Methyl-Substituted Cyclopropylcarbinyl (Alias Vinyl-Bridged Ethylene) Carbocations. Molecular Orbital Calculations and Criteria for Structure Representation–Nomenclature Decisions

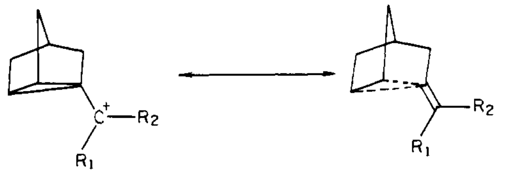
Lawrence R. Schmitz and Ted S. Sorensen*

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4.

Received August 17, 1981

Abstract: The question of whether nortricyclylcarbinyl cations **1** have an enhanced vinyl-bridging 2-norbornyl **1b** character has been probed by means of molecular orbital calculations. In order to do this, one needs data on model methyl-substituted cyclopropylcarbinyl cations, and 14 different systems, together with the parent cation, have been included in this study. Optimized geometries were evaluated by using the MNDO procedure and energies obtained by the STO-3G ab initio method. Calculated heats of formation agree well with experiment and the stabilizing influence of methyl groups on the parent cyclopropylcarbinyl cation correlate well with solvolysis data. The HOMO level for most of the cations is the π-MO, a result at variance with a simple perturbation treatment but one which can be easily rationalized. Two procedures are suggested for semiquantitatively evaluating the "mix" of the two extreme resonance structures in the actual structure, and both of these methods give similar results. Applying one of these criteria to the nortricyclylcarbinyl cation case, one finds indeed that there is an enhanced vinyl-bridging character compared to the simple cyclopropylcarbinyl model.

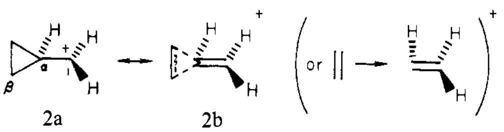
In the preceding article,[1] we have described the in situ preparation of a homologous series of *bisected*, *static*, primary, secondary, and tertiary cyclopropylcarbinyl cations **1**.



1a 1b

These cations represent a key *structural link* between cyclopropylcarbinyl and bridged 2-norbornyl cation families. Structures **1a** and **1b** are, of course, extreme representations of a resonance system, and it is largely futile to argue the fine points of which is the closer representation to the actual structure, based only on NMR spectra. We were therefore interested in what MO theory had to say in this regard, particularly whether the bridged representation **1b** might be enhanced in this case.

The parent cyclopropylcarbinyl cation **2** has been very extensively computed,[2] probably most often in connection with the potential energy surface of the well-known cyclopropylcarbinyl–cyclobutyl–allylcarbinyl interchange. As many have pointed out, cation **2** is, in resonance terminology, some "mix" of extreme structures **2a** and **2b**.[3]



2a 2b

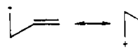
As a reference point for a "normal structure" comparison, cation **1** can be approximated as an α,β,β'-trimethyl-substituted cyclopropylcarbinyl cation **6**, and we therefore wished to study such systems. However, for completeness, and because methyl-substituted cyclopropylcarbinyl cations have not been systematically studied computationally,[4] we decided to look at a selected number of these in addition to **6**. Thus, although the calculations were initiated with a specific question in mind, they have been expanded to include a relatively complete study of methyl-substituted cyclopropylcarbinyl cations. The MO calculations have focused on total energies, resonance or stabilization energies, individual orbital energies, optimized geometries, charge delocalization, barriers for rotation about the C_α–C_1 bond and the C_α–C_β "bonds", and, relevant to the problem at hand, trying to devise better criteria for deciding the relative importance of the two extreme resonance

---

(1) Schmitz, L. R.; Sorensen, T. S., preceding article in this issue.

(2) (a) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5537. (b) Dewar, M. J. S.; Haddon, R. C.; Komornicki, A.; Rzepa, H. *Ibid.* **1977**, *99*, 377. (c) Hehre, W. J.; Hiberty, P. C. *Ibid.* **1974**, *96*, 302. (d) Hehre, W. J.; Hiberty, P. C. *Ibid.* **1972**, *94*, 5917. (e) Olah, G. A.; Spear, R. J.; Hiberty, P. C.; Hehre, W. J. *Ibid.* **1976**, *98*, 7470. (f) Radom, L.; Pople, J. A.; Buss, V.; Schleyer, P. v. R. *Ibid.* **1970**, *92*, 6380. (g) Wiberg, K. B.; Szeimies, G. *Ibid.* **1970**, *92*, 571. (h) Baldwin, J. E.; Foglesong, W. D. *Ibid.* **1968**, *90*, 4311. (i) Trindle, C.; Sinanoglu, *Ibid.* **1969**, *91*, 4054. (j) Hoffmann, R. *J. Chem. Phys.* **1964**, *40*, 2480. (k) Kollmar, H.; Smith, H. O. *Tetrahedron Lett.* **1970**, 3133. (l) Isaacs, N. *Tetrahedron* **1969**, *25*, 3555. (m) Wiberg, K. B. *Ibid.* **1968**, *24*, 1083. (n) Davies, R. E.; Ohno, A. *Ibid.* **1968**, *24*, 2063. (o) Wilcox, C. F.; Loew, L. M.; Hoffmann, R. *J. Am. Chem. Soc.* **1973**, *95*, 8192. (p) Hehre, W. J. *Acc. Chem. Res.* **1975**, *8*, 369. (q) Bach, R. D.; Blanchette, P. E. *J. Am. Chem. Soc.* **1979**, *101*, 46. (r) Dill, J. D.; Greenberg, A.; Liebmann, J. F. *Ibid.* **1979**, *101*, 6814. (s) Khalil, S. M.; Shanshal, M. *Theor. Chim. Acta* **1977**, *46*, 23. (t) Danen, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 4835. (u) Yonezawa, T.; Nakatsuji, H.; Kato, H. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2788. (v) Shanshal, M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem. Biophys., Biol.* **1972**, *27B*, 1665. (w) Shanshal, M. *Theor. Chim. Acta* **1971**, *20*, 405. (x) Wolf, J. F.; Harch, P. G.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1975**, *97*, 2904. (y) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1972**, *94*, 5935. (z) Yurtsever, E.; Morehead, J.; Shillady, D. *Chem. Phys. Lett.* **1975**, *36*, 365. (aa) Schleyer, P. v. R.; Buss, V. *J. Am. Chem. Soc.* **1969**, *91*, 5880. (bb) Buss, V.; Gleiter, R.; Schleyer, P. v. R. *Ibid.* **1971**, *93*, 3927. (cc) Wiberg, K. B.; Pfeiffer, J. G. *Ibid.* **1970**, *92*, 553. (dd) Haselbach, E.; Schmelzer, A. *Helv. Chim. Acta* **1971**, *54*, 1299. (ee) Tremper, H. S.; Shillady, D. D. *J. Am. Chem. Soc.* **1969**, *91*, 6341. (ff) Andrist, A. H. *J. Chem. Soc., Chem. Commun.* **1975**, 446. (gg) Andrist, A. H. *J. Am. Chem. Soc.* **1973**, *95*, 7531. (hh) Kispert, L. D.; Engelman, C.; Dyas, C.; Pittman, C. U. *Ibid.* **1971**, *93*, 6948.

