larly the directive influence of substituents which are not simply classified as $\pi$ donors or acceptors (*e.g.*, $CF_3$[30]) remains to be worked out.

Finally an interesting historical sidelight on our arguments is that in some cases we were led to the conclusion that the activation energy for a reaction is more influenced by the effect of substituents on reactant or product than their effect on the transition state. Now this is the way substituent effects were explained many years ago. Then the focus changed, perhaps too sharply, to the effect of substituents on the transition state or intermediate in a reaction. We look forward to a balanced theory of substituent effects.

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# An INDO Theoretical Study of Conjugation into and through the Cyclopropane Ring

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**Abstract:** Semiempirical calculations, in the INDO approximation, were performed on a series of *trans*-2-vinylcyclopropylcarbinyl derivatives, **a–f**, where the carbinyl group was $CH_3$ (**a**), $CH_2\cdot$ (**b**), $CH_2^+$ (**c**), $CF_2\cdot$ (**d**), $CF_2^+$ (**e**), or $BH_2$ (**f**), as well as on the acyclic 4-penten-1-yl cation and radical. From a consideration of optimized bond lengths, barriers to rotation, preferred conformations, charge densities, unpaired spin densities, and $\pi$-bond orders it was concluded that strong conjugation of the cyclopropyl ring with the carbinyl carbon existed, and the strength of this interaction increased as the electron demand of the carbinyl carbon increased. However, these calculations did not support a measurable transmission of conjugation through the ring into the vinyl group except in **c**. Even in **c** the magnitude of this transmitted conjugation was small. The preferred geometry of the carbinyl carbon in difluoro radical **d** was nonplanar despite conjugative interactions with the ring and fluorines. Conversely, the planar geometry was more stable in difluorocarbonium ion where these conjugative interactions were stronger.

To evaluate the magnitude of conjugation, both into and through the cyclopropyl ring, we undertook a theoretical study of a series of cyclopropylcarbinyl cations, radicals, and boron derivatives using the INDO method first developed by Pople and coworkers.[3] The basic model molecule chosen was *trans*-2-vinylcyclopropylcarbinyl system **1**, where X = $CH_3$, $CH_2\cdot$, $CH_2^+$, $CF_2\cdot$, $CF_2^+$, and $BH_2$. The degree of conjugation into and through the ring was evaluated by obtaining charge densities (or unpaired spin densities) at each atom, optimized bond lengths, barriers to rotation about the ring–carbinyl carbon and ring–vinyl group bonds, $\pi$-bond order in the ring–vinyl group bond, and the preferred conformations of **1a–f**.

**Delocalization into Ring.** It has been known for some time that cyclopropyl groups stabilize adjacent carbonium ion[4] and radical[5,6] centers. For example, cyclopropylcarbinyl derivatives solvolyze at markedly enhanced rates compared to their acyclic counterparts. Cyclopropylcarbonium ions have been directly observed by nmr spectroscopy and extensive charge delocalization into the ring was demonstrated by large downfield shifts of the $\beta$-cyclopropyl hydrogens.[4e–g,j] The barrier to cyclopropyl rotation in tertiary cyclopropylcarbinyl cations is 12–14 kcal/mol with the

**1a**, X = $CH_3$
**b**, X = $CH_2\cdot$
**c**, X = $CH_2^+$
**d**, X = $CF_2\cdot$
**e**, X = $CF_2^+$
**f**, X = $BH_2$

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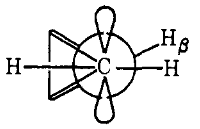
"bisected" conformation preferred.[4f,g] The interaction of the cyclopropyl ring with the carbinyl carbon



bisected conformation

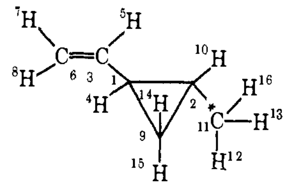
varies with its electron demand in solution.[4j] Compared to their cations, in cyclopropylcarbinyl radicals there is a lower electron demand made upon the ring, but conjugation into the ring has been observed where radical-forming reactions have been accelerated by the introduction of a cyclopropyl ring directly on the incipient radical center.[5]

Conjugation of unpaired spin density into a cyclopropyl ring is maximized in the "bisected" conformation in electron-deficient radicals,[5] but if the radical center is made sufficiently electron rich (as in some radical anions) the preferred conformation changes to the "symmetrical" conformation.[6b] The parent cyclopropylcarbinyl radical has now been directly observed by esr at temperatures below −140°.[6c] It exists in the bisected conformation.

