produced by attachment of a second molecule of X, *regardless of the ratio* $[P_0]/[X_0]$. By the definition of the equilibrium constants, the amount of complex formation varies with the absolute concentrations $[P_0]$ and $[X_0]$, not with their ratio, which is concentration independent. Thus for systems in which $K_2\epsilon_2/K_1\epsilon_1$ is appreciably larger than 0.01, eq 15 is inapplicable at *any* concentration of X. We might also reemphasize that when [X] becomes very small, the saturation fraction (depending on the values of the formation constants) approaches zero, and we enter a region where it may be difficult or impossible to determine accurate values of the limiting slope or intercepts of the plots.[1]

Finally, we note that methods commonly in use[22,23] for "proving" the existence of 1:1 complexes, such as Job's method,[24] have been shown to be inappropriate for systems in which more than one molecule of X is bound, leading to erroneous values for the formation constants.[25] It can be concluded from a careful examination of the literature that there are few if any weak complexes determined by spectroscopic means which have been rigorously proven to consist only of 1:1 complexes, other than those which are isolable as crystalline complexes amenable to chemical analysis.

Acknowledgment. This work was supported by the National Institutes of Health and the Swiss National Foundation for Scientific Research, Grants No. 3426 and 4883.

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(22) M. J. S. Dewar and C. C. Thompson, *Tetrahedron Suppl.*, 7, 97 (1966).

(23) P. R. Hammond, *J. Phys. Chem.*, 72, 2272 (1968).

(24) P. Job, *Ann. Chim.* (Paris), 9, 113 (1928).

(25) *Cf.* discussions by Rossotti and Rossotti.[12]

Local Orbital Guide to Allowed Interconversions of $C_4H_7^+$ Ions

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Abstract: A guide to adiabatic reaction pathways, parallel to the method of Hoffmann and Woodward but convenient for three-dimensional molecules of low symmetry, is developed in terms of localized molecular orbitals. Calculations on the $C_4H_7^+$ system illustrate the technique; several predictions are made. The *syn*-allylcarbinyl ion closes to cyclobutyl ion by a disrotatory motion. The cyclopropylcarbinyl cation rearranges to a nonplanar cyclobutyl ion by bending the *exo*-methylene toward a ring carbon. The CH bond at the formally charged carbon naturally assumes the axial position essential to a stable cyclobutyl ion. The protonated planar methylene cyclopropane may undergo a pseudorotation by conrotatory motion of the *exo*- and a ring methylene. A detailed description of delocalization in these ions is given by a newly developed semiempirical local orbital analysis.

I. Introduction

The Hoffmann–Woodward rules provide an invaluable guide to low-energy paths in chemical reactions and are widely verified by experiment.[2] The arguments leading to these rules rest upon the correlation between orbitals of an original geometry A and a final geometry B. At first decisions were based on the fate of the highest occupied orbital in A; if this orbital passes into an occupied orbital of B, the nuclear motion probably requires little energy. It is "thermally allowed." If the orbital correlates instead with an excited orbital of B, A goes to B only by free-radical, multistep, or photochemical processes. Since these pathways are either very demanding of energy or require special experimental conditions, they are easily distinguished from the thermally allowed reactions. At the suggestion of Longuet-Higgins and Abrahamson,[3] the arguments were put on a firmer basis by consideration of the correspondence of each member of the set of occupied orbitals in A with its counterpart in B.

Application of the Hoffmann–Woodward approach and arguments analogous to it becomes more difficult in large, three-dimensional systems of low symmetry. In this report, we describe a reformulation of the Hoffmann–Woodward approach, in the language of localized molecular orbitals, which avoids this difficulty. We rely on the fact that, if a set of molecular orbitals ΦA correlates with another set ΦB, one may form arbitrary linear combinations within the sets without destroying their correspondence. The energy localized orbitals[4] are particularly suitable linear combinations in this context because of the high degree of transferability of many local orbitals. The transferability makes the correspondence of individual orbitals very easy to discern: a CH bond orbital of A usually corresponds to a similar CH bond orbital in B, for example. The localized orbitals (LO's) we refer to in

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(2) (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968); J. J. Vollmer and K. L. Servis, *J. Chem. Educ.*, 45, 214 (1968); (b) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, 87, 2046, 4389 (1965).

(3) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2045 (1965).

(4) (a) J. E. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc.* (London), A202, 446 (1950); A210, 190 (1951); (b) C. Edmiston and K. Reudenberg, *Rev. Mod. Phys.*, 35, 457 (1963); *J. Chem. Phys.*, 43, S97 (1965); (c) C. Trindle and O. Sinanoğlu, *ibid.*, 49, 65 (1968).

this paper are those that result from the criterion of "minimum exchange"[4a] between different orbitals. A *nonempirical* procedure for obtaining them for small molecules was devised by Ruedenberg and coworkers.[4b] The procedure requires, however, nonempirical SCF MO's and the multicenter integrals and so becomes difficult for applications in organic chemistry. A semiempirical method which starts with semiempirical MO's and yields the LO's of organic molecules while demanding little computer time[4c] will be used in the present paper.

The local orbital correspondence method is illustrated by calculations and diagrams for several geometries of the $C_4H_7^+$ system, which has been widely discussed due to its importance in the carbonium ion reactions of allylcarbinyl, cyclopropylcarbinyl, and cyclobutyl derivatives.[5]

A by-product of the localization calculations is a detailed description of delocalization in these ions: hyperconjugation and nonclassical character can be precisely characterized.

In section II, we briefly recount the localization method, which we have discussed in more detail elsewhere.[4c] The "localization defect," a measure of delocalization, is defined, with examples of its application.

Section III demonstrates the ease of determining correspondence between LO's for different geometries, by the examples of the *syn–anti* rotation of allylcarbinyl cation, and the ring closing to cyclobutyl cation.

Section IV shows that the pyramidal $C_4H_7^+$ ion once proposed as an intermediate in solvolysis reactions is subject to major Jahn–Teller instability and relaxes to the cyclopropylcarbinyl cation in which the CH bonds of the *exo*-methylene group lie in the plane of symmetry.

In section V, the route of formation of a bicyclobutyl carbonium ion from the cyclopropylcarbinyl ion is indicated; the cyclobutyl ion is seen to be accessible from this intermediate. A cyclopropylcarbinyl species in which the four carbons lie in a plane containing the *exo*-methylene CH bonds (essentially a protonated alkene) is predicted to undergo a conrotatory motion of the methylenes producing a pseudorotation of the molecule.

Section VI is a discussion of delocalization in the $C_4H_7^+$ systems as described by the localized orbitals and the bond indices.