(3) These extreme structures are meant to show that in **2a**, there are *two* C_α–C_β bonds (the two Walsh orbitals) and *no* C_1–C_α π bond, whereas in **2b**, there is *one* C_α–C_β bonding pair (the remaining symmetrical Walsh orbital) and a *full* C_1–C_α π bond. Dewar (Dewar, M. J. S.; Marchand, A. P. *Annu. Rev. Phys. Chem.* **1965**, *16*, 321) uses the single arrow representation shown in **2b**, while others prefer the VB formulation shown.

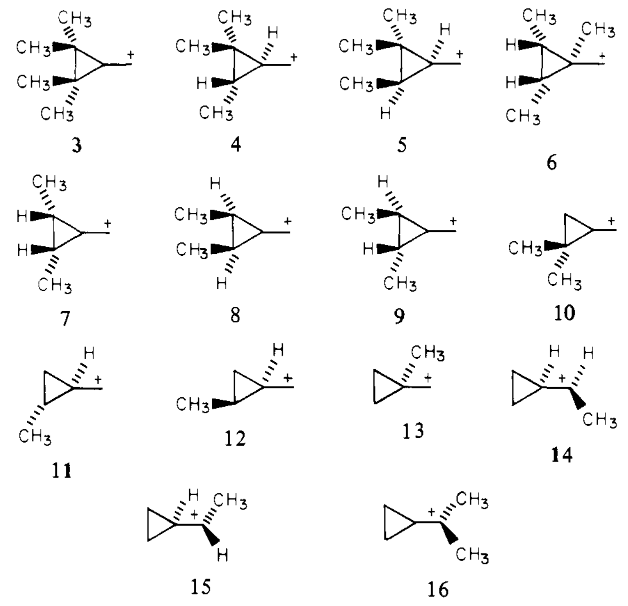


2b

The important point is that **2b**, even though it contains a three-center two-electron "bond" is still an *extreme* resonance canonical form. Dewar's formulation is perhaps the most satisfactory of the three.

(4) References 2a, 2c, 2e, 2f, 2o, 2q, 2r, 2x, and 2y deal also with methyl-substituted cyclopropylcarbinyl cations.

Chart I



structures, as represented by cations **1a** ↔ **1b** or **2a** ↔ **2b**. For example, the question of whether **1b** is a more stable "structure" than a trimethyl analogue of **2b**, i.e., **6b**? This latter point also leads to such questions as to how one should both depict and name these cations. In an era where sophisticated MO calculations are easily done, it has been argued that it is a retrogressive step to use the concepts of VB theory and to artificially compute parameters related to VB resonance structures. However, in a pedagogical sense and also for historical reasons, we find it easier to "visualize" a molecule as some "mix" of extreme VB resonance structures.

Where possible, all results have been compared to appropriate experimental data.

Cations Selected for Study. Excluding optical isomers, there are 79 possible mono, di, tri, etc. methyl-substituted cyclopropylcarbinyl cations. Of these, 14 (**3**–**16**) have been chosen, including the expected structural extremes **3** and **16** (maximum C_β and C_1 carbon stabilization, respectively).

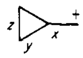
Computational Methods. All structures were first calculated using the MNDO semiempirical method of Dewar and Thiele[5] and were fully geometry optimized except for some methyl group dihedral angles. For the symmetrical ions, the imposition of fixed C_s symmetry gave similar results to calculations involving no symmetry constraints, showing that the "bisected" conformation is, as expected, the ground state in all those cases which were specifically tested. The unsymmetrical cations **4**, **5**, **9**, **10**, **11**, and **12** gave distorted "bisected" ground states. In the case of **10**, the distortion is large and, furthermore, only a shallow local minimum exists for this geometry.

MO calculations were also carried out on an additional group of neutral and cationic molecules needed for various isodesmic reactions. Calculations were aslo made on a group of "perpendicular" cyclopropylcarbinyl cations and on a group of "planar" vinyl-bridged ethylene cations. Special aspects involving all of these calculations are discussed in later sections.

With use of these optimized MNDO geometries, single point STO-3G ab initio calculations[6] were then carried out. All of our results pertaining to energies, unless otherwise specified, involve the STO-3G results. This minimal basis set satisfactorily reproduces experimental ΔH_f data.

Of perhaps more concern are the differences in optimized geometries, as a function of the type of MO calculation. These are given in Table I for the parent cation **2**. Significantly, the MNDO and STO-3G geometries are quite similar but considerably less distorted than the 4-31G basis set results. This latter geometry is confirmed at the 6-31G* level, the energy being 7.5 kcal/mol lower than with the MNDO geometry (Table II) (vs. a difference of 7.7 kcal/mol between MNDO and 4-31G geometries, using the 4-31G basis set). The actual energy difference could be lowered somewhat by using shorter C–H bonds in the MNDO geometries.

Table I. Different Optimized Geometries Using Different Basis Sets

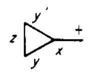


type of MO calcn	bond lengths, Å			ref
	x	*y*	*z*	
CNDO/2	1.41	1.58	1.46	2k
MINDO/3	1.378	1.599	1.426	2b
MNDO	1.400	1.615	1.474	this work
STO-3G	1.384	1.609	1.454	2c
4-31G	1.347	1.664	1.412	2a

Table II. Relative Energies of the 4-31G and MNDO Optimized Geometries of 2 as a Function of the Type of Calculation

type of MO calcn	relative energy, kcal/mol	
	MNDO geometry	4-31G geometry
MNDO	0	+8.89
STO-3G	0	−0.34
4-31G	0	−7.73
6-31G*	0	−7.52

Table III. Important Geometry Parameters for the MNDO-Optimized Geometries[a]



cation	bond lengths, Å			
	x	*y*	*y'*	*z*
3	1.394	1.640		1.505
4	1.393	1.691[b]	1.595[b]	1.492
5	1.393	1.681	1.599	1.492
6	1.407	1.644		1.482
7	1.397	1.624		1.486
8	1.395	1.629		1.483
9	1.396	1.632 (anti-CH_3)	1.623 (syn-CH_3)	1.482
10	1.393	1.701	1.576	1.483
11	1.397	1.651	1.592	1.480
12	1.396	1.657	1.591	1.478
13	1.407	1.630		1.472
2	1.400	1.615		1.474
14	1.416	1.600		1.481
15	1.418	1.601		1.481
16	1.436	1.590		1.486

[a] Optimized Z matrices are available as supplementary material. [b] The longer bond is invariably the one to the most substituted β-carbon.

