π system, there are also interactions present in the σ system which favor a pyramidal heteroatom, i.e., a nonplanar geometry. In pyrrole, these σ interactions are small and the geometry is determined by the aromaticity in the π system. However, in phosphole these σ interactions are larger and dictate a nonplanar geometry as a compromise.[26] We conclude that the nonplanar geometry of phosphole is due to σ interactions and not to a lack of aromaticity of the π system, as has been suggested by Palmer.[27,28]

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(19) The values of $S(C(6)-P)$ and $S(C(6)-N)$ have been calculated for the optimized geometries of $^+CH_2PH_2$ and $^+CH_2NH_2$, respectively. F. Bernardi and N. D. Epiotis, submitted for publication.
(20) The AO overlap integrals have been obtained for the optimized geometries of $^+CH_2PH_2$ and $^+CH_2NH_2$ (see ref 19). The orbital energies of the "lone pair" AO's were taken from photoelectron spectroscopy data of the model compounds NH_3 and PH_3. Finally, the oribtal energy of the e_{2u} MO of benzene was set equal to $-\epsilon_{1g} + \Delta E$, where ΔE is the HOMO − LUMO energy gap of benzene as calculated by the INDO method. The PE spectroscopic results were taken from the following references: (a) NH_3; G. R. Branton, D. C. Frost, F. G. Herring, CA. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, **3**, 581 (1969); (b) PH_3; G. R. Branton, D. C. Frost, C. A. McDowell, and I. A. Stenhouse, *ibid.*, **5**, 1 (1970); (c) benzene; L. Asbrink, E. Lindholm, and O. Edquist, *ibid.*, **5**, 609 (1970).
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Theoretical Approaches to Rearrangements in Carbocations. 3. The Homocyclopropenyl Cation[1]

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Abstract: The geometrical structures and relative energies of several isomeric forms of $C_4H_5^+$ have been investigated using single determinant ab initio molecular orbital theory. Of lowest energy is the methyl-substituted cyclopropenyl cation, which displays the enhanced stability of the aromatic 2π electron cyclic on which it is based. The homocyclopropenyl cation is much better depicted in terms of a cyclobutenyl-like geometry rather than that corresponding to a true bicyclic arrangement. As was the case for the related homoaromatic systems, the bicyclo[3.1.0]hexenyl and homotropylium ions, the homocyclopropenyl cation is predicted by the calculations to readily undergo degenerate circumambulatory rearrangement. Only this time does rearrangement proceed in a Woodward–Hoffmann forbidden manner, the explanation for which is given in terms of the control of the migration process by an orbital subjacent to the highest occupied. The effects of substituents, both on the geometrical structure of the homocyclopropenyl cation and the energetics of its degenerate rearrangement are briefly considered.

Introduction

There has been intense interest in recent years in detecting and, if possible, characterizing molecules which are expected to show either exceptional stability because of aromatic conjugation or lability due to their incorporation of cyclic antiaromatic arrays. The characterization of the aromatic 2π electron cyclopropenyl cation is an example of the former;[3] the

quest for cyclobutadiene, the latter.[4] One set of molecular species which are especially fascinating in this regard are those in which the cyclic aromatic array has been interrupted in one or more places by alkyl chains. A number of these so termed homoaromatic and homoantiaromatic arrangements have already been observed experimentally.[5] Among the better characterized are included the 6π electron homotropylium ion

and the 4π system, bicyclo[3.1.0]hexenyl cation. Although the simplest possible member of this series of ions, the 2π electron homocyclopropenium cation, was the first to be depicted as a possible homoaromatic, it was not until many years after the initial solvolysis experiments of Roberts and Applequist[6] that even highly substituted derivatives of the system were actually observed as stable species. The NMR spectrum of the parent homocyclopropenium ion itself has only been reported in the last year.[7]

In the present paper, we continue our theoretical investigations into the nature of homoaromatic stabilization and into the structure of homoconjugated molecules[1b] by now focusing attention on the homocyclopropenyl cation. As in our previous studies, we shall make use of simple levels of ab initio molecular orbital theory. Our primary concern here will be a characterization, as far as is possible, of the geometrical and electronic structures of the homocyclopropenyl cation and in the elucidation of any pathways by which it might undergo rearrangement. We shall also be interested in describing what effects simple substituents have upon the structural and energetic properties of the ion. In so doing not only should we be able to probe the distribution of charge in the homoaromatic ion, but also we should be placed in a favorable position to construct substituted systems which might behave in predetermined manners.

Quantum Mechanical Methods

Standard single-determinant molecular orbital theory has been used throughout. As in our previous works we have employed the STO-3G minimal basis set[8] for the optimization of molecular equilibrium geometry. Our results are to be found in Figure 1. A single calculation was then performed at this "best" STO-3G geometry using the split-valence-shell 4-31G basis.[9] This is in order that we be able to more accurately assess the relative energies of the individual isomers. We have also performed additional calculations on the cyclobutenyl cation for values of the ring puckering angle other than that reported as optimum. The individual geometries here have been optimized at the STO-3G level much in the same manner as those for equilibrium structures. Only the ring puckering angle was kept fixed. Here, we have attempted to provide a potential curve for ring flipping in parent cyclobutenyl system in order that we might investigate the effects of simple substitutents on the geometry of the ion. Thus, single point STO-3G calculations have been carried out along this potential for various placements of standard model[10] methyl and phenyl substituents. These have been attached at the same angles as the hydrogens which they replaced and at connecting bond lengths of 1.50 and 1.40 Å, respectively. We have also performed a number of individual STO-3G calculations on a variety of methyl- and phenyl-substituted cyclopropenylcarbinyl cations. Our purpose here was to investigate the effects of these substituents on barrier to degenerate circumambulation in the cyclobutenyl cation and on the potential-hindering methylene rotation in the cyclopropenylcarbinyl transition state. Geometries were constructed as before. All energetic data are to be found in Table I.