II. Semiempirical Localization

This study is based on an analysis which starts with molecular orbital wave functions. The system is of considerable size, so an approximate semiempirical MO treatment is indicated. Since the molecules are charged, a self-consistent procedure is essential.[6] The CNDO/2 approximation to the Roothaan equations of the SCF–MO theory developed by Pople and Segal[8] seems most suitable for these and other reasons: we deal with three-dimensional systems for which no unique choice of the atomic coordinate systems exists, so the invariance to arbitrary rotation of these axes guaranteed in CNDO calculations is most desirable. Since the localized orbitals are often easily represented in terms of hybridized atomic functions, the invariance of CNDO expectation values of hybridization of the basis set is advantageous. This advantage is gained at the cost of a drastic approximation: that Coulomb integrals containing p orbitals are indistinguishable from Coulomb integrals involving only s orbitals. Surprisingly, the CNDO wave functions yield a consistent account of s and p character in individual hybrids.[9] Finally, a CNDO program is listed with the Quantum Chemistry Program Exchange,[10] so the calculations similar to those we describe are feasible for many chemists.

The properties of many molecules can be described as if local bond orbitals exist, only slightly influenced by the other bond orbitals of the system. However, calculations based on the Roothaan equations (including Hückel[11] as well as CNDO methods) yield orbitals delocalized throughout the molecule, classified by their response to the symmetry operations of the molecular point group. The invariance of expectation values to unitary transform of the set of occupied orbitals allows the combination of the set of MO's into functions resembling bonds, cores, and lone pairs. In highly symmetric molecules, group theoretic methods determine the localization transform;[12] in general, however, a physical criterion of localization is necessary. The condition that local orbitals have a minimum exchange interaction, proposed by Lennard-Jones and Pople and made practicable by Edmiston and Reudenberg[4b] for *ab initio* calculation, has been adapted for semiempirical work.[4c]

Briefly, molecular orbitals are subjected to a series of 2 × 2 transformations, which have the effect of forming the combinations of two orbitals which have minimum exchange.

The pairwise combinations may be expressed in terms of a single parameter α_{ij}.

$$u_i = (\phi_i)\cos\alpha_{ij} - (\phi_j)\sin\alpha_{ij}$$

$$u_j = (\phi_i)\sin\alpha_{ij} + (\phi_j)\cos\alpha_{ij}$$

The angle α_{ij} is defined in terms of the Coulomb integrals and the MO coefficients by the following relations.

$$\cos 4\alpha_{ij} = -A_{ij}/(A_{ij}^2 + B_{ij}^2)^{1/2}$$

$$\sin 4\alpha_{ij} = B_{ij}/(A_{ij}^2 + B_{ij}^2)^{1/2}$$

$$A_{ij} = \sum_{rt}[rr|tt]\{a_{ir}a_{jr}a_{it}a_{jt} - {}^1/_4(a_{ir}^2 - a_{jr}^2)(a_{jt}^2 - a_{it}^2)\}$$

$$B_{ij} = \sum_{rt}[rr|tt]\{(a_{ir}^2 - a_{jr}^2)a_{it}a_{jt}\}$$

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(5) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, to be submitted for publication.

(6) The appreciation of the averaged, long-range portion of the electronic repulsion built into the SCF formalism is central to the credibility of predictions of hyperconjugative delocalization. According to Dewar,[7a] neglect of correlation as in many Hückel calculations must lead to overestimates of delocalization. The SCF procedure should give an account of the charge distribution adequate to our purpose, since more detailed attention to correlation does not lead to significant changes in this one-electron function.[7b]

(7) (a) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, Chapter II, but see S. Ehrenson, *J. Am. Chem. Soc.*, **83**, 4493 (1961); (b) O. Sinanoğlu and D. F. T. Tuan, *J. Chem. Phys.*, **38**, 1740 (1963), discusses effects of correlation or orbitals.

(8) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966).

(9) C. Trindle and O. Sinanoğlu, *J. Am. Chem. Soc.*, **91**, 853 (1969).

(10) Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47001.

(11) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(12) G. G. Hall, *Proc. Roy. Soc.* (London), **A202**, 336 (1950); **A205**, 541 (1951); G. G. Hall and J. E. Lennard-Jones, *ibid.*, **A202**, 155 (1950); **A205**, 357 (1951).

Here $[rr|tt] = \int X_r^*(1)X_r(1)(1/r_{12})X_t(2)X_t(2)\, dV_1V_2$, the X's being atomic orbitals, and the a_{ir} the LCAO expansion coefficient for the rth atomic orbital in the ith molecular orbital.

All pairs of orbitals are transformed in succession, in an iterative process: the localization is complete when B_{ij} is zero for all i and j.

In the computer version of this calculation, the matrix of interatomic distances, the atomic numbers of the several atoms, and the CNDO–LCAO coefficients are supplied to the program,[4c] and the coefficients of the localized orbitals and the transformation matrix are returned.

There are potential difficulties with the localization procedure which can complicate its application. Edmiston and Reudenberg[4b] have shown that there are an infinite number of equivalent localization transforms for the π orbitals of benzene and the lone pairs of F_2. This ambiguity is an example of the general problem of multiple relative minima in the exchange interaction. There is no way of proceeding with complete confidence to the absolute minimum, or of knowing that there is only one. However, in our experience with the semiempirical localization, only two examples of ambiguous localization have occurred, ethylene oxide and trifluoromethane. It made its presence felt by slowing down convergence drastically.

Perhaps a more disappointing aspect of localization is the occasional determination of LO's which depart substantially from chemical intuition. This difficulty is rare; besides the examples mentioned above, we have never encountered it. Unconventional angles between hybrids, such as the 90° between OH hybrids in H_2O found by Edmiston and Reudenberg,[4b] affect none of the arguments below.

The extensive and detailed information contained in the local orbitals is essential to the discussions of nuclear motion presented in the following sections. However, one important aspect of the wave function, the degree and extent of delocalization, can be characterized in a less cumbersome way by the bond indices.