It is not feasible to use either the 4-31G or 6-31G* geometry optimization calculations for the series of cations **3**–**16**.

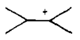
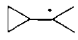
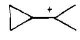
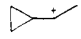
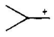
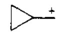
Optimized Geometries for Cations 2–16. Table III lists the important bond distances for these cations. Methyl substitution at C_1 will stabilize resonance canonical structure **a**, while substitution at C_β will stabilize **b**. The observed geometry changes are resonably consistent with this. Thus, in going from **16** to **2** to **3**, the C_1–C_α bond shortens, the C_α–C_β bonds lengthens and the C_β–C_β bond shortens from **16** to **2** and then lengthens in **3**. This latter change is very likely due to eclipsing methyl interactions

---

(5) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

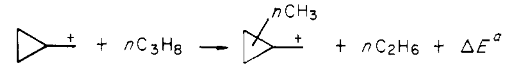
(6) Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. Program No. 368 (Gaussian 76), Quantum Chemistry Program Exchange; Indiana Unversity: Bloomington, IN.

Table IV. Calculated and Experimental Heat of Reaction Data

reaction				$\Delta H_{reaction}$[a,c]		ΔH_f[b,c]	
I	II	III	IV	calcd	exptl	calcd	exptl
	+  →	 16	+ 	−11.04	−8.9	+176.86	179
$(CH_3)_3C^+$	+  →	 16	+ CH_4	−14.52	−13.7	+178.18	179
$CH_3\text{-}\overset{+}{C}H\text{-}CH_3$	+  →	 15	+ CH_4	−20.92	−20.8	+196.88	197
	+  →	 2	+ 	−20.95	−22.5	+215.55	214
$CH_3\overset{+}{C}H_2$	+  →	 2	+ CH_4	−29.59	−35.6	+220.01	214

[a] $\Delta H_{reaction} = \Delta H_{IV(calcd)} + \Delta H_{III(calcd)} - \Delta H_{II(calcd)} - \Delta H_{I(calcd)}$. [b] $\Delta H_{f(III(calcd))} = \Delta H_{f(II(exptl))} + \Delta H_{f(I(exptl))} + \Delta H_{(reaction(calcd))} - \Delta H_{f(IV(exptl))}$. [c] In kcal/mol.

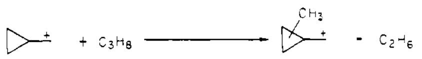
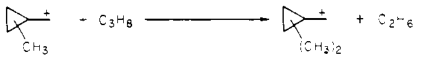
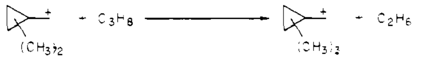
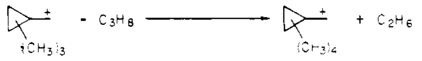
Table V. Electronic Stabilization of Cyclopropylcarbinyl Cations by the Addition of Methyl Groups



ion	n	$-E/n$	$-\Delta E$
3	4	4.13	16.52
4	3	5.30	15.90
5	3	4.76	14.28
6	3	4.12	12.37
7	2	5.95	11.89
8	2	4.49	8.98
9	2	5.88	11.77
10	2	5.85	11.71
11	1	6.74	6.74
12	1	5.22	5.22
13	1	4.23	4.23
14	1	14.48	14.48
15	1	16.29	16.29
16	2	14.68	29.36

[a] In kcal/mol.

Table VI. Average Incremental Stabilizations of Cyclopropylcarbinyl Cations by the Addition of Methyl Groups to the β-Carbons

reaction	$-\Delta E$[a]	av of cations
	5.98	2 → 11 and 12
	5.11	11 and 12 → 7, 8, 9, and 10
	4.00	7, 8, 9, and 10 → 4 and 5
	1.43	4 and 5 → 3

[a] In kcal/mol.

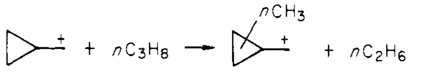
in **3**. The unsymmetrical ions **4**, **5**, **9**, **10**, **11** and **12** have uneven C_α–C_β bonds, smallest for **9**, intermediate for **4**, **5**, **11**, and **12**, and largest for **10**. These results are not unexpected.

X-ray data on cyclopropylcarbinyl salts are badly needed because no experimental bond distance data is available for comparison with the calculations.

Calculated Heats of Formation. Experimental $\Delta H_f°$ values are known[7] for cations **2**, **15**, and **16**, although the structure of the cation involved with **2** is probably not known with certainty, and could well be a mixture of cyclopropylcarbinyl and cyclobutyl cations. Similarly, the geometry at C_1 in **15** (i.e., **15** or **14**?) is not known for certain but probably corresponds to **15**. Using isodesmic reactions (all structures were calculated by the same procedure as used for **3**, **15**, and **16**, $C_2H_5^+$ being computed as a primary ion and not a hydrogen-bridged structure) and known $\Delta H_f°$ data for the other three species in the isodesmic reaction, one calculates the $\Delta H_f°$ values shown in Table IV.

With the best isodesmic reaction comparisons (the top one in each series), the calculated and experimental results are within about 2 kcal/mol.

Stabilization of 2 by Additional Methyl Groups. The stabilization of the parent cation **2** by additional methyl groups was arbitrarily evaluated by using isodesmic reaction 1. The absolute numbers obtained depend on the particular isodesmic reaction used but internal comparisons should be reasonably valid. These data are listed in Table V.



(1)

As expected, substitution at C_1 is most stabilizing, followed by the anti-β-position, the syn-β-position and least for the C_α position. Multiple substitution at the β-position eventually causes a partial saturation effect, perhaps partly for steric reasons. These data are shown in Table VI.