The calculations we report in this paper were all carried out using the GAUSSIAN 70 series of computer programs.[11]

Discussion of Results

Of the forms of $C_4H_5^+$ which we have investigated theoretically, the methylcyclopropenyl cation(I) is the most stable, not at all surprising in view of its incorporation of an aromatic 2π electron cycle. The geometrical structure of this ion has not been fully optimized at the STO-3G level. Rather, a "standard" methyl group[10] (tetrahedral, $r_{CH} = 1.09$ Å) has replaced one of the hydrogens in the theoretical equilibrium structure
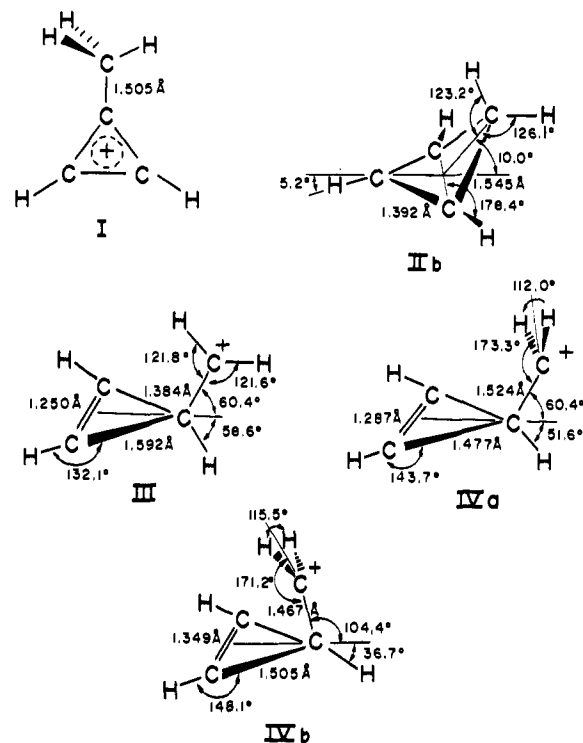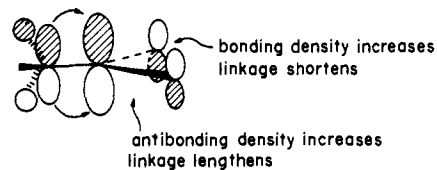

Figure 1. Theoretical (STO-3G) equilibrium geometries. Except for methylcyclopropenyl cation, all C–H bond lengths set at 1.10 Å. The calculated structure for the methylcyclopropenyl cation assumes a standard model CH_3 group attached to the theoretical equilibrium geometry of cyclic $C_3H_3^+$. Only the connecting bond length has been optimized.
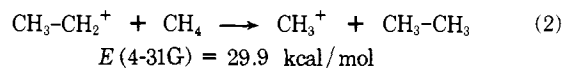
of parent $C_3H_3^+$,[12] the connecting linkage being optimized by STO-3G to a value of 1.505 Å. We expect that a fuller optimization of geometry would reveal a tendency for the small ring to adopt a structure in which two of its bonds have elongated and the other shortened, a consequence of charge transfer from the highest occupied molecular orbital on the methyl into the lowest empty (π symmetry) function associated with the three-membered ring. Stabilization due to methyl

bonding density increases
linkage shortens

antibonding density increases
linkage lengthens

substitution granted to the cyclopropenyl system, as measured by the energy of the *isodesmic*[13] process (1), is significantly

$$\Delta E\,(4\text{-}31G) = 18.4\ \text{kcal/mol}$$
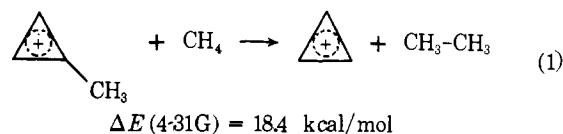
less than that afforded to a bare carbonium center (2), indicative of the delocalization of charge away from a single site.

$$CH_3\text{-}CH_2^+ + CH_4 \longrightarrow CH_3^+ + CH_3\text{-}CH_3 \qquad (2)$$
$$E\,(4\text{-}31G) = 29.9\ \text{kcal/mol}$$

Perhaps the most curious of the $C_4H_5^+$ isomers is the homocyclopropenyl cation (II), a molecule which presents us with