The bond index[13a] between two atomic orbitals a and b, W_{ab}, is simply the square of the bond order P_{ab}, familiar from the semiempirical theory of π systems. The sum of W_{ab} over the atomic orbitals b is proportional to the charge in the orbital a. The charge may be separated into charge which is involved in ionic structures W_{aa}, and charge involved in covalent bonding to other orbitals b.

$$2q_a = \sum_b W_{ab} = W_{aa} + \sum_{b \neq a} W_{ab}$$

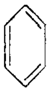
The latter charge is referred to as the "active charge." An alternate partitioning divides the active charge $q_a - {}^1/_2q_a{}^2$ into terms corresponding to charge involved in various localized valence-bond structures.[13b] For example, consider the active charge of a hydrogen atom in methane, illustrated in the following equation where $W(\text{H–C}_s)$ is the square of the bond order between the H 1s orbital and the C 2s orbital; $W(\text{H–C}_x)$, $W(\text{H–C}_y)$, and $W(\text{H–C}_z)$ are the squares of bond orders between the H 1s and the C $2p_x$, $2p_y$, and $2p_z$ orbitals, respectively. The remainder D_L contains terms describing bonding between hydrogens.

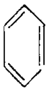
$$q^A(\text{H}) = \frac{1}{2}[2q(\text{H}) - q(\text{H})^2] = \frac{1}{2}[W(\text{H–C}_s) + W(\text{H–C}_x) + W(\text{H–C}_y) + W(\text{H–C}_z)] + D_L = \frac{1}{2}W_{\text{CH}} + D_L$$

The first four terms at right pertain to the CH bonds of the usual valence-bond (VB) structure for methane and account for 99.8% of the proton's active charge. The remainder D_L is defined here as the *localization defect* and is a measure of the adequacy of a representation of a molecule by a single VB structure. A more general expression parallel to eq 2 defines the localization defect for any structure B.

$$q^A = \sum_{ab \text{ in B}}[(W_{ab}/2) + D_L(\text{B})]$$

This definition requires some elaboration for systems in which several important VB structures can be written which have a portion in common. A specific example illustrates the problem. Consider benzene, for which B might be one of the Kekulé structures. B fails to account for an important aspect of the bonding, represented by the other Kekulé structure C. Note that the σ structure is common to these forms. In this case we account for 99% of the active charge in the σ system by the common structure, but only 44% of the active π charge by one Kekulé structure, according to an analysis of a CNDO wave function. In this case, the major portion of the localization defect is to be found in the π system, as we may expect.

B =


C =


In general, if the localization defect is very small, we know that a single VB structure is a good description of the system, and that a localized orbital representation is feasible.

In the following discussion, calculated localized orbitals are the base for all conclusions. However, the bond indices and the localization defects will be convenient means for the discussion of delocalization (see Table I).

III. Correspondence between Localized Orbitals in Interconvertible Species. Allylcarbinyl and Cyclobutyl Cations

As we mentioned above, decisions whether a nuclear motion leading to interconversion of species is allowed are made on the basis of orbital correlation diagrams such as the one shown schematically in Figure 1. If an orbital occupied in configuration A correlates with a virtual (unoccupied) orbital of B, the nuclear motion leading from A to B is unlikely, dependent on multistep or free-radical processes which are usually very demanding energetically. If, however, each of the occupied orbitals of A corresponds to occupied orbitals in B, the nuclear motion is adiabatic and requires less activation energy. In systems with high symmetry, drawing the relations between A and B orbitals is fairly simple. However, as the symmetry is reduced, the connections become less obvious: as the size of the

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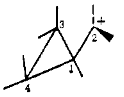
(13) (a) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968); "Bond Orders and Bond Indices," private communication; (b) C. Trindle, *J. Am. Chem. Soc.*, 91, 219 (1969).

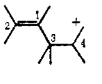
Table I. Bond Indices and Localization Defects for the Configurations of the $C_4H_7{}^+$ System Discussed in the Text[a]

I. Bent "outplane" cyclopropylcarbinyl cation



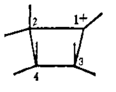
$W(C_1C_2) = 1.14$ $W(C_2H) = 0.93$
$W(C_1C_3) = 0.91$ $W(CH) = 0.96$
$W(C_1H) = 0.85$ $D_L = 1.59$

II. *anti*-Allylcarbinyl cation



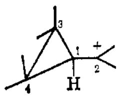
$W(C_3H_4) = 1.18\ (0.20\pi)$ $W(C_1C_3) = 0.99$
$W(C_1C_2) = 2.00\ (1.00\pi)$ $W(CH) = 0.96$
$W(C_3H) = 0.87$ $D_L = 1.12$

III. Cyclobutyl cation



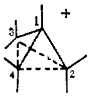
$W(C_1C_2) = 1.094$ $W(CH) = 0.96$
$W(C_2C_4) = 1.00$
$W(C_2H) = 0.91$ $D_L = 1.59$

IV. Planar outplane cyclopropylcarbinyl cation



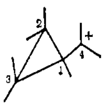
$W(C_1C_2) = 1.34$ $W(CH) = 0.96$
$W(C_1C_3) = 0.94$
$W(C_1H) = 0.62$ $D_L = 2.10$

V. Pyramidal $C_4H_7{}^+$



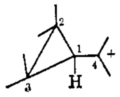
$W(C_1C_2) = 1.07$ $W(C_1C_3) = 0.92$
$W(C_3C_4) = 0.76$ $W(C_2C_3) = 0.11$
$W(C_1H) = 0.95$
$W(CH) = 0.97$ $D_L = 1.36$

VI. Bent "inplane" cyclopropylcarbinyl cation



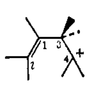
$W(C_1C_2) = 0.79$ $W(C_1C_4) = 1.40\ (0.41\pi)$
$W(C_2C_3) = 1.06$
$W(CH) = 0.95$ $D_L = 1.74$

VII. Planar inplane cyclopropylcarbinyl cation



$W(C_1C_2) = 0.79$ $W(C_1C_4) = 1.41\ (0.42\pi)$
$W(C_2C_3) = 1.07$ $W(C_1H) = 0.89$
$W(CH) = 0.96$ $D_L = 1.82$

VIII. *syn*-Allylcarbinyl cation



$W(C_1C_2) = 2.00$ $W(C_1C_3) = 0.94$
$W(C_3C_4) = 1.41$ $W(C_3H) = 0.78$
$W(C_4H) = 0.93$
$W(CH) = 0.96$ $D_L = 1.92$

[a] The bond index is the square of the bond order, while the localization defect is a measure of the departure of the charge distribution from a single valence-bond structure. Fully localized CH bonds generally have a bond index of 0.98–1.00, while localized CC single and double bonds have indices very near 1.00 and 2.00, respectively. Localization defects for localized systems are very small; if these $C_4H_7{}^+$ systems were as localized as alkanes usually are, no localization defect would exceed 0.20 unit of charge. $W(AB)$, where A and B are atoms, is defined as the sum of all W_{ab}, where a denotes an atomic orbital on atom A and b denotes an atomic orbital on atom B.

system increases, the problem becomes rapidly unwieldy.