The data shown in Table V correlate roughly with known solvolysis rate constant data,[8] and this is shown in Figure 1. The partial saturation effect of C_β methyl substitution has been noted previously in the solvolysis data.

Strictly speaking, the Figure 1 plot should be of the calculated energy difference between neutral and cationic speices, but one expects that the effect of added methyls in the neutral compounds will be relatively small. Even accounting for this error, the calculated energy changes are still much larger than the corresponding $RT \ln K_{rel}$ numbers ($\Delta\Delta G^\ddagger$), and this must partly be because no account of solvation is involved in the calculations and also the transition states do not correspond to fully developed carbocations.

Orbital Energies. The usual simple picture of the bonding in a "bisected" cyclopropylcarbinyl cation is that given in Figure 2.

Since the antisymmetric Walsh orbital has the correct symmetry for a π-type overlap with C^+, the resulting four centre MO is herein called the π-MO. The remaining symmetric Walsh orbital in the cyclopropylcarbinyl cation will be referred to as the σ-MO and of course has no $2p_z$ C^+ component in it.

---

(7) (a) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979, Vol. II, p 1. (b) McLaughlin, R. G.; Traeger, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5791. (c) Dewar, M. J. S.; Thiel, W. *Ibid.* **1977**, *99*, 4907.

(8) Schleyer, P. v. R.; Van Dine, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 2321.

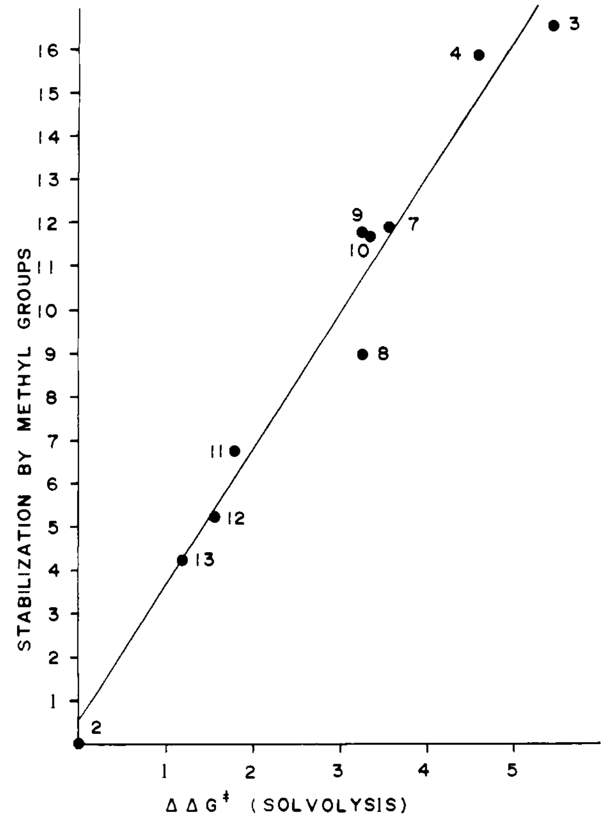


Figure 1. Plot of solvolysis rate data from ref 8 vs. the stabilization of the parent cyclopropylcarbinyl cation by added methyl groups, as calculated in Table V.

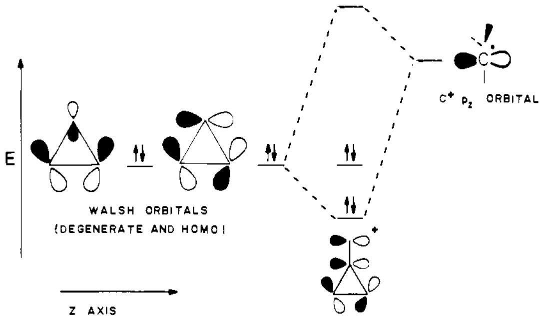


Figure 2. The simple fragment interaction diagram for constructing the two highest MO's of the cyclopropylcarbinyl cation.

This simple perturbational approach predicts that the π-MO should drop in energy below the σ-MO and indeed this is the order given in ref 9. However, calculations of the parent cyclopropylcarbinyl cation at the MNDO, STO-3G, 4-31G, and 6-31G* levels, as well as calculations involving some CI,[10] all show the π-MO to be the higher in energy (actually the HOMO for the ion).

Like other attractive and simple perturbation treatments, that shown in Figure 2 is valid, providing there are no gross geometric distortions after the fragments are joined. However, in the "bisected" cyclopropylcarbinyl cation case, this distortion is large and the Figure 2 diagram, while conceptually very useful, is not really correct.

The explanation for this reversal seems straightforward. The "need" for charge delocalization from the ring toward the "empty" C_1 carbon provides the basic starting point. However, this electron density must come from the C_α–C_β bonds, and these are therefore weakened. The C_β–C_β interaction is antibonding in the π-MO, and loss of electron density from the β-carbons decreases this unfavorable interaction. At this point the Figure 2 diagram applies, and as expected from this, the C_1–C_α bond shortens and the C_α–C_β bonds weaken.

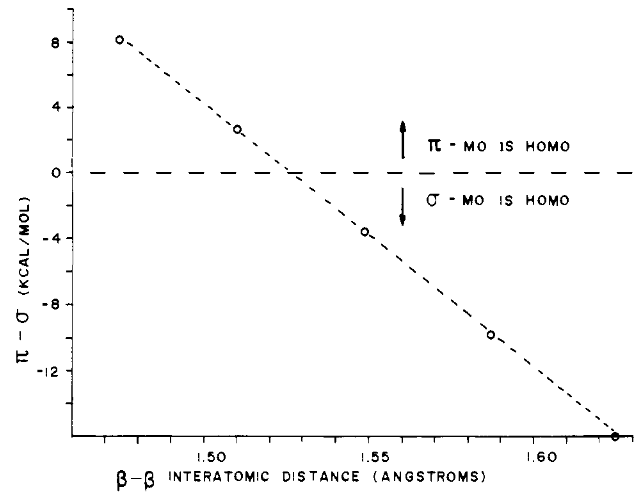


Figure 3. Variation of the π–σ MO energy difference (MNDO) in cation 2 as a function of the C_β–C_β bond distance. The C_β–C_β bond length was varied by changing the C_β–C_α–C_β angle while keeping all other gometry parameters constant. The optimized geometry is the point at the top left.