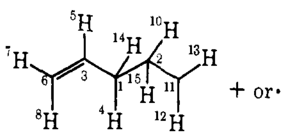
**Transmission of Conjugation.** While conjugation from electron-deficient carbinyl carbon into the cyclopropyl ring has been clearly established, transmission of conjugation through the ring has not been unequivocally demonstrated. Transmission of conjugation in the ground electronic state has been investigated by Raman[7] and infrared[8] spectroscopy, molar refractivity,[9] heats of combustion,[10] Hammett $\rho$ values,[11] and Michael addition to 2-vinylcyclopropane-1,1-dicarboxylate.[12] This evidence has been controversial. The ability of cyclopropylcarbinyl radicals and cations to transmit conjugation is not known.

## Method

The INDO and CNDO/2 programs (CNINDO) QCPE No. 141 were obtained from the Quantum Chemistry Program Exchange, Indiana University, and were modified for use on a Univac 1108. The structures were generated using the Gordon–Pople model builder program, QCPE No. 135, which determined the cartesian coordinates of the atoms when bond lengths and angles were supplied. Calculations were performed on an IBM Model 360/50 and on a Univac 1108. The numbering systems used are shown in **2** and **3** below (note that H-16 is not present in the radicals or carbonium ions). Considerable attention was directed to picking reasonable bond distances, since bonds 1–3, 2–11, B–H, and C–F were the only bonds which were optimized by calculation in **1a–f**. Rather than use standard bond lengths and angles, the experimental values used for this model system were from DeMeijere and Luttke's[13] electron-diffraction study of vinylcyclopropane (summarized in Table I).



**2**, *C or B



**3a**, cation
**b**, radical

**Table I.** Molecular Geometry Used in INDO Calculations of **1a–f**

| Bond | Lengths, Å |
|---|---|
| C—C | |
| 1–2, 1–9, 2–9, | 1.510 |
| 1–3, 2–11 | optimized |
| C=C | |
| 3–6 | 1.334 |
| C—H | |
| 1–4, 2–10, 3–5, 6–7, 6–8, 9–14, 9–16 | 1.08 |
| 11–16, 11–13,[a] 11–12[a] | 1.09 |

| Angle | Deg | Angle | Deg |
|---|---|---|---|
| 2–1–3 | 118.7 | 10–2–9 | 116.8 |
| 3–1–9 | 118.7 | 11–2–1 | 117.5 |
| 4–1–2 | 116.8 | 11–2–10 | 114.4 |
| 4–1–3 | 115.7 | 12–11–2[b] | 109.5 |
| 5–3–1 | 116.7 | 13–11–12[b] | 109.5 |
| 6–3–1 | 123.6 | 13–11–2[b] | 109.5 |
| 6–3–5 | 119.7 | 16–11–13 | 109.5 |
| 7–6–3 | 120.0 | 16–11–12 | 109.5 |
| 8–6–3 | 120.0 | 14–9–1 | 116.8 |
| 9–1–3 | 118.7 | 14–9–2 | 116.8 |
| 9–1–2 | 60.0 | 15–9–1 | 116.8 |
| 10–2–1 | 116.8 | 15–9–14 | 118.2 |

[a] The 11–13 and 11–2 distances were shortened in the radical **1b** to 1.08 and in ion **1c** to 1.05 Å. [b] The angles were converted to 120° in the carbonium ions, radicals, and $BH_2$ cases except in the out-of-plane calculations where 13 and 12 were F. These are stated in the text.