If the set of orbitals occupied in geometry A has a one-to-one correspondence with the set of orbitals occupied in geometry B, formation of combinations within each of these sets does not destroy their correspondence. The symmetry labels of the orbitals lose their significance as combinations with components of differing symmetry are constructed. However, this loss is usually more than compensated by the fact that most of the local orbitals will be transferable from A to B. For these orbitals, the correspondence will be easy to see.

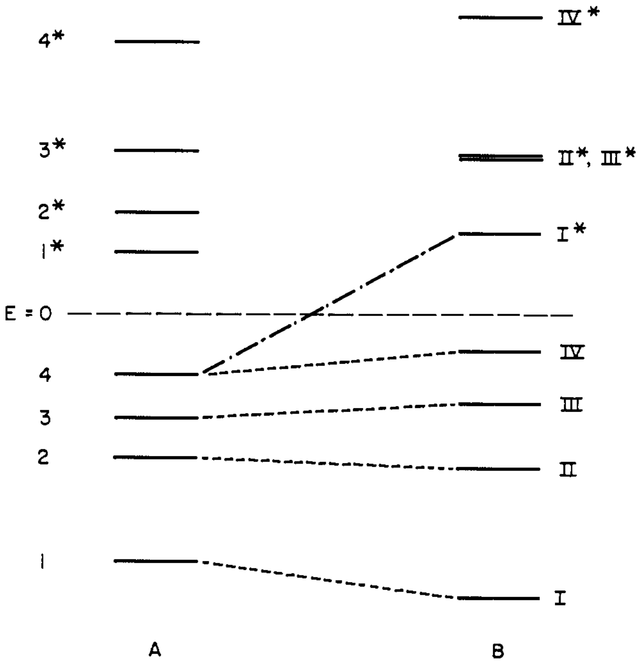


Figure 1. A correlation diagram used in making a decision whether a given nuclear motion connecting geometries A and B is allowed. If all the occupied orbitals of A pass into occupied orbitals of B (dashed lines), the process is allowed. If an occupied orbital of A correlated with an excited orbital of B (as in the connection of 4 (A) with I* (B) shown), the process is thermally forbidden.

The correlations of local orbitals can be obtained by examination of tables of orbital coefficients, such as Table II. However, it seems convenient to represent the local orbitals by single schematic contours, and to inspect the diagrams rather than the numerical coefficients. Figures 1–5 are diagrams of this type: LO's of positive sign are given open contours, while negatively signed LO's have shaded contours. The LO coefficients of all the carbonium ions may be obtained from one of us (C. T.) if necessary to clarify the construction of the diagrams.

Consider the rotation of allylcarbinyl cation from its *anti* form to the *syn* configuration, a preparation for the ring closing to cyclobutyl ion. As the sketches in Figure 2 show (and as the LO coefficients bear out in greater detail), the local orbitals of *anti*-allylcarbinyl ion bear strong resemblance to the respective orbitals in *syn*-allylcarbinyl ion, both in contour and in sign. The only major difference, that of orientation, is closely associated with the nuclear motion.

The sign given each local orbital by the unitary transform T, which assembles the local orbitals L from the set of symmetry orbitals C ($TC = L$), is very significant.[14] For example, consider the drawings of local

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(14) The signs of molecular orbitals are not fixed by the usual MO computation. That is, any MO ϕ_i can be replaced by $-\phi_i$ without affecting any expectation values (the physically significant quantities). For the signs of local orbitals to have meaning, a consistent phase (sign) convention must be applied to the MO's. In the present work we required that the atoms be numbered in a given order, and that the first coefficient in the vector $((C)_{in})$ which is not zero by symmetry be positive. Given that the phases of the MO's are fixed, and that the localization transform is unitary, of the form given in section II of the text, the signs of the LO's are meaningful. In constructing correlations of LO's of different molecular geometries, not only the contours, *but also the signs*, must agree. The fact that T is unitary allows the reversal of sign of any *even* number of local orbitals. This freedom facilitates the perception of correspondences, but does not alter the predictions based thereon.

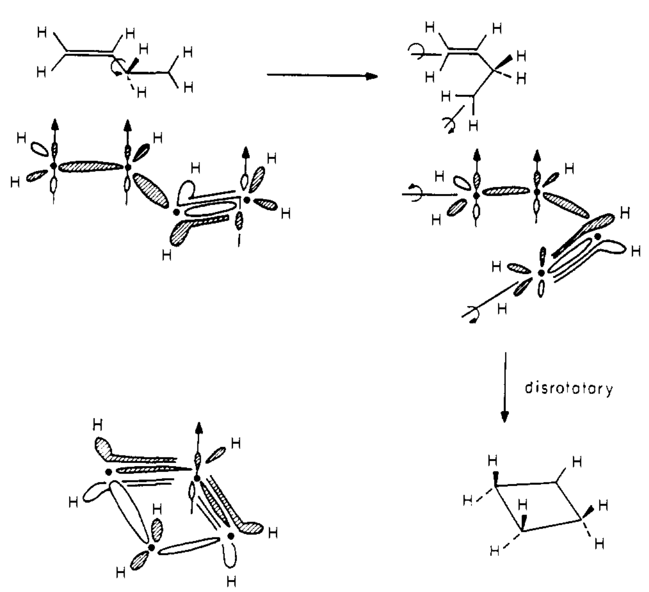

Figure 2. The correlation of local orbitals in the *anti*-allylcarbinyl–*syn*-allylcarbinyl cyclobutyl interconversion. The *anti* to *syn* rotation leaves all signs and contours unaltered (the shaded LO's are negative in sign; the unshaded LO's are positive). The *syn* LO's pass smoothly into the cyclobutyl LO's by disrotatory motion of the terminal methylenes. The conrotatory motion leads to a node in the region of the desired ring-closing bond. π-Type p_z orbitals are marked by arrows parallel to the *z* axis.

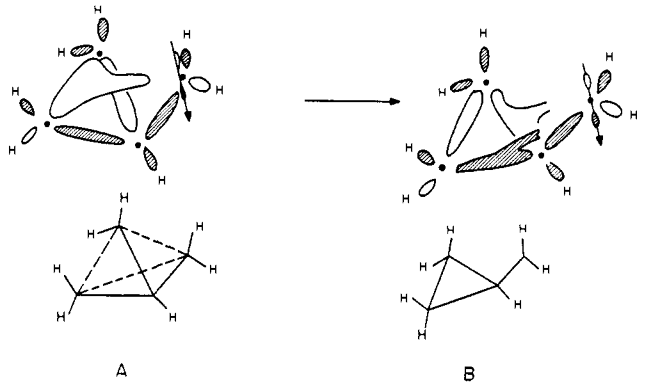

Figure 3. The relaxation of pyramidal $C_4H_7^+$ to inplane cyclopropylcarbinyl ion allows an increase in delocalization and leaves the signs of the LO's unchanged.