Table I. Theoretical Energy Data
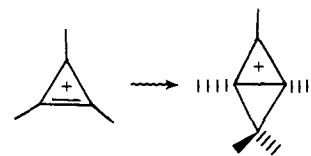
| Molecule		STO-3G E, hartrees	4-31G E, hartrees
Methylcyclopropenyl (I)		−152.23019	−153.81896
Cyclobutenyl (IIb)	0°	−152.20665	−153.79510
	10°	−152.20726	−153.79574
	30°	−152.20473	−153.79374
	50°	−152.17991	−153.76875
Bisected cyclopropenylcarbinyl (III)		−152.13722	−153.75315
Eclipsed cyclopropenylcarbinyl (IVa)		−152.09251	−153.70063
Eclipsed cyclopropenylcarbinyl (IVb)		−152.10123	−153.69285
2-Methylcyclobutenyl (V)	0°	−190.80144	
	10°	−190.80245	
	30°	−190.80161	
	50°	−190.77960	
2-Phenylcyclobutenyl (VI)	0°	−378.97414	
	10°	−378.97540	
	30°	−378.97658	
	50°	−378.95889	
4,4′-Dimethylcyclobutenyl (VII)	0°	−229.37775	
	10°	−229.37839	
	30°	−229.37612	
	50°	−229.35082	
Bisected 4,4′-dimethylcyclopropenylcarbinyl (VIII)		−229.34018	
Eclipsed 4′,4′-dimethylcyclopropenylcarbinyl (IXa)		−229.31803	
Eclipsed 4′,4′-dimethylcyclopropenylcarbinyl (IXb)		−229.27109	

the possibility of a 2π electron homoaromatic arrangement. Here, one might consider such a system to be constructed by replacement of the formal double bond in the cyclopropenyl cation by a cyclopropane moiety, the logic behind such a move being easily suggested by the overall similarity between the highest filled π and lowest empty π^* orbitals on an unsaturated linkage (A, B) to the occupied valence pair of (Walsh) orbitals
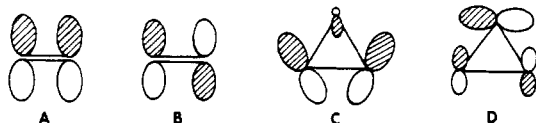

on the small ring (C, D).[14] Two extreme geometrical structures may result from such a substitution. The first, one in which the integrity of the cyclopropane ring has largely been maintained, might properly be termed a bicyclobutyl cation (IIa). The

bicyclobutyl cation   cyclobutenyl cation

IIa   IIb
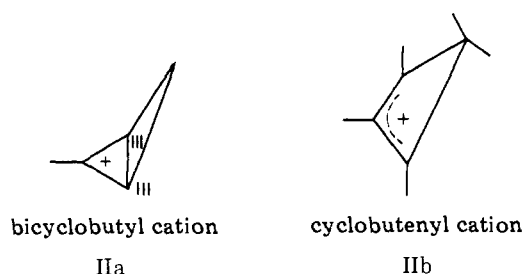
other, where the ring-fused bond has opened, would be better described as a cyclobutenyl cation, IIb. One might anticipate that any equilibrium between these two forms
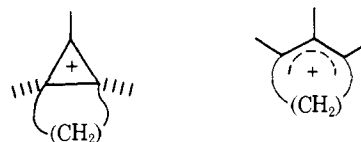
IIa $\rightleftharpoons$ IIb
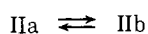
would be very much the same as the equilibrium between the cyclopropyl and allyl cations, the only difference being the
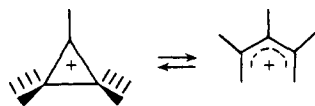

constraint that the two termini are tied together by a single methylene group (see structures below).

Pople and co-workers have carefully explored the $C_3H_5^+$ surface,[15] and in particular the equilibrium between the allyl
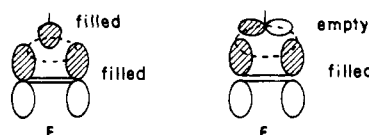

and cyclopropyl cations. They report that the cyclopropyl system is unstable with respect to disrotatory ring opening in the direction of the allyl cation. One can easily see the reason behind the instability here. Consider the cyclopropyl cation to be formed as a result of interaction of ethylene with a $C-H^+$ fragment. The important terms involved in such an interaction
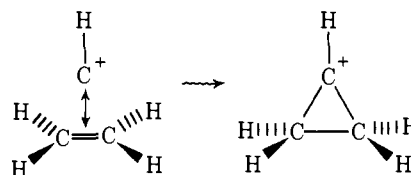
are given in Figure 2. Term 1 between the highest (doubly) occupied molecular orbitals on each of the ethylene and CH^+ fragments involves a total of four electrons, and hence is repulsive. Although terms 2 and 3 are two-electron interactions, to a first approximation they do not lead to energetic stabilization because of zero overlap between the component fragments. Overlap between the two lowest empty molecular orbitals (interaction 4), while allowed on symmetry grounds, leads neither to energetic stabilization or destabilization. This is simply because no electrons are involved.

An alternative, but completely equivalent, manner in which to visualize the unfavorable energetic situation here is to consider the nature of the orbital arrangement in the resulting complex between $C-H^+$ and ethylene. One might think of it as either a four-electron Huckel cycle (E) or an equally unfa-


vorable two-electron Mobius arrangement arrangement (F).[16]

In either representation the cyclopropyl cation stands out as an antiaromatic system.

