical bridged one (Figure 1b), a knowledge of the relative stabilities of both forms and the activation barrier between them is needed for a better understanding of their chemistry. In the absence of experimental data, these properties have to be deduced from theoretical calculations done on the parent system $C_2H_3^+$. The ab initio calculations reported in this communication, which include an accurate evaluation of correlation effects through extensive configuration interaction (CI), lead to the following chemical predictions after a critical estimation of all errors which can arise from defects in the calculations. (i) The two structures, both corresponding to minima in the potential energy surface, have the same energy to within 1-2 kcal/mol, the bridged structure probably having the lower energy. (ii) Molecular conformations along the lowest energy path for rearrangement from linear to bridged structures are planar. (iii) The barrier to rearrangement is small, less than 1-3 kcal/mol.

Previous calculations have addressed the question of the relative stabilities of the two structures, but have not given a definitive answer: semiempirical methods are known to strongly overestimate the stabilities of the nonclassical ions,[2,3] ab initio self consistent field (SCF) calculations[4,5] do not include correlation effects, and the independent-electron-pair approximation used in the CI approach of Zurawski et al.[6] lacks the so-called additivity corrections.[7] There have been no previous predictions of the rearrangement path. In our calculations, two levels of wave functions were computed for each nuclear conformation, (i) an SCF wave function for the dominant closed shell configuration in which occupied orbitals are expanded in a contracted Gaussian basis of "double-ζ plus polarization" quality, and (ii) a CI wave function, obtained by diagonalizing the Hamiltonian in an n-particle space spanned by the SCF configuration and all configurations derivable from it by single and double electron excitation into the unoccupied SCF orbitals. Energy differences between the SCF and CI wave functions give the correlation corrections to the potential energy surface. The calculations will be fully described elsewhere.[8,9]

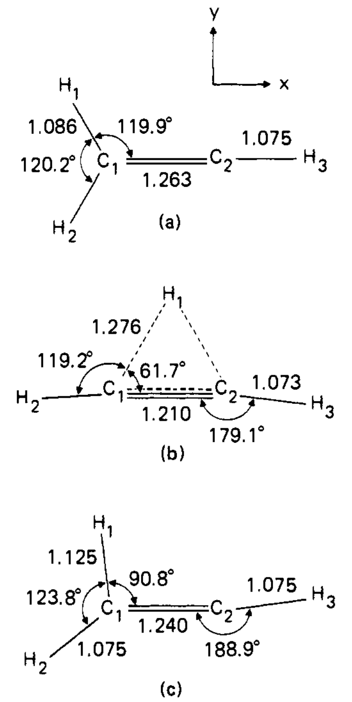

Figure 1. Optimized geometries for the vinyl cation: (a) classical (C_{2v}); (b) bridged (C_{2v}); (c) intermediate α = 90.8°. Internuclear distances are in Å.

SCF energies of the linear and bridged structures have been minimized with respect to all geometrical parameters, whose optimum values are shown in Figures 1a and 1b. We have determined computationally that these minimum energy structures are planar C_{2v}. Three points on the reaction path were chosen to give equal increments in the angle $H_1C_1C_2$ (Figure 1) between the linear and bridged structures. Having fixed this angle, α, the SCF energies were minimized with respect to variation of all the remaining geometrical parameters. Figure 1c shows the optimized conformation when angle α is halfway between its linear and bridged values (α = 90.8°). All points on the minimum energy reaction path, presented in Figure 2, have been shown computationally to be planar. We have determined that during the migration of H_1 (Figure 1) along the reaction coordinate, the atom H_3 moves trans to H_2, with angle $C_1C_2H_3$ equal to 188.9° when α = 90.8°, and then back through the linear position to a final $C_1C_2H_3$ angle of 179.1°. This emphasizes the necessity of geometrical optimization; assumed interpolations using only the linear and bridged geometries can result in errors of several kilocalories per mole in the energy along the reaction path. It is noteworthy that the $H_2C_1C_2H_3$ conformation in the bridged structure has a geometry very close to that of acetylene; π-protonation of acetylene causes very little distortion.