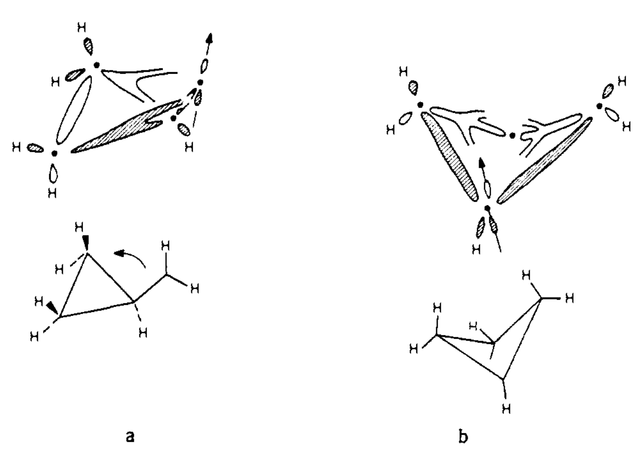

Figure 4. The bicyclobutonium ion is formed from cyclopropylcarbinyl ion by bending the *exo*-methylene group (Cl) toward one of the ring carbons (say C_4). The C_1C_4 bond is strengthened as the C_1–C_3 interaction is weakened. The signs of the local orbitals correspond, indicating that the process is thermally allowed. The bicyclobutonium ion is allowed to achieve the planar cyclobutyl geometry; *cf.* Figure 2.

orbitals for *syn*-allylcarbinyl ion and cyclobutyl ion, Figure 2. The hyperconjugative interaction of the α-hydrogens in cyclobutyl ion with the "vacant" p orbital at the formally charged carbon fixes the sign of the α-CH bond orbitals. This restriction and the signs of the *syn*-allylcarbinyl LO's make clear that the disrotatory motion shown is the allowed ring closing node.[15] The opposite conrotatory motion would merely produce a node in the region of the desired ring-closing bond. The conclusion is in accord with calculations of Wiberg and Szeimes[16] on the ring *opening* of *bent* cyclobutyl ion. Comparison of such apparently disparate processes is justified by (a) the fact that dihedral bending of the cyclobutyl ion is an allowed process, and (b) the principle of detailed balancing, which allows arguments concerning the forward course of a reaction to apply to the opposite reaction, where equilibration is possible.

IV. The Pyramidal $C_4H_7^+$ Ion

The symmetric pyramidal ion was once proposed as an intermediate in the solvolysis of cyclopropylcarbinyl and cyclobutyl compounds.[17] The C_{3v} form (Figure 3A) is appealing because of its high symmetry but is not a significant species. Its ground state is apparently a triplet,[18] hence inaccessible from the singlet ions which we discuss. The singlet species is degenerate, and thus subject to Jahn–Teller distortion.[19] A *very* small distortion ($C_{3v} \rightarrow C_s$) such that the C_3–C_4 distance is only 0.3% shorter than the equal C_2–C_3 and C_2–C_4 distances leads to profound departures in the charge distribution from threefold symmetry (Figure 3A). The slightly smaller C_3–C_4 region attracts 77% of the active charge in the three-center bond in the base of the pyramid, for example. The C_1–C_2 bond assumes relatively great π character (20%) relative to the C_1–C_3 and C_1–C_4 bonds (3%). The contours and signs of the local orbitals shown in Figure 3 indicate that the pyramidal ion can achieve the cyclopropylcarbinyl geometry, with the *exo*-methylene CH bonds lying in the plane of symmetry of the molecule. The cyclopropylcarbinyl ion is far more stable than the slightly distorted pyramidal ion, 0.5 in the CNDO energy units (nominally over 300 kcal/mole). The pyramidal ion is not a significant intermediate, according to these computations.

V. Nuclear Motion in the Cyclopropylcarbinyl Cation

Rearrangement to the Cyclobutyl Ion. Cyclopropylcarbinyl cation is presumed to attain a bicyclobutyl ion

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(15) The allylcarbinyl cation could be considered a protonated butadiene; a naive view might lead to prediction of conrotatory closing to protonated cyclobutene, by analogy to the unprotonated system. That this is not the case is confirmed by a conventional Hoffmann–Woodward analysis.

(16) K. B. Wiberg and G. Szeimes, to be submitted for publication.

(17) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

(18) R. E. Davis and A. Ohno, *Tetrahedron*, **24**, 2063 (1968).

(19) H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), A161, 220 (1937); see G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1966, p 41 ff.

Table II. Local Orbital Coefficients for Local Orbitals (LO) in Bent Inplane Cyclopropylcarbinyl Cation[a]

	C_1–C_3	C_2–H_5	C_3–H_7	C_1–C_2	C_1–H_3	C_4–H_1
C_1–2s	0.3038	0.0042	−0.0044	−0.3033	−0.3924	−0.1116
C_2–2s	0.0676	0.4176	0.0034	−0.2489	−0.0004	−0.0076
C_3–2s	0.2482	−0.0035	−0.4177	−0.0680	0.0001	−0.0072
C_4–2s	−0.0058	0.0197	−0.0199	0.0059	0.0109	0.4361
C_1–2p_x	−0.5348	0.0154	0.0156	−0.5351	−0.0004	0.0000
C_2–2p_x	−0.0970	0.2962	0.0056	0.0350	0.0043	0.0016
C_3–2p_x	0.0340	0.0056	0.2962	−0.0981	−0.0043	−0.0019
C_4–2p_x	−0.2999	−0.0549	−0.0548	−0.3001	−0.0002	0.0000
C_1–2p_y	−0.3368	−0.0102	0.0103	0.3372	−0.3336	−0.0280
C_2–2p_y	0.1138	−0.1360	0.0096	−0.5705	0.0040	−0.0063
C_3–2p_y	0.5713	−0.0097	0.1357	−0.1128	0.0043	−0.0065
C_4–2p_y	0.0248	−0.0093	0.0094	0.0247	−0.0386	−0.2232
C_1–2p_z	−0.0032	−0.0389	0.0389	0.0031	0.5154	0.0116
C_2–2p_z	−0.0004	−0.5045	0.0388	−0.0053	0.0366	−0.0008
C_3–2p_z	0.0056	−0.0389	0.5045	0.0004	0.0366	0.0001
C_4–2p_z	0.0101	−0.0166	0.0164	−0.0103	0.0334	0.5628
H_1–1s	−0.0109	−0.0010	0.0007	0.0109	−0.0447	0.6639
H_2–1s	0.0232	−0.0058	0.0058	−0.0232	0.0289	−0.0102
H_3–1s	−0.0051	−0.0292	0.0291	0.0056	−0.6764	0.0325
H_4–1s	0.0174	−0.0132	−0.0324	0.0115	−0.0295	0.0025
H_5–1s	0.0139	0.6744	0.0258	0.0140	0.0285	0.0036
H_6–1s	−0.0113	0.0324	0.0132	−0.0174	−0.0295	0.0026
H_7–1s	−0.0143	−0.0258	−0.6744	−0.0138	−0.0285	0.0022