Table VII. Energy Separation (π–σ MO's) as a Function of Geometry and Type of Calculation

	energy sepn,[a] kcal/mol	
type of calculation	4-31G geometry	MNDO geometry
MNDO	20.23	8.20
STO-3G	30.85	13.66
4-31G	29.30	13.67
6-31G	29.55	
6-31G*		14.63

[a] In all cases the σ-MO is the lower in energy.

Table VIII. Energy Separation (π–σ MO's) as a Function of Methyl Group Substitution

cation	energy separation[a]	HOMO
3	−3.94	σ
7	−0.29	σ
8	0.16	π
6	13.11	π
2	13.66	π
16	12.98	π
14	14.30	π
15	15.01	π
13	25.42	π
20	7.51	π
21	11.15	π
22	11.10	π
23	10.92	π
24	5.09	π

[a] In kcal/mol.

However, the actual distortion goes farther, and one sees also a well-known shortening of the C_β–C_β bond. This raises the antibonding interaction in the π-MO (*decreases* bonding) but *increases* the bonding in the σ-MO, so rather subtle factors are obviously involved in the decision as to where the most stable arrangement will occur. In any case, in most of the cations studied, the σ-MO drops in energy well below the π-MO.

The π–σ MO separation for the parent cyclopropylcarbinyl cation also varies considerably depending on the calculation, and these results are shown in Table VII. Note however that the π–σ MO *order* is clearly the same even at the highest level ab initio calculation. The opposing nature of the C_β–C_β interaction in the π- and σ-MO's is likely the major reason why one can get rather

---

(9) Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

(10) Rauk, A., personal communication.

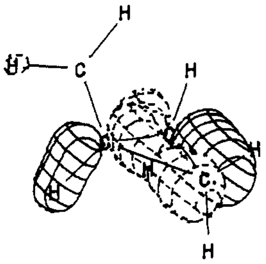


Figure 4. Wave function plot of the σ-MO in cation **2**.

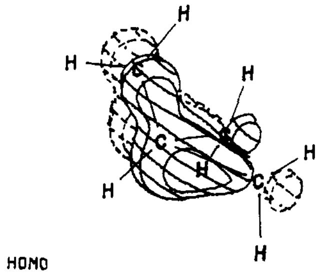


Figure 5. Wave function plot of the π-MO in cation **2**.

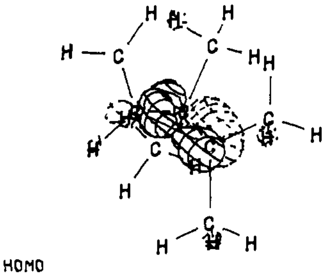


Figure 6. Wave function plot of the σ-MO in cation **3**.

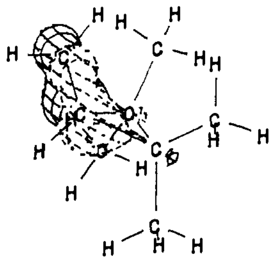


Figure 7. Wave function plot of the π-MO in cation **3**.

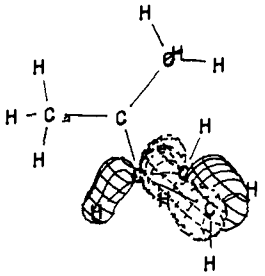


Figure 8. Wave function plot of the σ-MO in cation **16**.

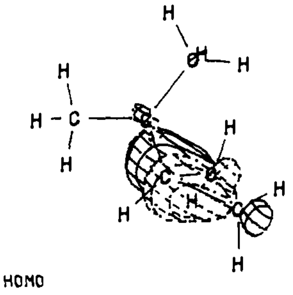


Figure 9. Wave function plot of the π-MO in cation **16**.

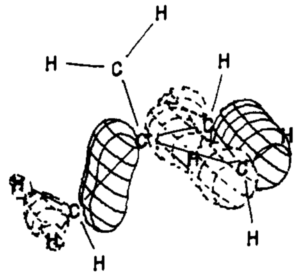


Figure 10. Wave function plot of the σ-MO in cation **13**.

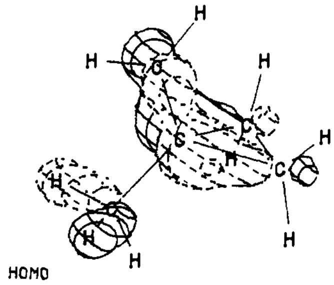


Figure 11. Wave function plot of the π-MO in cation **13**.

large geometry distortions with different basis sets. In other words, if the distortion did involve a nearly equal stabilization and destabilization of the σ- and π-MO's, then the total energy would not be a very sensitive function of geometry[11]. In agreement with this, in the more distorted 4-31G geometry, there is a much larger separation of the π- and σ-MO's (see Table VII).

The quantitative effect of the C_β–C_β bond length on the π-σ MO energy separation is also readily apparent if we fix all of the optimized parameters in the MNDO calculation and simply open up this bond. This is shown in Figure 3. Similarly, at the 4-31G level, fixing the three cyclopropane bonds at either 1.51 or 1.54 Å also leads to the Figure 2 MO energy ordering (σ higher than π by 9.6 and 10.8 kcal/mol, respectively.)

π–σ MO Energy Separation in Methyl-Substituted Cyclopropylcarbinyl Cations. This energy separation varies with structure, and the values are reported in Table VIII. Note the reversal of the π–σ MO levels to the "normal" order in the case of the tetramethyl cation **3**. In this cation, the electron density on the β-carbons is further lowered compared to that of **2**, and hence the antibonding interaction is reduced in the π-MO. In this case, however, there is no further shortening of the C_β–C_β bond so the π-MO stays lowered in energy. The π- and σ-MO's for cations **2** and **3**, as well as for **13** and **16** are shown in Figures 4–11,[13] and these illustrate the features described above, e.g., the small antibonding interaction in the π-MO of **3**.

The α-methyl cation **13** is an interesting case, in that the π–σ MO separation is even larger than in the parent cation, in spite of this ion having the smallest methyl energy stabilization of any of the ions (see Table V). The MO plots in Figures 10 and 11 illustrate clearly the off-setting bonding and antibonding character of the α-methyl group in the two MO's.

Unsymmetrical bisected structures such as ions **4**, **5**, **10**, **11**,

---

[11] In all these and subsequent discussions one has to be careful. Geometry changes are based on total energy, which in turn involves all occupied orbitals.

[12] These absolute values are undoubtedly a sensitive function of the optimized geometry of any given cation. We have previously noted the more distorted 4-31G geometry, compared to MNDO, for the parent **2** (and hence large π–σ MO energy difference). On methyl substitution, we would expect *similar trends* no matter which geometry (MNDO-like or 4-31G-like) was used. It is not feasible at this time to get 4-31G-optimized geometries for **3**–**16**.