In light of Pople's observations on the allyl–cyclopropyl equilibrium, it is not surprising that we find only a single potential minima on the $C_4H_5^+$ surface corresponding to a four-membered ring, and that this structure resembles far more closely what we would call a cyclobutenyl cation (IIb), in which the ring-fused bond has opened, than a bicyclobutyl form (IIa), in which this linkage remains closed. Thus, the theoretical (STO-3G) structure which we report for the $C_4H_5^+$ homoaromatic is one in which the four-membered ring deviates only slightly from planarity (an angle of 10° between the pair of three-membered rings is calculated) and one in which the "ring-fused" linkage has elongated to 1.99 Å. Inversion through an ion with a wholly planar carbon skeleton is predicted at the 4-31G level to require only 0.4 kcal/mol.

It is easy to see why it is that the cyclobutenyl cation would not wish to adopt a wholly planar carbon skeleton. Consider the system to be formed as a result of association of an allyl cation and methylene. Here, if all four centers lie in a common plane, then the potentially stabilizing two-electron interaction between the lowest unoccupied allyl cation molecular orbital and the filled p-orbital symmetry function at methylene is zero for lack of overlap. Raising the methylene center slightly from the plane of the other three carbons breaks the symmetry constraint, thus allowing stabilization to occur.

in - plane
overlap zero

out - of - plane
overlap finite
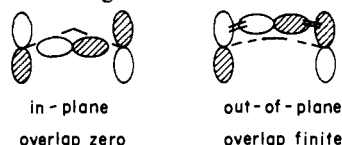
There are at least two published crystal structures of substituted cyclobutenyl cations. That of a tetramethyl derivative[17a] (complexed to $AlCl_3^-$) shows ring bond lengths which are almost identical with those suggested by the calculation, but a carbon skeleton which is puckered to a greater extent. A structure of the chloride salt of the tetraphenylcyclobutenyl cation shows, on the other hand, a planar ring skeleton.[17b]

angle between ring planes = 31.5°
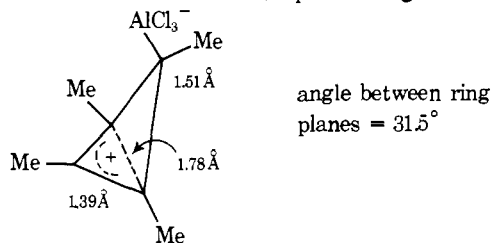
The ^{13}C and ^1H NMR spectra of parent $C_4H_5^+$, as well as a number of its simple derivatives, have recently been reported by Olah and co-workers.[7] Here, under conditions of long life in super-acid media, the ion has been established to have a puckered carbon skeleton and to undergo what appears to be ring inversion through a planar arrangement, with a barrier of 8.4 kcal/mol.

What is even more disturbing than the lack of agreement between the calculated and experimental barriers to ring inversion are a series of NMR spectral observations which Olah and co-workers have made on the parent and methyl- and phenyl-substituted homocyclopropenyl cations. Whereas the ^{13}C chemical shifts of such species
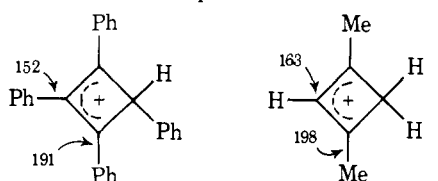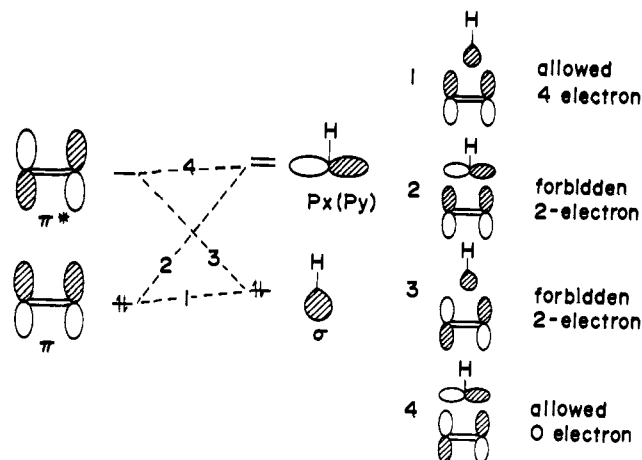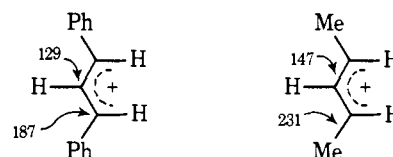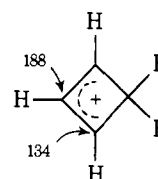
parts per million relative to Me_4Si (ref 7b)

Figure 2. Interaction of the valence orbitals of CH^+ with those of a double bond leads to the formation of the cyclopropyl cation.

closely parallel those in the analogous allyl cations

parts per million relative to Me_4Si (ref 18)

those in the parent system do not.

parts per million relative to Me_4Si (ref 7b)

Olah interprets his NMR data as evidence for a structure of $C_4H_5^+$, which is fundamentally different from one based on allyl cation, and in particular one in which there is significant 1,3-bonding.
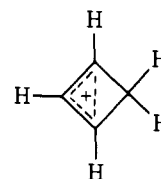
This is seemingly in contrast to the theoretical (STO-3G) structure for parent cyclobutenyl ion, which incorporates a nearly "normal" allylic moiety (at least as far as carbon–carbon bond lengths are concerned). The STO-3G calculated π