When discussing the angle of rotation about the 1–3 bond, the dihedral angle reported is defined by 5–3–1–4.[13] For the case X = $CH_3$, **1a**, the dihedral angle 12–11–2–10 was chosen to define rotation about the 2–11 bond. The minimum energy rotational conformations about the 1–3 and 2–11 bonds were determined by performing calculations every 5°. After obtaining the minimum energy conformation, bond distances were optimized by calculations every 0.02 Å, plotting the results, and reporting the minimum in these curves to the nearest 0.01 Å. The rotational

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Table II. Calculated Bond Lengths, Rotational Barriers, and Most Stable Conformations **1a–f**

| X | Type calcn | Bond length, Å 1–3 | Bond length, Å 2–11 | Rotational barriers, kcal/mol 1–3 | Rotational barriers, kcal/mol 2–11 | Dihedral angle of most stable conformn, deg 1–3 | Dihedral angle of most stable conformn, deg 2–11 | Total energy, hartrees |
|---|---|---|---|---|---|---|---|---|
| $CH_3$ | CNDO/2 | 1.47 | 1.48 | 4.58 | 2.38 | 180 | 30 | −50.27882 |
| | INDO–CNDO/2[a] | 1.47 | 1.48 | 3.76 | 1.15 | 180 | 30 | −48.74846 |
| | INDO | 1.46 | 1.47 | 3.86 | 1.19 | 180 | 30 | −48.74846 |
| $\dot{C}H_2$ | CNDO/2 | 1.44 | 1.41 | 5.78 | 11.20 | 180 | 180 | −49.33103 |
| | INDO–CNDO/2[a] | 1.44 | 1.41 | 4.68 | 9.46 | 180 | 180 | −47.80715 |
| | INDO | 1.46 | 1.42 | 3.99 | 8.35 | 180 | 180 | −47.80785 |
| $\overset{+}{C}H_2$ | CNDO/2 | 1.44 | 1.36 | 3.66 | 41.2 | 180 | 180 | −49.04167 |
| | INDO–CNDO/2[a] | 1.44 | 1.36 | 4.51 | 47.3 | 180 | 180 | −47.52052 |
| | INDO | 1.45 | 1.36 | 4.32 | 47.3 | 180 | 180 | −47.52050 |
| $\dot{C}F_2$ | INDO[b] | 1.46 | 1.43 | 3.71 | 2.75 | 180 | 180 | −99.189532 |
| $\overset{+}{C}F_2$ | INDO[c] | 1.46 | 1.39 | 3.69 | 25.0 | 180 | 180 | −98.910076 |
| $BH_2$ | INDO[d] | 1.46 | 1.47 | 3.64 | 18.90 | 180 | 180 | −44.849031 |

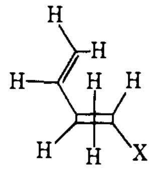
[a] INDO calculations performed on a structure whose optimized bond distances were determined by CNDO/2. [b] The INDO optimized C–F bond length was 1.34 Å. [c] The INDO optimized C–F bond length was 1.31 Å. [d] The INDO optimized B–H bond length was 1.20 Å.

Table III. Calculated Bond Lengths, Rotational Barriers, and Preferred Conformations of the 4-Penten-1-yl Cation **3a** and Radical **3b**[a]

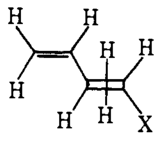
| Structure | Bond length, Å, optimized 2–11 | 1–2 | 1–3 | 3–6 | Rotational barriers, kcal/mol 2–11 | 1–3 | Dihedral angles of most stable conformn,[b] deg 2–11 | 1–2 | 1–3 | Total energy, hartrees |
|---|---|---|---|---|---|---|---|---|---|---|
| **3a**[c] | 1.38 | 1.48 | 1.46 | 1.33 | 21.70 | 4.37 | 90 | 180 | 60 | −40.60453 |
| **3b**[c] | 1.44 | 1.49 | 1.47 | 1.33 | 2.21 | 3.98 | 90 | 180 | 70 | −40.93314 |

[a] All INDO calculations; standard bond angles and lengths (except those which were optimized) were used. [b] The conformations are completely defined by the three dihedral angles. The dihedral angles listed in the table were 13–11–2–1 (for 2–11 rotation), 11–2–1–3 (for 1–2 rotation), and 2–1–3–6 (for 1–3 rotation). See structures **3a** and **b** for numbering. [c] Dipole moments **3a** = 17.545 D, **3b** = 0.262 D.