	C_1–C_4	C_3–H_6	C_2–C_3	C_4–H_2	C_2–H_4
C_1–2s	−0.3547	−0.0071	0.0348	0.0152	−0.0071
C_2–2s	−0.0019	−0.0020	0.2882	−0.0102	−0.4082
C_3–2s	−0.0018	−0.4081	0.2886	−0.0102	−0.0020
C_4–2s	−0.4654	0.0210	0.0138	−0.4200	0.0204
C_1–2p_x	−0.0002	0.0011	−0.0011	0.0000	−0.0012
C_2–2p_x	0.0057	0.0042	−0.5589	0.0039	−0.2906
C_3–2p_x	−0.0057	0.2906	0.5588	−0.0039	−0.0042
C_4–2p_x	0.0001	−0.0119	−0.0006	0.0000	0.0118
C_1–2p_y	−0.3179	0.0048	−0.1123	−0.0197	0.0049
C_2–2p_y	0.0016	0.0014	−0.3119	−0.0141	0.1536
C_3–2p_y	0.0018	0.1537	−0.3109	−0.0141	0.0014
C_4–2p_y	0.3291	−0.0074	−0.0048	−0.6175	−0.0070
C_1–2p_z	−0.4618	−0.0376	−0.0011	0.0285	−0.0377
C_2–2p_z	−0.0312	−0.0379	−0.0018	0.0038	−0.5030
C_3–2p_z	−0.0312	−0.5031	−0.0018	0.0038	−0.0379
C_4–2p_z	0.4797	−0.0143	−0.0155	0.0303	−0.0151
H_1–1s	−0.0021	−0.0005	0.0006	0.0298	−0.0015
H_2–1s	−0.0096	−0.0080	−0.0022	−0.6617	−0.0080
H_3–1s	0.0001	−0.0296	0.0231	0.0235	−0.0296
H_4–1s	0.0248	0.0292	−0.0095	−0.0041	−0.6823
H_5–1s	−0.0272	−0.0316	−0.0068	0.0061	0.0134
H_6–1s	0.0248	−0.6823	−0.0096	−0.0041	0.0293
H_7–1s	−0.0271	0.0135	−0.0068	0.0061	−0.0315

[a] Each LO is shown in a column; the leftmost column contains the atomic orbital labels, while the bonds represented by each orbital are specified in the top row. The numbering of the atoms is that of Table I: the plane of symmetry is the *yz* plane, and the C_3–C_2 vector is parallel to the *x* axis, in the coordinate system fixing the orientation of the p orbitals.

intermediate on its way to the cyclobutyl ion.[20] The LO's in Figure 4a of cyclopropylcarbinyl ion show a substantial interaction between C_2 and C_3, and equivalently (due to the existence of the plane of symmetry) a like interaction between C_2 and C_4. An intuitively reasonable motion of C_2 is the bend toward (say) C_3, strengthening the partial C_2–C_3 bond while concomitantly weakening the partial C_2–C_4 bond. The result of this motion is the bicyclobutonium ion shown in Figure 4b. The cross-ring (C_1–C_3) binding accounts for the "bicyclo" label. Note that the hydrogen at the formally charged carbon naturally assumes the axial position (the term referring to the eventual cyclobutyl ring, in the bent form). The axial conformation of this CH bond is associated with a stable cyclobutyl ion by ample experimental evidence.[21] As the bicyclobutyl ion is bent toward a planar form, the local orbitals pass into those of the planar cyclobutyl ion, and cross-ring bonding vanishes. This account of the cyclopropylcarbinyl–cyclobutyl rearrangement is in complete accord with the conclusions of Wiberg and Szeimes,[16] who made extensive CNDO calculations with a parametrization obtained by fitting the energies of simple hydrocarbons, and found the route outlined above to be much lower in energy than alternate paths. The barrier was estimated as *ca.* 0.02 au, opposed to values in excess of 0.22 for other apparently plausible paths.

The Outplane Cyclopropylcarbinyl Ion. The CNDO energies obtained with the Pople parametrization (Table III) present a complex picture. The outplane cyclopropylcarbinyl ion evidently prefers a geometry in which the four carbons are coplanar: the molecule

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[20] K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 3773 (1964); **87**, 1331 (1965).

[21] K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, 1273 (1963); K. B. Wiberg and B. A. Hess, Jr., *J. Am. Chem. Soc.*, **89**, 3015 (1967).

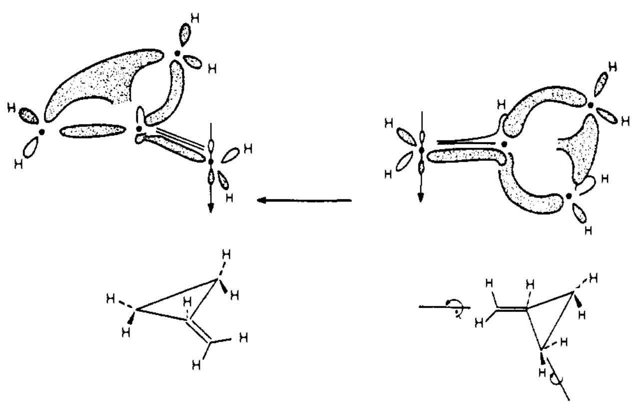

Figure 5. A symmetry-allowed conrotatory motion of the *exo-* and a ring methylene leads to a pseudorotation of the protonated alkene shown. The disrotatory motion forms a node between C_1 and C_2, resulting in a net bond breaking, and is energetically prohibited as a concerted thermal process.

in this form is essentially a protonated alkene. This molecule is not easily interconvertible with the inplane species. The rotation of the *exo*-methylene relative to the ring encounters a considerable barrier: *ca.* 0.038 au in the planar form and a surprising 0.207 au in the bent form. This value is reduced to 0.027 au (17 kcal/mole) in the bent species if the Wiberg parametrization is chosen. Whether the Wiberg parametrization, which is determined so that the energy of normal alkenes is matched in CNDO computation, is preferable in a crowded, charged system to the Pople parametrization, which was chosen so that SCF wave functions of diatomic molecules would be matched, is not clear. We believe that considerations of the charge distribution, which are the basis for the analyses in this paper, should be less sensitive to the parametrization than are decisions based on variations in the total energy of less than 0.5%.