1.392Å   1.385 Å
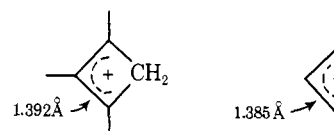
charges for both planar and puckered forms of the cyclobutenyl system are also markedly similar to those of the allyl cation. That is to say, the positions adjacent to the methylene carbon

-0.025   -0.012   -0.020
+0.510   +0.463   +0.510
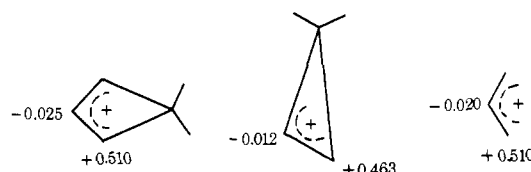
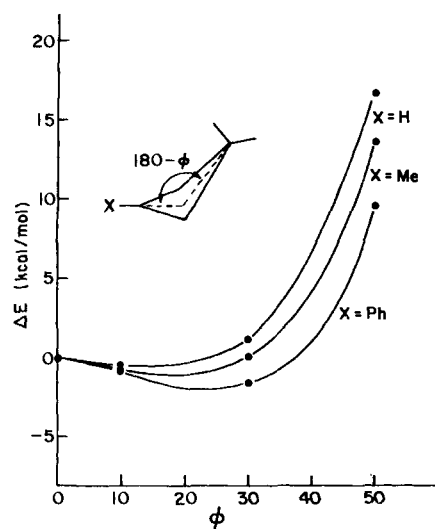in the two ring systems are positively charged, while that op-

Figure 3. Theoretical (STO-3G) potentials for ring puckering in cyclobutenyl cation and its (2-substituted) methyl and phenyl derivatives.

posite to it is actually slightly negative. Although the detailed pattern of charge localization which characterizes the allyl system is most closely mimicked by the planar cyclobutenyl cation, ring puckering does not seem to cause major disruptions. We strongly suspect that even for puckering angles two or three times larger than that predicted by the STO-3G method, the cyclobutenyl systems will exhibit charge distributions reminiscent of the allyl cation.[19] If, then, one is willing to accept the notion of a gross parallel between ^{13}C chemical shifts and molecular charges,[20] one is forced to admit that the theoretical calculations are in fundamental disaccord with Olah's NMR data. Perhaps we are indeed witnessing a breakdown of the assumed shift–charge relationship, or perhaps the ion's geometrical and electronic structure is actually being altered by the presence of the super-acid media. Possibly instead, the quantitative molecular orbital calculations have failed to properly describe the gross structure of the cyclobutenyl cation. With regard to this last point, it is quite conceivable that the ab initio STO-3G calculations have seriously underestimated the degree to which the cyclobutenyl cation is actually puckered. Thus, the theory's assignment for the deviation from planarity of the carbon skeleton in cyclobutane (6.9° at the STO-3G level) is only about a fourth of what is observed experimentally.[21] Also the barrier to ring inversion in cyclobutane (0.1 kcal/mol using the 4-31G basis set at optimum STO-3G geometries) is more than an order of magnitude below the experimental value of 1.28 kcal/mol. Despite this failing of the theoretical method with regard to the degree to which the ground state $C_4H_5^+$ ion is actually puckered, we suspect that gross features of our calculated cyclobutenyl cation structure such as the carbon–carbon bond lengths will stand up to further scrutiny.[22] Further investigation is necessary, both into the nature of the assumed charge–shift relationships and into the possible role of the solvent on the equilibrium structure of the ion.

In addition to their studies on the parent $C_3H_5^+$ systems, Radom, Pople, and Schleyer have observed that the energy difference between the allyl and cyclopropyl cations may be significantly reduced by substitution.[23] For example, a single methyl group at the 2 position reduces the separation between the two by more than half, from 39.2 kcal/mol in the parent ions to 18.8 kcal/mol for the substituted systems. Substitution by strong π donor σ acceptor groups such as amino or hydroxy is actually predicted by the calculations to lead to a reversal in the energies of the isomeric cations, making the small-ring compound the more stable. It is interesting, then, to see what effects, if any, substituents might have on the structure of the

cyclobutenyl cation. Toward this goal we have taken two steps. First we have traced a one dimensional potential corresponding to the motion of ring puckering required to go between the open, cyclobutenyl, and closed, bicyclobutyl, cations. This has been accomplished by complete optimization of geometrical structure subject only to the constraint that the puckering angle, φ, is held fixed. The results, displayed in Figure 3, show a single and shallow energy minimum around $\varphi = 10°$. (It should be commented that individual 4-31G calculated energies for the $\varphi = 0$, 10, 30, and 50° points are nearly superimposible on the STO-3G values.) Without further geometrical optimization we have next proceeded to replace the hydrogen at the 2 position in the cyclobutenyl cation by methyl and phenyl groups. The ring puckering potentials which result from such a substitution are also plotted in Figure 3. Paralleling the case with the allyl–cyclopropyl system, substitution by methyl leads to an increase in the degree to which the cyclobutenyl cation is puckered. Replacement of hydrogen by a phenyl group furthers this trend.

We have also investigated the effect of a pair of CH_3 substituents at the methylene carbon on the structure of the cyclobutenyl cation, and on its barrier to ring inversion. The potential which results is virtually identical with that for the unsubstituted ion.