barriers were then redetermined using the minimized bond lengths.



s-cis



s-trans

## Results

**Preferred Conformations.** In structures **1a–f**, the s-cis and s-trans conformations represented energy minima in rotation about the 1–3 bond; however, the s-trans was more stable than the s-cis form by 1.36, 1.40, 2.63, 1.40, 2.36, and 1.75 kcal/mol, respectively. Rotating 90° about the 1–3 bond from the s-trans conformation resulted in energy maxima in each of molecules **1a–f**. The "bisected" conformation was always the minimum energy conformation in rotation about the 2–11 bond in **1b–f**. Calculations showed that rotation about the 1–3 bond in **1a**, where X = $CH_3$, exhibits energy minima when the 12–11–2–10 dihedral angle has values of 30, 60, and 90°. Maximum energy conformations occurred at 0 and 120°. The minimum at 30° is 0.99 kcal/mol more stable than the 90° conformation and 0.98 kcal/mol more stable than the 60° conformation.

**Bond Lengths and Rotational Barriers.** The optimized bond distances for the 1–3, 2–11, C–F, and B–H bonds are listed in Table II. The changes in the 2–11 bond lengths are striking. Going from X = $CH_3$ to $CH_2\cdot$ the 2–11 bond length decreased by 0.05 Å (INDO) from 1.47 to 1.42 Å. The 2–11 bond length further decreases going from 1.42 Å where X = $CH_2\cdot$ to 1.36 when X = $CH_2^+$. This 0.06-Å decrease makes the 2–11 bond resemble a double bond. The 2–11 bond length shortens to 1.43 Å where X = $CF_2\cdot$ and further to 1.39 Å where X = $CF_2^+$. Where X = $BH_2$ the 2–11 length has not decreased substantially and is 1.47 Å. However, this system (isoelectronic with X = $CH_2^+$) is difficult to compare since different atoms are joined in the 2–11 bond.

INDO calculations show no change in the 1–3 bond distance going from X = $CH_3$ to X = $CH_2\cdot$, $CF_2^+$, $CF_2\cdot$, or $BH_2$ and only a very small (0.01 Å) decrease when X = $CH_2^+$. The CNDO/2 calculations do indicate a small decrease in the 1–3 length from 1.47 Å when X = $CH_3$ to 1.44 Å when X = $CH_2\cdot$ or $CH_2^+$.

INDO calculations show dramatic changes in the 2–11 rotational barriers but only tiny changes in the 1–3 barriers when X is varied. The marked change in the 2–11 barrier from 1.19 kcal/mol (X = $CH_3$) to 8.35 (X = $CH_2\cdot$), 47.3 (X = $CH_2^+$), 25.0 (X = $CF_2^+$), 18.90 (X = $BH_2$), and 2.75 kcal/mol (X = $CF_2\cdot$) can be correlated to the large changes in 2–11 bond length. On the other hand, the rotational barriers about the 1–3 bond are virtually unchanged when X is varied. The variation from 3.86 to 4.32 kcal/mol going from X = $CH_3$ to $CH_2^+$ was the largest change by a wide margin. The barrier actually decreased slightly going from X = $CH_3$ to $BH_2$, $CF_2\cdot$, or $CF_2^+$.

The 4-penten-1-yl cation and radical were then examined. All the carbon–carbon bonds were optimized before the rotational barriers were calculated. The most stable conformations, bond lengths, barriers, and dipole moments are listed in Table III. The 2–11 length is greatly shortened to 1.38 Å in cation **3a**. This is a decrease of 0.06 Å from the radical, but this is still longer than the 2–11 length in **1c**.