[13] The figures were generated by using the plotting program of Jorgensen: Jorgensen, W. L. Program No. 340, Quantum Chemistry Program Exchange; Indiana University: Bloomington, Indiana.

Table IX. Energies of Isomerization of "Bisected" to "Perpendicular" Cyclopropylcarbinyl Cations

ion	ΔE, kcal/mol
3	31.80
2	26.31[a]
16	13.21[b]

[a] Previously reported, using the STO-3G basis set and geometry optimization, as either 25.7[2e] or 26.3 kcal/mol.[2d] Our use of the optimized MNDO geometries obviously gives similar results. Some older estimates have also appeared. [b] Previously reported, using an STO-3G basis set and geometry as 12.3 kcal/mol[2e]. Also reported using unoptimized geometry as 17.54 kcal/mol[2f] (STO-3G) and as 16.6 kcal/mol (no details).[2c] Some older estimates using semiempirical procedures have also been reported.

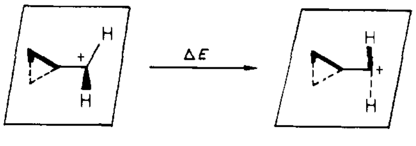
and **12** tend to mix π- and σ-MO's and these have not been further analyzed.

It is not obvious that the reversed π–σ energy levels in **2**, or the "normal" order in **3**, have any direct chemical significance other than to show the pitfalls involved in simple perturbation analysis. However, spectroscopic properties, e.g., PE spectroscopy, might show some changes. Furthermore, in looking at ways to stabilize these cations, one should focus on the σ-MO as well as the π-MO. For example, a C_α substituent might be made very stabilizing if we could find some bonding interaction in the σ-MO, as shown by methyl, and lessen the antibonding properties shown by this particular group in the π-MO.

In concluding the discussion on the π–σ MO's, we wish to emphasize the synergistic effects involved here. Obviously the π-MO is the important orbital interaction involved in the charge delocalization. This however ultimately allows the σ-MO to be the more stabilized (except in the case of **3** and **7**).

Resonance or Stabilization Energies. No rigorous, unambiguous definition of the resonance energy of a cyclopropylcarbinyl cation seems possible to us. There are, however, two reasonable procedures which one can apply, although we will later show that one has to be careful that one has in fact chosen the appropriate reference compound.

Energy Differences between "Bisected" and "Perpendicular" Cyclopropylcarbinyl Cations. The resonance energy of allyl cations has been evaluated as the energy difference between the planar and 90° twisted form.[14] Likewise, one can evaluate the energy difference between the ground-state "bisected" form and the 90° twisted form, the "perpendicular" geometry. The "perpendicular" geometry, like the allyl equivalent, has no π overlap of the C^+ center with the ring, but as has been noted in the previous section, the σ-MO is also involved here and this is a complicating feature peculiar to the cyclopropylcarbinyl cations.

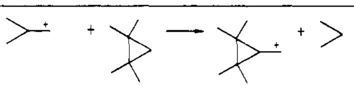
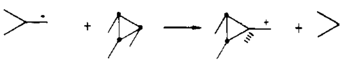
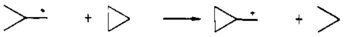
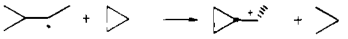
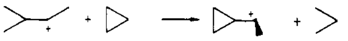


"bisected" "perpendicular"

We have evaluated the energy difference between the "bisected" and "perpendicular" geometries for cations **2**, **3**, and **16**, and these are shown in Table IX. Two of the cations, **2** and **16**, have previously been computed, and in the latter case an experimental rotation barrier (C_α–C_1) is known[15,16] (13.7 kcal/mol).

The 90° twist energies in Table IX show the expected increase in going from **16** to **3**; i.e., the importance of the vinyl-bridged canonical form (e.g., **2b**) is expected to increase in this order. This change is also apparent from a visual comparison of the π-MO's in **3**, **2**, and **16**; see Figures 5, 7, and 9. In the case of **16**, the C_1–C_α overlap is very small, while in **3**, this is dominant.

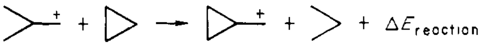
Table X. Resonance Energies of Cyclopropylcarbinyl Cations Determined by Isodesmic Reactions

reaction	ion formed	$-\Delta E$,[a] kcal/mol
	3	35.66
	6	32.79
	7	31.41
	8	28.50
	2	20.95
	15	14.37
	14	12.56
	16	11.04

[a] These reactions can also be used to calculate ΔH_f values for these cations (see Table IV).

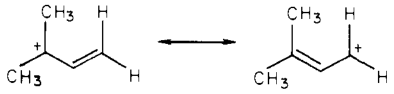
One has to realize however that the π-MO is *only partly* (and probably indirectly from an energy standpoint) responsible for the stabilization of the "bisected" cation. One is looking, of course, at the *total energy difference* between the two geometries. It is therefore much too simplistic to simply look at the C_1–C_α electron density in the π-MO. We believe that this shows up, in fact, in the 1,1-dimethyl species **16**, where the π-MO in Figure 9 shows only a small C_1–C_α overlap electron density. The calculated barrier for rotating the C^+ group by 90° is sizeable however (13.2 kcal/mol).

Isodesmic Reactions as Models for Cyclopropylcarbinyl Resonance Energies. A second procedure for obtaining resonance or stabilization energies involves the previously discussed isodesmic reactions (Table IV), i.e.



A more complete listing of $\Delta E_{\text{reaction}}$ values is given in Table X. These data parallel rather closely the energy differences between "bisected" and "perpendicular" cyclopropylcarbinyl cations. This is expected, of course, if the "perpendicular" cations behave energy-wise like simple aliphatic carbocations, i.e., with no "special" stabilization modes.

Criteria for Defining Resonance Energies and the "Best" Single-Structure Canonical Form for Cyclopropylcarbinyl Cations. The fallacy with our previous definition of the resonance energy of **2**–**16** is that we have presupposed the cyclopropylcarbinyl canonical form, e.g., **2a**, to be the most important contributor to the actual structure. One can illustrate the potential pitfall of such an assumption by using the unsymmetrical allyl cation **17**, whose extreme resonance forms are **17a** and **17b**.