Our initial interest in the homocyclopropenyl cation centered around the possibility of it undergoing degenerate stereospecific isomerization by way of circumambulation of the external methylene group around the base of the three-membered ring polyene. Recall that the corresponding migration process in
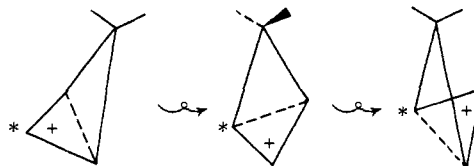
the 4π electron system, bicyclo[3.1.0]hexenyl cation, goes with stereochemical inversion at the methylene carbon;[24] that is to say, it proceeds through a bisected cyclopentadienylcarbinyl cation (X → XI → X) rather than an eclipsed one (X → XII → X). This is simply in order to maintain continuity of overlap
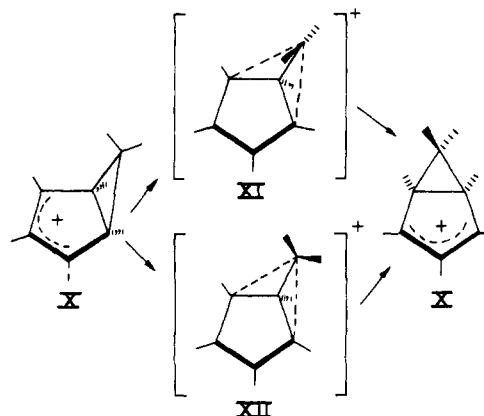

between the empty p lobe at the migrating methylene group and the highest occupied molecular orbital on the base polyene (G).[25] Migration with retention at methylene would necessitate
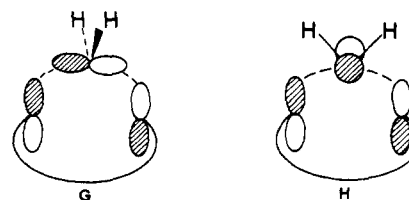

a break in overlap at one point along the way (H). The situation

is quite the opposite for the 6π electron homotropylium ion. Here the termini of the base polyene highest occupied molecular orbital are of the same sign. This time migration with inversion would be the symmetry forbidden processs, and that with retention the allowed (J, K). Although degenerate
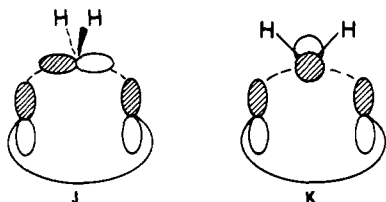

methylene circumambulation has never been experimentally observed in homotropylium,[26] theoretical ab initio calculations indicate[1b,27] a strong preference for the symmetry allowed mechanism (XIII → XV → XIII) over the forbidden (XIII → XIV → XIII).
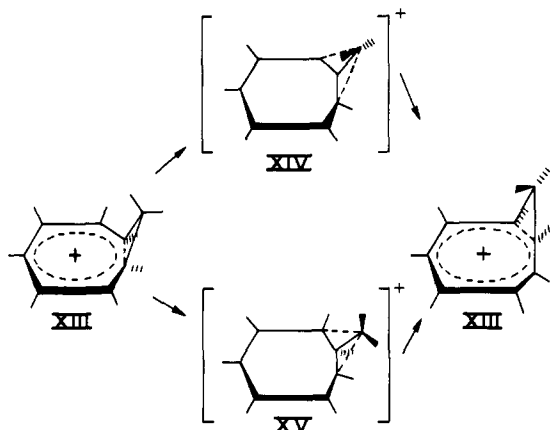
Migration of the methylene in $C_4H_5^+$, another $(4N + 2)\pi$ electron system, should follow the same pattern as in homotropylium. That is to say, progression through an eclipsed cyclopropenylcarbinyl cation should be the allowed process, as far as interaction between the empty lobe at methylene and the polyene HOMO goes, while passage via a bisected structure, the forbidden. The results of the ab initio calculations are,
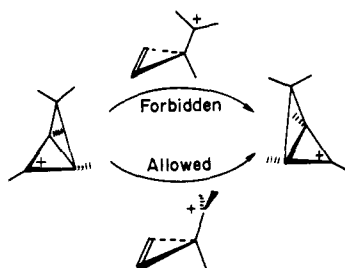

however, not in agreement with this simple notion. Indeed, at the 4-31G level, the bisected cyclopropenylcarbinyl cation is energetically favored over the corresponding eclipsed structure by more than 30 kcal/mol. To understand this apparent violation of orbital symmetry control, consider interaction of the vacant p lobe on the migrating methylene group with each member of the manifold of cyclopropene valence molecular orbitals, and not just the π symmetry highest occupied function to which we have limited our attention until now. Immediately below the highest occupied π is a pair of in-plane functions, intimately related to the degenerate set of Walsh orbitals on cyclopropane. Here the degeneracy is split in such a way as to place the symmetric member of the duo at the lower energy. This ordering of orbital energies is presumably due to the fact that one of the three linkages in the cyclopropene ring is shorter than the other two. Thus, the symmetric Walsh component, which is strongly bonding between a single pair of ring atoms,
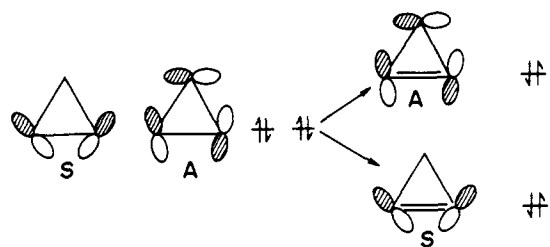