**Table IV.** The $\pi$-Bond Orders of the 1–3 Bonds and Charge Densities[a] in the $2p_y$ Orbital of Carbon-1 and -3

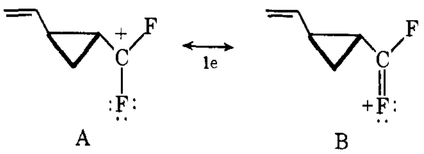
| Species | **1a**<br>$-CH_3$ | **1b**<br>$-CH_2\cdot$ | **1c**<br>$-CH_2^+$ | **1d**<br>$CF_2\cdot$ | **1e**<br>$CF_2^+$ | **1f**<br>$BH_2$ | **3a**<br>$CH_2^+$ | **3b**<br>$CH_2\cdot$ |
|---|---|---|---|---|---|---|---|---|
| $C_1$–$C_3$ $\pi_y$ bond order | 0.2281 | 0.2344 | 0.2426 | 0.2316[b] | 0.2344 | 0.2300 | 0.2359 | 0.2224 |
| $C_1$ $2p_y$ | 698 | 662 | 147 | 648[b] | 662 | 432 | −1107 | −179 |
| $C_3$ $2p_y$ | −267 | −246 | 308 | −196[b] | −246 | −154 | +423 | −255 |

[a] Charge densities given $(1 - q) \times 10^4$. [b] For the nonplanar optimized structure the $C_1$–$C_3$ $\pi_y$ bond order was 0.2311, the charge density in $C_1$ $2p_y$ = 569, and in $C_3$ $2p_y$ = −180.

**$\pi$-Bond Orders, Charge Densities, s-Orbital Spin Densities.** The $\pi$-bond order in the 1–3 bonds of **1a–f** and **10a** and **b** are listed in Table IV with the charge densities in the $2p_y$ orbital of C-1 and C-3. These were examined to see if any large increase in $\pi$ bonding had occurred which would indicate transmission of conjugation through the ring. The largest $\pi$-bond order was found when X = $CH_2^+$ and throughout the series **1b–f** the $\pi$-bond orders were slightly larger than in **1a** (X = $CH_3$). However, these increases are small, reaching a maximum $\Delta\pi$ bond order = 0.0145 going from X = $CH_3$ to X = $CH_2^+$. When cyclopropylcarbinyl radical **1b** and cation **1c** are compared to their acyclic analog **3b** and **3a**, respectively, it is apparent that the 1–3 $\pi$-bond orders are only slightly higher in the cyclopropyl compounds. No dramatic increase in $\pi$-bond order across the 1–3 bond is found even when an exceedingly powerful electron demand is made upon the ring by $CH_2^+$.

As expected, the charge density found for the carbinyl carbon, C-11, of the carbonium ions **1c**, **e**, and acyclic **10a** bore the largest amount of charge.[14] More charge was localized at C-11 in acyclic **3a** (+0.3531) than in **1c** (+0.2458). As expected, C-1 in **3a**, which is $\beta$ to the carbonium ion site, bore a large charge (0.1616). In **1c** there are two such $\beta$ carbons. Together they bore substantially more charge than the single C-1 in **3a** (*i.e.* (in **1c**), C-1, 0.1723; C-9, 0.0687). Since **1c** has more atoms over which the charge may be dispersed, this result indicates "delocalization" into the ring. More charge was localized at the tertiary C-1 than at C-9 in **1c**. The sum of positive charge localized at the vinyl carbons (C-3, C-6) totaled 0.0539 in **1c**, 0.0448 in **3a**, and 0.0449 in **1e** with more at C-6 in each case. These sums may be compared to the corresponding values of 0.0061 in **1f**, X = $BH_2$, and −0.0027 in **1a**, X = $CH_3$. The small difference between **1c** and **3a** (0.0090) would be larger if **3a** had as many atoms as **1c** over which to disperse the charge.