17a 17b

If we were to measure the C_2–C_3 rotation barrier or formulate an isodesmic reaction giving **17b**, we would arrive at a much higher "resonance" energy than if we used the major contributor **17a** (C_1–C_2 rotation barrier). However, **17a** would be the correct reference comparison.

Dewar[2b] has applied bond order and charge delocalization comparisons to deduce the relative importance of **2a** and **2b** to the structure of **2**. His conclusion is that **2b** comes closer than **2a** to the actual structure. Obviously, on this basis, our "resonance" models would indeed be suspect. However, bond order

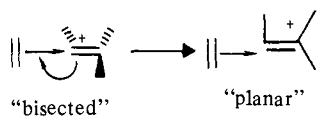
---

(14) (a) Mayr, H.; Forner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032. (b) Radon, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1973**, *95*, 6531.

(15) Kabakoff, D. S.; Namanworth, E. *J. Am. Chem. Soc.* **1970**, *92*, 3234.

(16) The rotation barrier could conceivably be higher than the "bisected"–"perpendicular" energy difference. However, Bach and Blanchette[2q] have calculated some intermediate rotation energies, and these suggest a smooth curve maximizing at the 90° twist.

Table XI. Energies of Isomerization of "Bisected" to "Planar" Cyclopropylcarbinyl Cations[a]



ion	ΔE, kcal/mol
3	29.33
2	42.9
16	60.45

[a] Dewar's structural representations are particularly useful for showing this process.

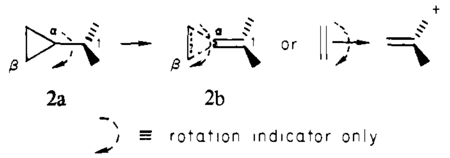
Table XII. Comparisons of Resonance Energies (ΔE) Obtained Using Either "Bond" Rotations or Isodesmic Reactions

	ΔE(carbinyl model)[a]		ΔE(vinyl-bridging model)[a]		fraction of vinyl-bridging character[b]	
ion	isomerization[c]	isodesmic[d]	isomerization[e]	isodesmic[f]	isomerization	isodesmic
3	31.80	35.66	29.33	27.96	0.52	0.56
2	26.31	20.95	42.92	33.98	0.38	0.38
16	13.21	11.04	60.45	56.75	0.18	0.16

[a] In kcal/mol. [b] Calculated[20] as ΔE(carbinyl model)/ΔE(carbinyl model) + ΔE(vinyl-bridging model). [c] Table IX. [d] Table X. [e] Table XI. [f] Table XIII.

comparisons are often complicated by other factors, and we believe that alternative procedures need to be devised. We therefore suggest two completely general procedures[17] for deciding the relative importance of resonance forms **2a** and **2b** etc., both based on *energy* considerations.

C_α–C_β vs. C_1–C_α 90° Twist Energy Comparisons. Rotation of the C_1–C_α bond in **2**–**16** by 90° formally destroys the "extra" π overlap of a cyclopropylcarbinyl canonical form, e.g., **2a**, while 90° rotation about the C_α–C_β bond in **2b** etc. formally destroys the "extra" π overlap of a bridging vinyl cation canonical form.[18] The more the *actual* structure resembles **2a**, the lower the C_1–C_α 90° twist energy difference and the higher that for the C_α–C_β 90° twist. The more the actual structure resembles **2b**, the lower the C_α–C_β 90° twist energy difference and the higher the C_1–C_α value.



The C_1–C_α values have been given in Table IX, while those for the C_α–C_β twist difference are given in Table XI. The comparisons have been limited to the parent ion **2** and the two extreme cyclopropylcarbinyl cations **3** and **16** and are given in Table XII.

Only in the case of ion **3** do we find the bridging vinyl cation structure marginally dominant.[20] Cation **16** is much better represented by the cyclopropylcarbinyl canonical form, as expected.

Isodesmic Reactions as a Criteria for Determining Resonance Energies and the "Best" Canonical Structure. The two isodesmic reactions eq 2 and 3, express the same intent as the two 90° twist energy differences.

Thus, the stabilization energy in the first case is the "extra" stabilization of a cyclopropylcarbinyl cation relative to an aliphatic cation, while that in the second is the "extra" stabilization relative to an alkyl-bridged ethylene cation. Data for the first case (eq 2) have already been presented in Tables IV and X and are shown here only for comparison purposes. Data for eq 3 are given in Table XIII,[21] and a comparison of eq 2 and 3 for cations **2**, **3**, and **16** is given in Table XII, in which the data for the two procedures, the 90° twist energy differences, and the isodesmic reactions are collected together and compared. It is gratifying to note the similarity in the data.

Table XIII. Resonance Energies of "Vinyl-Bridged Ethylene" Cations Using Isodesmic Reactions

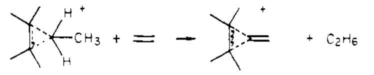
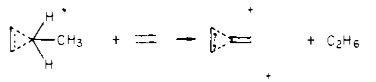
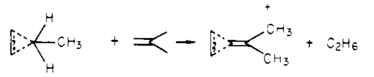
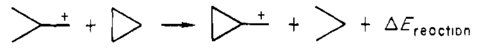
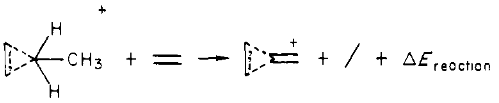
reaction	ion formed	−ΔE, kcal/mol
	3	27.96
	2	33.98
	16	56.75

Table XIV. Formal Charges in the Cyclopropylcarbinyl Cations

	charge		
ion	β region	α region	C_1 region
3	0.614	−0.022	0.407
4	0.604	−0.014	0.409
5	0.602	−0.016	0.414
6	0.536	+0.050	0.414
7	0.562	−0.005	0.443
8	0.567	−0.007	0.440
9	0.564	−0.006	0.442
10	0.583	−0.005	0.423
11	0.538	+0.003	0.459
12	0.540	+0.002	0.457
13	0.472	+0.070	0.457
2	0.499	+0.014	0.487
14	0.430	−0.005	0.574
15	0.425	−0.003	0.577
16	0.370	−0.014	0.645



(2)



(3)

Overall, we believe that these procedures allow for a reasonably objective evaluation of the relative importance of the two canonical forms (e.g., **2a** and **2b**) in the cyclopropylcarbinyl cation. In terms of a *single structure* representation, **16** is correctly written without dotted lines since the structure is much closer to **16a** than to even an average of **16a** and **16b**. Cations **2** and **3** are obviously close to a true hybrid of extreme structures **2a** or **3a** and **2b** or **3b**, and this should somehow be conveyed in a written structure. The usual depiction of this is structure **18**, with a dotted line between C_1 and C_α. In contrast to our extreme structure **2a**, the dotted C_α–C_β "bonds" have *additional* electron density from the π-MO. Although one uses a dotted line in both cases, one must mentally make a distinction between these for the purposes of the discussion

---

(17) Although general, the definitions are still arbitrary.