Cyclopropane   **Cyclopropene**

is lowered in energy, while the asymmetric member of the duo, which is antibonding between this same set of centers, is raised. So we must now contend with a situation where the migrating carbonium center may interact not only with the cyclopropene π system, but also with the pair of valence Walsh orbitals on the small ring. Thus, the Woodward–Hoffmann allowed eclipsed cyclopropenylcarbinyl transition-state structure is further stabilized by way of a two-electron interaction with the lower energy symmetric Walsh orbital. We would, however, expect this additional stabilization to be rather small, for not only are the interacting filled and empty orbitals far removed in energy, but overlap between them is minimal. The bisected cyclopropenylcarbinyl structure has only a single two-electron
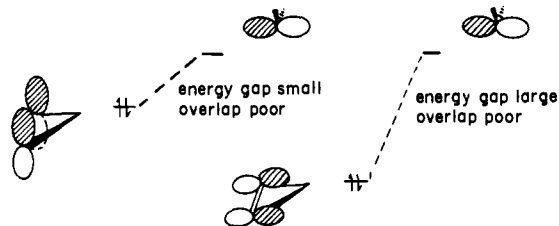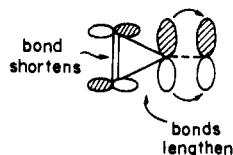

interaction available to provide energetic stabilization, that involving the antisymmetric, and higher energy, member of the Walsh pair. Although, on energy grounds alone, this term should not be as effective in stabilizing the carbonium center as that involving the small ring π system, on the basis of overlap considerations, it is far superior. That is to say, unlike the p–π interaction open to the system in its eclipsed geometry, this interaction involves overlap between two centers which are already connected by a σ linkage. We have, then, uncovered
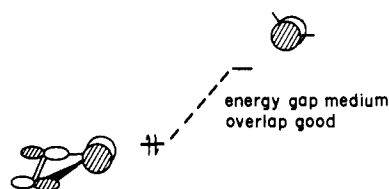

an extreme example of what has been termed *subjacent orbital control*;[28] a situation where, because of favorable overlap conditions, a molecular orbital beneath that which is highest occupied provides the dominant force dictating stereochemical control.

Our contention that the two-electron interaction between the carbonium center and the antisymmetric Walsh component is of far greater importance than that involving either the ring π system or the symmetric Walsh orbital may be further substantiated by careful scrutiny of the calculated STO-3G geometries of the bisected and eclipsed cyclopropenylcarbinyl cations. Two-electron interaction between the carbonium center and the antisymmetric Walsh component present in bisected cyclopropenylcarbinyl results in charge transfer away from the small ring and into the linkage connecting the two fragments. As a direct consequence, bonding electron density is removed from two of the small ring's linkages, resulting in their lengthening (from 1.49 Å in cyclopropene at the STO-3G level[29] to 1.59 Å in the ion). In addition, the charge withdrawal leads to a lessening of the antibonding character of the re-

maining cyclopropene linkage. It actually shortens in response (to 1.25 Å in bisected cyclopropenylcarbinyl down from 1.28 Å in the cyclic alkene). Interaction of the positively charged center in its eclipsed arrangement with either the cyclopropene π orbital or its symmetric Walsh component leads to a lengthening of just one of the small ring's linkages. Such a
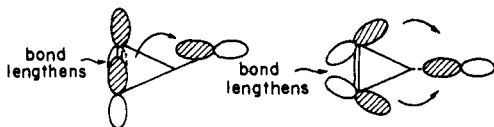
distortion is indeed observed in the geometrical structure of the eclipsed cyclopropenylcarbinyl cation, though its magnitude is far smaller than the effects noted in the bisected system (the ring C=C bond length in eclipsed cyclopropenylcarbinyl is 1.29 Å, only 0.01 Å longer than that for cyclopropene itself). Further indication of the difference in strengths between the two-electron interactions possible for the bisected and eclipsed conformations of cyclopropenylcarbinyl may be seen in the theoretical values for the lengths of the bonds connecting the small ring to the carbonium center. Thus the ring–carbonium center bond in bisected cyclopropenylcarbinyl is very much shorter than that in, say, methylcyclopropane (1.38 vs. ≃1.52 Å), while that in the eclipsed conformer (1.52 Å) is little different. It might be commented that the geometrical distortions observed in these two systems closely parallel those already noted for interaction of a carbonium center with the saturated cyclopropane ring.[30] Indeed, even the magnitude of the effects in the two sets of systems is nearly identical.