In the difluoro cation **1e**, the fluorines still bore a net negative charge despite being attached to a positively charged carbon (F-12 = −0.1126 and F-13 = −0.1162). However, this still represents a substantial decrease in charge density at fluorine compared to fluoroethane and 1,1,1,-trifluoroethane where INDO calculations indicate charges on the fluorines of −0.205 and −0.216, respectively [3b] This can be explained by invoking hybrid structures A and B for **1e**. However, efficient delocalization of charge into the ring would reduce the degree to which hybrid B contributes compared to such contribution, for example, in the methyldifluorocarbonium ion. To the degree that b contributes in **1e**, one would expect a decrease in $\pi$-bond order between C-2 and -11. In this regard, the decrease in rotational barrier from 47.3 to 25.0 kcal/mol going from X = $CH_2^+$ to $CF_2^+$ makes sense. If hybrid B does contribute, the $CF_2^+$ group might actually make a smaller electron demand upon the ring than does $CH_2^+$. The sum of the charge densities on ring carbons 2, 1, and 9 in **1c** *vs.* **1e** supports this view. For **1c**, this sum is +0.3246, while it is only +0.1823 for the difluoro analog **1e**. Furthermore, the charge density in the vinyl carbons of **1e** (C-3 + C-6 = 0.449) is smaller than that found for **1c**. If transmission of conjugation is significant, the greater electron demand made by $CH_2^+$ over $CF_2^+$ on the ring should be reflected by an increased plus charge density in the vinyl group of **1c** *vs.* **1e**. Summing these densities for atoms 3, 6, 5, 7, and 8, one finds this is true, but the magnitude of the difference between these sums is small. Any transmission effect, as represented by these charge densities, is not of sufficient magnitude to be sensitive to this difference in electron demand.



A B

The calculated hyperfine couplings for radical **1b** (X = $CH_2\cdot$) are in very close agreement with those observed in the esr studies of the cyclopropylcarbinyl radical by Kochi and Krusic.[6c] This agreement demonstrates no unusual structure need be invoked for **1b**. Of particular interest, the calculated values of the valence densities, 2-orbital spin densities, and hyperfine couplings of the vinyl hydrogens (5, 7, and 8) and vinyl carbons (3, 6) were very small for each of the radicals **1b** and **e**.[14] For example, hyperfine couplings at the vinyl hydrogens (5, 7, and 8) were less than 1 G and at the vinyl carbons (3, 6) were 2 G or less for both radicals **1b** and **1e**. Furthermore, very similar values were obtained for acyclic **3b** (for example, the hyperfine couplings at all vinyl group atoms were less than 1 G) with no trend evident going from the acyclic to the cyclic system. Thus, these values provide no evidence of any special transmission of conjugation through the ring into the vinyl group.

Calculations were next performed on **1d** and **e** to determine if the preferred geometry of the carbinyl carbon, containing directly bonded fluorine, was planar or nonplanar. These calculations demonstrated that the most stable conformation of difluoro radical **1d** was nonplanar while that of difluoro cation **1e** was planar. Systematic variation of the C–C–F and F–C–F bond angles showed that radical **1d** was most

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(14) Complete tables of charge densities, s-orbital spin densities, and hyperfine couplings covering all calculations performed are available on request from the authors for **1a–f** and **3a** and **b**.

stable when the C–C–F angles were 121° and F–C–F angle was 106°. This conformation was 8.6 kcal/mol more stable than the planar conformation. Conversely, deforming the carbinyl carbon geometry out of the plane in cation **1e** resulted in a loss of stability. When the C–C–F angles were 120° and F–C–F angle was varied only 2–118°, the stability of **1d** decreased by 0.7 kcal/mol. Deforming these angles to those of the most stable geometry of radical **1d** resulted in a decrease in stability of 13.99 kcal/mol relative to the planar geometry.

## Discussion and Conclusions

After careful examination of the 2–11 bond distances and rotational barriers, the charge densities on the ring carbons, the preference shown for the bisected conformation, and the unpaired spin densities on the ring, it is clear that the cyclopropyl ring has a strong electronic interaction with the carbinyl groups $CH_2^+$, $CF_2^+$, $CH_2\cdot$, $CF_2\cdot$, and $BH_2$. This interaction is strongest for $CH_2^+$ which makes a greater electron demand upon the ring than $CF_2^+$. Both cation centers interact more strongly than the corresponding $CH_2\cdot$ and $CF_2\cdot$ groups. It is very difficult to authoritatively divide this interaction into $\sigma$ and $\pi$ contributions due to the complicated geometry and to our choice of the $x$, $y$, and $z$ axis system. However, the substantial decreases in the 2–11 bond length in cations **1c** and **e** are only partially due to a general shrinkage of the C-2 van der Waals radius. A $\pi$-type interaction (resonance) between the cyclopropane ring and the carbinyl carbon best explains the decreased 2–11 length, the large increase in the 2–11 rotational barrier, the large charge density on the $\beta$-cyclopropyl carbons, the decrease in the 2–11 rotational barrier going from a planar carbinyl $-CH_2^+$ to planar $-CF_2^+$, the much greater dipole moment of the acyclic cation **3a** (17.55 D) compared to **1c** (5.48 D), and the preference for the bisected structure. This interaction is also significant but weaker in radicals **1b** and **d** and in borane **1f**. Thus, *resonance delocalization into the cyclopropyl ring from trigonal carbon (or boron) is substantial and its magnitude increases as the electron demand made by the trigonal center increases.*