Figure 2 shows the reaction path computed with CI wave

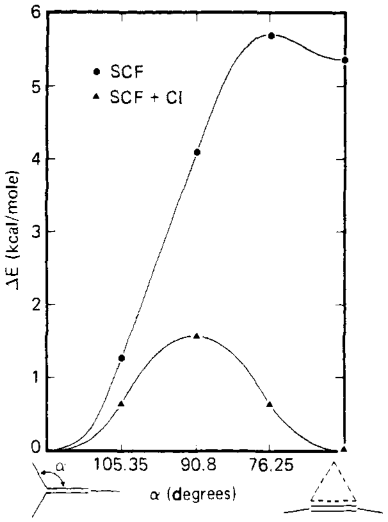

Figure 2. Section of the potential surface corresponding to the optimum transformation path of the classical to the bridged vinyl cation. For both curves, the difference $\Delta E = E - E$(linear form) is plotted against the reaction coordinate α.

functions at SCF optimized geometries. The qualitative difference between the CI and SCF (shown on the same figure) reaction paths demonstrates that the change in correlation effects with structure plays an important role in carbonium ion rearrangement. While Figure 2 shows equal (to within 0.01 kcal/mol) CI energies for the linear and bridged structures, and a barrier of 1.6 kcal/mol, we must establish error bars on these numbers to make chemical predictions. These error bars, established through computation both on this and on other molecules, estimate the effect of deficiencies in the 1-particle basis, the n-particle basis, and errors in diagonalization and geometrical optimization. When applied to the results of Figure 2 they result in the predictions made at the beginning of our letter. Finally we have calculated for both structures the first vertical singlet-singlet $\pi \rightarrow \sigma^*$ excitation energy by doing separate SCF calculations on the ground and excited states. Due to important differences in the electronic structure of the two forms, these transitions occur at very different energies: 2.37 eV in the linear structure, 6.53 eV in the bridged one. This very low $\pi \rightarrow \sigma^*$ excitation energy for the linear cation leads to the conclusion that it should be colored and suggests that it could be easily identified if experimental techniques succeed in producing vinyl cations with long enough lifetimes. Such an observation could confirm our prediction that the bridged structure cannot be significantly lower in energy than the linear.

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J. Weber, A. D. McLean*
IBM Research Laboratory
San Jose, California 95193

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*Book Reviews**

Finite Groups and Quantum Theory. By D. B. CHESNUT (Duke University). Wiley-Interscience Publishers, New York, N.Y. 1972. xii + 254 pp. $14.95.

There is no scarcity of books on group theory and a question which naturally arises is why publish another book on this subject?

The author is clearly aware of the many companions that his book will find on the reader's bookshelf; thus he has prepared a text which is of quite useful character. The text is designed to be educational. It explains well the basic mathematical ideas and structure behind the theory of point groups and its application in quantum mechanics. Besides presenting derivations, proofs, and formulas, good problems and solutions are given at the end of each chapter. It is worth emphasizing that one only learns the subject of group theory well by practice, and the preparation of relevant problems and their solutions should then allow the reader to learn the subject with sufficient practice, without getting bogged down by his temporary inability to visualize the solutions of some important problems.

The book is divided into several basic areas. The first five chapters deal with abstract theory, which may appear to be brief and somewhat difficult for beginning students. Chapters 6 through 11, which deal with reducible and irreducible representations, the group character, the orthogonality relations, character tables, functional and coordinate transformations, and projection operators, are presented in more detail. These details are important as they represent the mathematical essence of group theory. Chapter 12 shows the essential connection of quantum mechanics with group theory. The symmetry of the Hamiltonian and its eigenfunction are treated clearly. The final three chapters are concerned with applications, and one should find the important techniques used in these chapters useful in the field of molecular quantum mechanics.

While this book has commendable features, its style is probably too terse to be matched to the needs of a beginning student who is trying to teach himself group theory. However, those who have already been exposed to the subject or are being guided by an instructor, will find this a worthwhile book. By working through the derivations and manipulations given in the book, they will undoubtedly gain much greater confidence in using the basic and fundamental techniques of group theory. The book is well suited to serve as lecture material for a one-semester course on group theory for students in physical chemistry or chemical physics.

C. H. Wang, *University of Utah*