The form of eclipsed cyclopropenylcarbinyl which we have hitherto discussed is one whose geometrical structure is related to that of the bisected ion by a 90° twist at the methylene center. In terms of its highest occupied molecular orbital it may be depicted as (L). There exists the possibility of a second energy minima on the $C_4H_5^+$ potential surface which might also be said to correspond to eclipsed cyclopropenylcarbinyl. The ring–carbonium center bond in this species (IVb) has bent up
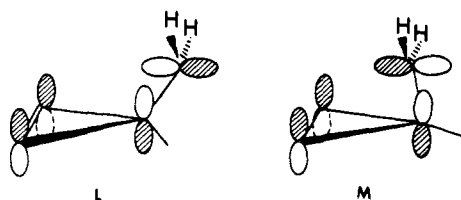
so that now it is nearly orthogonal to the plane of the three-membered cycle. In so doing, interaction between the vacant p lobe at C^+ and the cyclopropene π system has been considerably enhanced (M). According to the theoretical STO-3G calculations, this second "closed" form of eclipsed cyclopropenylcarbinyl is a separate entity from the "open" structure (IVa), and actually slightly (5.5 kcal/mol) the lower in energy. A barrier (IVb → IVa) of slightly more than a half a kcal/mol is predicted between the two structures. Calculations using the split-valence shell 4-31G basis suggest, however, that this is not the case and that only a single potential minima for cyclopropenylcarbinyl, the open structure (IVa), actually exists.

In the hope of further probing the electronic structure of the cyclobutenyl and cyclopropenylcarbinyl cations, we have carried out calculations in which both methylene hydrogens have been replaced by CH_3 groups. As before, the geometry of the methyls is as given by the standard model, and they are

Table II. Relative Energies of $C_4H_6^+$ Cations[a]

Comparison	Unsub-stituted	4,4'-Dimethyl-substituted
Cyclobutenyl/bisected cyclopropenylcarbinyl	26.7	6.7
Cyclobutenyl/open eclipsed cyclopropenylcarbinyl	59.7	25.6
Cyclobutenyl/closed eclipsed cyclopropenylcarbinyl	64.5	65.3
Bisected/open eclipsed cyclopropenylcarbinyl	33.0	18.8

[a] In kilocalories per mole at 4-31G level. Approximate 4-31G relative values for dimethyl-substituted systems obtained by combining the STO-3G energies for *isodesmic* processes: VII + III → II + VIII, VII + IVa → II + IXa, VII + IVb → II + IXb, VIII + IVa → III + IXa, with the calculated 4-31G energy differences for the parent molecules.

connected to the parent ions with bond lengths of 1.50 Å. A number of interesting energetic comparisons among these substituted ions are given in Table II along with the corresponding values for the unsubstituted systems.

Both the symmetry allowed and forbidden pathways to degenerate methylene circumambulation in the cyclobutenyl cation are lowered as a result of methyl substitution. Although the Woodward–Hoffmann preferred pathway gains the more (34 kcal/mol), the energy lowering of the symmetry-forbidden mode is great enough (20 kcal/mol) such that it is still the favored. The observation that the eclipsed cyclopropenylcarbinyl cation benefits more from substitution at the positively charged center than does the bisected structure may be taken as evidence for the extreme difference in the pattern of electron distribution present in the two species. In particular, it would appear that, whereas conjugation with the cyclopropene ring in the bisected ion leads to a dispersal of positive charge throughout the entire molecular skeleton, and hence a diminishment of substituent effect at any given site, the mere fact that the carbonium center in eclipsed cyclopropenylcarbinyl is "isolated" from the remainder of the ion means that substitution here will be of major consequence. The activation required for passage through the closed form of eclipsed cyclopropenylcarbinyl is unaffected by substitution at methylene. This latter observation suggests the delocalized nature of the closed cyclopropenylcarbinyl cation, indicating, perhaps, that what one might term the formal carbonium center actually bears but a small portion of the total positive charge. The effect of methyl substitution on the barrier to methylene rotation in cyclopropenylcarbinyl is interesting, in that it closely parallels what we have already observed for the analogous torsional process in the saturated cyclopropylcarbinyl cation.[31] The reduction in rotation barrier in both of these systems—from 33 to 19 kcal/mol in cyclopropenylcarbinyl; from 31 to 17 kcal/mol in the saturated analogue—is indicative of the extent to which electrons are delocalized in the bisected and eclipsed conformations of these cations. That is to say, while charge is extensively delocalized throughout the molecular framework in the bisected cyclopropenyl- and cyclopropylcarbinyl cations, reducing the impact of the methyl substituents, it is highly developed on the methylene center in the eclipsed structures where conjugation with the small ring systems is no longer as significant.

Conclusion

We have investigated the geometrical structures and relative energies of the homocyclopropenyl and related $C_4H_5^+$ cations using ab initio molecular orbital theory. The following points are worthy of special mention.

The homocyclopropenyl cation is not the lowest energy form on the $C_4H_5^+$ potential surface. This distinction belongs to a methyl derivative of the 2π electron aromatic cyclopropenyl cation.

The calculated geometry of the homocyclopropenyl cation is closer to that expected of an open "cyclobutenyl" structure rather than a tightly bridged bicyclic form. The theoretical assignment of the structure of the ion does not appear to be entirely in agreement with the conclusions reached by Olah in his recent NMR spectroscopy study of the parent ion.

Of the pathways open to degenerate rearrangement in the homocyclopropenyl cation, that which is formally forbidden on orbital symmetry grounds is found to be the preferred. Explanation is provided in terms of participation of an orbital subjacent to the highest occupied in the Woodward–Hoffmann forbidden transition state, the bisected cyclopropenylcarbinyl cation.

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