The changes in (1) 1–3 bond lengths, (2) 1–3 rotational barriers, (3) the vinyl group positive charge or unpaired spin densities, (4) the 1–3 $\pi$-bond order, and (5) the $\Delta E$ between the s-trans and s-cis conformations are all small going from **1a** to **1b-f** or when comparing **1b-f** to **3a** and **b**. *Thus, transmission of "conjugation" from the carbinyl group through the ring into the vinyl group is either small or nonexistent. Only in* **1c** *($X = CH_2^+$) can a consistent case be made for possible transmission of conjugation.* Here, a small increase in 1–3 $\pi$-bond order, the 1–3 rotational barrier, the charge density on the vinyl group, and $\Delta E$ between the s-trans and s-cis can be interpreted as a manifestation of a small "through transmission of conjugation." These calculations do not consider any solvation or medium effects. Thus, the calculated parameters represent a far stronger electron demand by the carbinyl group than would be experienced in solution chemistry. It is difficult to imagine any realistic functional group, intermediate, or transition-state structure at the carbinyl group which would make a stronger demand upon the ring than $CH_2^+$ in **1c**.

Results of these INDO calculations compare favorably with the literature. Close agreement exists between the calculated hyperfine coupling constants of **1b** and the esr observations of Kochi and Krusic.[6c] The calculated energy difference (1.36 kcal/mol) between the "s-trans" and s-cis" conformations in **1a** agrees with the measured enthalpy difference of 1.1 ± 0.2 kcal/mol reported by Luttke.[13] The bisected structure of the cyclopropylcarbinyl cation was favored in the previous calculations of Hoffmann[15] (extended Hückel), Yonezawa[16] (ASMO–SCF), Wiberg[17] (CNDO), Schleyer[18] (NNDO), and Pople[19] (*ab initio* STO-3G). The discrepancy between our 47-kcal/mol 2–11 barrier and that of Wiberg (25 kcal/mol) can be largely accounted for by the short (1.36 Å) 2–11 bond length we obtained by optimization *vs.* Wiberg's 1.54 Å. A similar discrepancy exists in the 2–11 barrier for the 1-pent-4-enyl cation **3a**, where our 21.7 kcal/mol value is much larger than *ab initio* results.[19] The most stable conformation of **3a** occurs where the "empty" p orbital on C-11 is coplanar with the 2–1 bond in agreement with the results of Pople.[19]

Theoretical treatments uniformly agree that carbonium ions prefer a planar structure[19,20] although nonplanar bridgehead cations are well known.[21] Similarly, hydrocarbon free radicals prefer the planar structure.[22] However, upon substitution of a radical center with F, planarity is lost and the preferred geometry tends toward tetrahedral.[23] For example, $CF_3\cdot$, $CF_2H\cdot$, and $CFH_2\cdot$ are nonplanar. Important factors determining the relative energies of the planar and nonplanar geometries include the occupancy of the carbon 2s orbital, the 2s–2p promotion energy, the dependence of the C–X bond energy on the amount of s character of the carbon bonding orbitals,[22] and, as Pauling[24] pointed out, the difference in electronegativity of atoms C and X. Where the electronegativity of X is substantially more than carbon's, an increasingly nonplanar geometry is favored. However, where partial multiple bonding between C and X occurs,[25] the tendency toward nonplanarity is modified such that the nonplanar structure with minimum energy has a geometry closer to the planar structure than it would be without such multiple bonding. We find the minimum energy conformation of **1e** was nonplanar where the C–C–F angles were 121° and the F–C–F angle was 106°. This conformation is 8.6 kcal/mol more stable than the planar geometry. *Thus, resonance interaction with the cyclopropyl ring, in addition to partial double bond character*