Table III. Energies of C_4H_7 Species[a]

Species	Pople parameters	Wiberg parameters
syn-Allylcarbinyl cation	−33.0106	
anti-Allylcarbinyl cation	−33.1038	
Bent "inplane" cyclopropylcarbinyl cation	−33.3429	−31.9491
Planar "inplane" cyclopropylcarbinyl cation	−33.2476	
Bent "outplane" cyclopropylcarbinyl cation	−33.1363	−31.9220
Planar "outplane" cyclopropylcarbinyl cation	−33.2853	
Planar cyclobutyl cation	−33.3884	
Bent cyclobutyl cation (60° dihedral angle)	−33.3449	−32.0523
C_{3v}-symmetric C_4H_7	−32.8147	

[a] The total energies, relative to isolated cores and valence electrons, are given, in atomic units, in the Pople parametrization of the Pople–Segal CNDO–MO theory. For some species the energies obtained by the Wiberg parametrization of the theory are available. The discrepancies are discussed in the text.

Examination of the local orbitals for outplane cyclopropylcarbinyl cation represented in Figure 5 suggests the possibility of an unusual motion of the species. If the *exo*-methylene is rotated out of the molecular plane, a concerted conrotatory motion of one of the ring methylenes is allowed. The motion of the *exo*-methylene allows the negative lobe of the formally vacant p orbital to interact with the negatively signed CC bond orbital. Simultaneously a p orbital on the moving ring methylene is brought up out of the plane to interact with the center carbon's p–π orbital. The ring C–C bond which is apparently broken by the latter motion merely shifts part of its charge to the central carbon: there was considerable delocalization of that C–C bond to the central carbon already. As Figure 5 indicates, the net effect of this motion is a pseudorotation of the planar cyclopropylcarbinyl ion. While an extensive study of the energy surface for this motion is advisable before unequivocal conclusions may be made, this pseudorotation is at least an allowed process, which may help account for the extensive isotopic scrambling observed in the $C_4H_7^+$ system.

VI. Delocalization in the $C_4H_7^+$ System

The $C_4H_7^+$ system embraces a variety of kinds of carbonium ions. As we shall see, one finds primary and secondary classical ions and three- and four-center nonclassical ions. Delocalization alone is apparently not a simple guide to stability, at least in nonequilibrium geometries.

In our nomenclature, a classical carbonium ion may possess substantial delocalization, but this is largely attributable to hyperconjugation with α-CH bonds.[22] The bond indices for *anti*-allylcarbinyl cation (Table I) and the local orbitals show that the only LO's not completely identifiable with two-center bonds are the α-CH bonds. The sums of the bond indices appropriate to the valence-bond structure shown in Table I (21.07) falls short of accounting for the total active charge (22.19) by 1.12 units of charge. This localization defect is probably typical of the primary carbonium ion, since the ethylene fragment is highly localized. That portion of the molecule could be replaced by any highly localizable group without great impact on the localization defect.

When the *anti*-allylcarbinyl cation is rotated to the *syn* form, the hyperconjugative delocalization increases; the π bond index of the C_3–C_4 bond grows from 0.20 to 0.40. Simultaneously the cross-ring binding which is characteristic of the incipient bent cyclobutyl ion becomes noticeable: $W(C_1–C_4)$ becomes 0.035. The C_1–C_3 bond is weakened by a like amount, and, given the background of previous sections, it appears that the *syn*-allylcarbinyl ion can rearrange to the bent cyclobutyl ion. The increase in localization defect, from 1.12 to 1.92, is associated with a rather large *de*stabilization (0.09 au) which casts doubt on the notion that delocalization is always associated with stabilization.

According to the bond indices and local orbitals, the planar cyclobutyl ion is classical,[23] the delocalization being due to hyperconjugative interaction of the formally vacant p orbital at the charged carbon with the four α-CH bonds. The localization defect does not double upon passage from a primary to a secondary carbonium ion, as does the number of α-hydrogens. Rather it increases by *ca.* 50% as the number of anti-

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[22] This usage is parallel to the view of Davis and Ohno, ref 18.

[23] This result agrees with conclusions of Davis and Ohno,[18] and K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

symmetric combinations increases from two [p, ($s_a - s_b$)] to three [p, ($s_a - s_b$), and ($s_a' - s_b'$)]. Here s_a represents the CH_a bond orbital, and the added α-CH bonds in the cyclobutyl ion are primed.

The cyclopropylcarbinyl system exhibits widely varying localization as the geometry is altered. Consider first the planar outplane protonated alkene. The localization defect is 2.10 and is primarily due to the considerable remaining double-bond character in the C_1–O_2 bond, and the interaction with the cyclopropyl ring, which has considerable π character. The only bonds which are strictly confined to two centers are the CH bonds, excepting the loosely bound added proton H_7. All the other bond orbitals contain coefficients from third and sometimes fourth centers exceeding 0.05 in absolute value. (The number 0.05 is an arbitrary choice, but suggests that the contribution to the local orbital from these "off bond" atomic orbitals cannot be neglected.)

The bent outplane cyclopropylcarbinyl ion has far less delocalization: the defect is 1.61, comparable to that of the classical secondary planar cyclobutyl ion. The bent species is formally a primary ion, so the ring still stabilizes the ion somewhat. Even with the considerable strain of the three-membered ring, this compound is comparable in stability with *anti*-allylcarbinyl cation. It is, of course, far less stable than the planar species.

The slightly distorted pyramidal $C_4H_7^+$ ion is a rather special system. In this obviously nonclassical ion, with a three-center bond in the base of the pyramid, we expect substantial delocalization. However, the localization defect relative to a strongly bent inplane cyclopropylcarbinyl valence-bond structure is only 1.36 units. If we subtract the portion of the defect due to the three-center bond, the remaining defect is 1.13, that of a classical primary ion. The instability of primary carbonium ions apparently overshadows the feeble three-center bonding, and accounts for the high energy of this ion.