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*in the C–F bonds of* **1d**, *is not enough to cause the planar geometry to be as stable as the nonplanar geometry. Upon strengthening the resonance interaction with both the ring and the fluorines, a planar geometry is increasingly favored.* This effect is illustrated in the difluorocyclopropylcarbonium ion, **1e**, where the planar conformation is the most stable geometry. It is much more stable than any geometry with a significant out-of-plane deviation. This is in accord with Pauling's[24] expectation that the planar geometry is increasingly more stable relative to nonplanar geometry as the electronegativity difference between C and F decreases.

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# A Quantitative Investigation of the Ozonolysis Reaction. XV. Quantum Chemical Interpretation of the Substituent Effects on the Cleavage of 1,2,3-Trioxolanes[1a]

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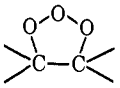
**Abstract:** Experimental distributions of the reaction paths of selected alkyl-substituted 1,2,3-trioxolanes to give (a) $R_1C^+HOO^-$ + $R_2CHO$ or (b) $R_1CHO$ + $R_2C^+HOO^-$ are compared with Mulliken overlap populations and with gross electron densities of the trioxolanes. In general, the preferential path of cleavage yields the zwitterion retaining the carbon atom having the highest C–O overlap in the trioxolane ring, and the cleavage appears to be initiated at the C–C bond. Both the EHMO and the CNDO/2 calculations indicate that the inductive effects, expressed in terms of net electron release by the substituents, are remarkably constant for the individual groups and correlate with Taft's polar $\sigma^*$ constants. Both methods indicate the participation of an additional effect, by which the preferentially formed zwitterion is the one in which the environment is electron richer, and is, thus, favored by alkyl groups in the order $CH_3 > \ldots >$ *tert*-$C_4H_9$. A consideration of this effect, together with the inductive effect, enables the consistent discussion of the reactivity of primary ozonides.

According to Criegee's mechanism of ozonolysis,[2] which is well supported by considerable experimental evidence,[3] ozone adds onto carbon–carbon double bonds to give the very unstable intermediate 1,2,3-trioxolanes (primary ozonides) I.

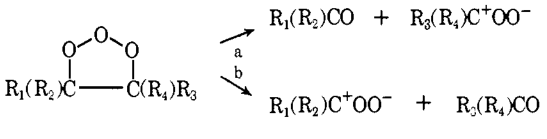


I

Evidence for the existence of the primary ozonides of some trans and cis alkenes has been given, and experimental findings confirm structure I.[4] However, owing to the extreme instability of the primary ozonides,[5] their conformational study is, at present, impossible with conventional experimental methods: quantum chemical LCAO–EHMO methods were used to gain information about the shape of selected alkyl-substituted primary ozonides.[6]

Their cleavage into zwitterion and carbonyl compound has been the object of recent detailed studies.[7–9] With unsymmetrical olefins $R_1(R_2)C{=}C(R_4)R_3$, two possible paths of cleavage are to be considered (Scheme I).

**Scheme I**



Because of the complexity of the reactions occurring in ozonolyses in inert solvents (*e.g.*, $CCl_4$, hexane),

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[1] (a) Paper presented at the Symposium on Cyclic Peroxides, Metrochem '71, San Juan, Puerto Rico, April 30, 1971. Abstracted in part from the Ph.D. Thesis of J. Renard, Université de Montréal, Montréal, Québec, Canada, 1969. (b) Department of Chemistry. (c) Faculty of Pharmacy.

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[5] The "most stable" primary ozonide (that of *trans*-di-*tert*-butylethylene) decomposes in an explosive way when "heated" up to −60°.[4a] The cis primary ozonides are reported to be even more unstable than the trans isomers,[4d] at temperatures as low as −110°.

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