Stable bent inplane cyclopropylcarbinyl cation is substantially delocalized, having a defect of 1.74 units. Clearly the ring has stabilized the formally primary ion by delocalization greater than that made possible by hyperconjugation in planar cyclobutyl ion. Bending this ion so that the four carbons are coplanar *increases* the localization defect slightly from 1.74 to 1.82, mainly by weakening the C_1–H bond. The molecule may be considered a protonated alkene, but the alkene is twisted; evidently this is an excited state of the alkene.

The bicyclobutyl cation remains to be considered. Two valence-bond structures could be drawn for this geometry. In the first, a proton has approached one of the bridgehead carbons. However, the very strong CH bonding at that point and (CH bond index = 0.93) the rather weak cross-ring bonding in this geometry (0.13) indicate that such a structure gives a poor account of the system. A preferable alternative is a bent cyclobutyl ion. Even in this representation the localization defect is large, 2.12 compared with the value of 1.59 for the classical planar cyclobutyl ion. The CNDO energies of these two species indicate that the planar ion is more stable. The opposite prediction might be made on the basis of this analysis of the charge distribution.[24] This situation also makes apparent the necessity for care in interpreting delocalization as a stabilizing influence.[25]

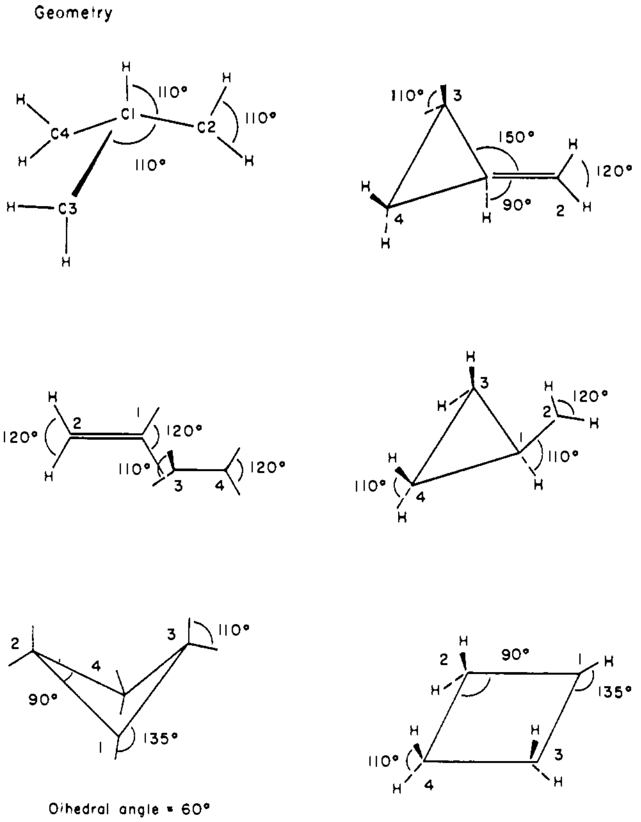

Figure 6. The geometry of some of the species discussed in the text is shown. Rather idealized geometries are assumed with all C–C bond distances equal to 1.5 Å except for the C_1C_2 bond length in allylcarbinyl ion equal to 135 Å and all bond CH lengths equal to 1.08 Å.

Summary and Conclusions

The contours and signs of localized molecular orbitals provide a guide to prediction of allowed nuclear motion, parallel to the methods of Hoffmann and Woodward. Although every prediction made in the local orbital analysis could be obtained by the Hoffmann–Woodward approach, the local orbital theory has certain definite advantages. Generally it is easier to correlate functions confined to a small region of a molecule, with single associated signs, than to correlate functions spread throughout a large molecule, with complicated alternations in sign. The changes in local orbitals as the geometry of a molecule is altered are easy to anticipate, since local orbitals often follow the nuclear motion with only slight modification. These advantages become most apparent in large asymmetric systems. In large systems, the orbital localization focuses attention on the critical but usually small regions where bonds are made or broken. In asymmetric systems, it becomes difficult to classify the molecular orbitals, and thus to establish their cor-

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(24) The Wiberg parametrization of the CNDO theory specifically for hydrocarbons leads to the prediction that the bent cyclobutyl ion is more stable than the planar form, and that there is appreciable cross-ring binding in the bent form.

(25) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 140; reprinted in" Nonclassical Ions," P. D. Bartlett, Ed., W. A. Benjamin, Inc., New York, N. Y., 1965, p 438.

relations. The local orbital method is not hampered by this problem; local symmetry is fully utilized when available but is not required.

Most of these points are illustrated in the reported study of the $C_4H_7^+$ system. Many conclusions on the properties of this system wrested from experimental data or extensive computation are reproduced by inspection of the signs and contours of the local orbitals. We find that the pyramidal $C_4H_7^+$ ion must relax to the inplane cyclopropylcarbinyl ion. The cation can achieve a "bicyclobutyl" configuration in which the CH bond at the formally charged carbon is in the axial orientation requisite to a stable cyclobutyl cation. The bicyclobutyl cation passes directly to a bent cyclobutyl ion which does not have a high barrier to inversion.

The outplane cyclopropylcarbinyl ion relaxes into a planar species, which is essentially a protonated alkene. A remarkable pseudorotation of this species is brought about by a concerted conrotatory motion of the *exo*- and a ring methylene.

A side product of the local orbital analysis is a detailed description of delocalization; this is of particular interest in the $C_4H_7^+$ system, in which the classical character has been the subject of some discussion.

The planar cyclobutyl ion is classical, the delocalization being largely due to hyperconjugative interaction of CH bonds with the "vacant" p orbital at the formally charged carbon. The bent cyclobutyl ion has considerable cross-ring bonding, and very large delocalization, perhaps because it is close to the transition state for the cyclopropylcarbinyl–cyclobutyl interconversion.

The *anti*-allylcarbinyl ion is also classical. As the molecule is rotated to the *syn* form, a geometry close to the transition state for the allylcarbinyl–cyclobutyl rearrangement, a dramatic increase in the delocalization is observed.

Distortion of the cyclopropylcarbinyl ion to a symmetric pyramidal form diminished delocalization: bending of the former species so that the carbons are coplanar increases the delocalization slightly. The stable cyclopropylcarbinyl ion must be considered nonclassical; although formally a primary ion, its localization defect exceeds that of a classical secondary ion due to the interaction of the p orbital at the charged carbon with the ring.

Acknowledgments. Our indebtedness to Professor Kenneth B. Wiberg is great. We thank him for supplying a preprint of his review of the chemistry of the allylcarbinyl–cyclopropylcarbinyl–cyclobutyl cation system, for stimulating discussion, and for reading the manuscript. Thanks go to Gunter Szeimes for discussion of his extensive CNDO calculations on this system. This work was supported by the National Science Foundation and the Alfred P. Sloan Foundation.