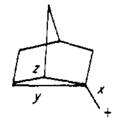
(18) There is an analogy here with bridged dialuminum compounds. With mixed alkyl and vinyl groups, the vinyl group is preferred at the bridging position because of the extra π-type overlap possible with empty aluminum orbitals.[19]

(19) (a) Albright, M. J.; Butler, W. M.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 3995. (b) Zweifel, G.; Clark, G. M. *Ibid.* **1971**, *93*, 527.

(20) There is no very obvious justification for assuming that these ΔE numbers are additive etc. However, the indicated mathematical manipulations seem intuitively reasonable as an *approximation* of canonical structure importance.

(21) "Perpendicular" cyclopropylcarbinyl cations were fully geometry-optimized within the restrictions of a fixed 90° twist and equal C_α–C_β bond lengths. They still possess C_s symmetry in the examples studied; i.e., both C_α–C_β bonds are equivalent. The C_α–C_β 90° twist structures also have C_s symmetry and form "planar" cyclopropylcarbinyl cations. However, the C_α–C_β "bonds" are not related by symmetry. We have however optimized the geometry of the "planar" cations, arbitrarily[16] making the C_α–C_β "bonds" equal. The bridged cation structures calculated for the isodesmic reactions have higher order (C_s) symmetry, and in all cases the C_α–C_β "bonds" are symmetry related. In any case, these "bonds" were always kept equal in the geometry optimizations.

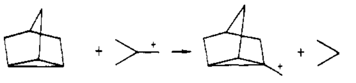
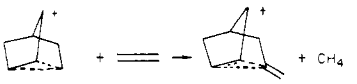
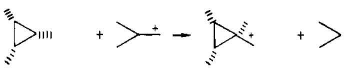
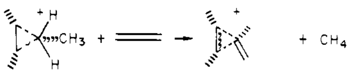
Table XV. Important Geometry Parameters for the MNDO-Optimized Geometries[a]



ion	bond lengths, Å		
	x	*y*	*z*
20	1.384	1.658	1.489
21	1.400	1.646	1.493
22	1.400	1.649	1.493
23	1.420	1.636	1.499
24	1.383	1.679	1.499

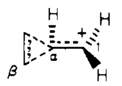
[a] Optimized Z matrices are available as supplementary material.

Table XVI. Isodesmic Reaction Comparisons for Cations 20 and 6

reaction	$-\Delta E$, kcal/mol	approx vinyl-bridging ethylene cation character[a]
 20a	36.85	0.57
 20b	27.95	
 6a	32.79	0.50
 6b	33.31	

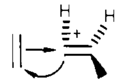
[a] See Table XII, footnote *b* for the definition of this quantity. See also ref 20.

in this paper. Dewar has used the double-arrow structure **19** to convey the same information with the single-arrow depiction corresponding to our extreme resonance form **2a**.[3]



18

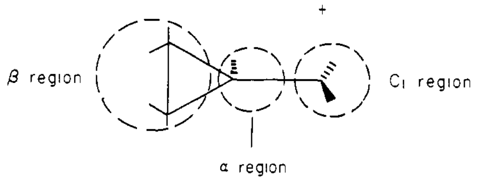
or



19

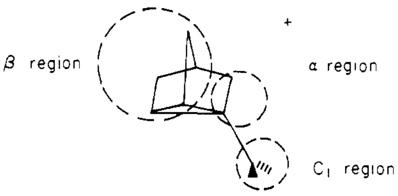
If one were to be totally logical in applying the criteria shown in Table XII, then cation **3** should be referred to as a vinyl-bridged tetramethylethylene cation.

Charge Delocalization. The STO-3G charge delocalizations are given in Table XIV. In order to compare nonisomeric species, we have simply broken the cation up into three regions, as shown.



The ratio of the charge at the C_1 region to that at the β region changes in the expected way as one varies the methyl substitution. The α-position is essentially neutral.

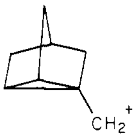
Table XVII. Formal Charges in the Nortricyclylcarbinyl Cations



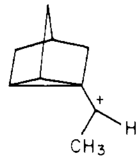
ion	charge		
	β region	α region	C_1 region
20	0.575	0.031	0.394
21	0.525	−0.006	0.481
22	0.526	−0.005	0.479
23	0.465	−0.020	0.555
24	0.651	0.001	0.349

Nature of the Nortricyclylcarbinyl Cations. Calculations have also been carried out on the nortricyclylcarbinyl cations **20–24**. The preparation of **20–23** has been described in the preceding article.[1]

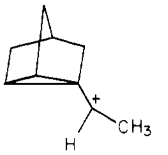
Optimized geometries are reported in Table XV. Our principle interest in this MO study was to see if calculations suggested a strengthening of the vinyl-bridged 2-norbornyl "character" in the primary cation **20**, relative to the α,β,β'-trimethylcyclopropylcarbinyl cation **6**. There is, of course, evidence that the 2-norbornyl geometry is especially favorable toward this kind of bridging.[22]



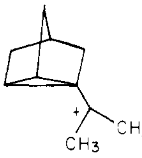
20



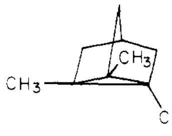
21



22



23



24

The pertinent isodesmic reaction comparisons are given in Table XVI. Clearly, on the basis of our previous discussion, cation **20** has a higher vinyl-bridging character than **6** and correspondingly a lower cyclopropylcarbinyl character. Indeed, from the figures in Table XVI we should name cation **20** as a vinyl-bridging 2-norbornyl cation.[23]

Data on the π-σMO energy separation in cations **20–24** are included in Table VII. Charge delocalization data are given in Table XVII and show the expected changes with structure.

Cation **24** has not yet been reported but should intuitively be an even better vinyl-bridging species, and this is corroborated by the MO calculations.

Acknowledgment. We thank the N.S.E.R.C. of Canada for financial support. We also appreciate the advice and help of Dr. A. Rauk and Mr. K. Wagstaff.

Registry No. 2, 14973-56-9; **3**, 80997-20-2; **4**, 80997-21-3; **5**, 80997-22-4; **6**, 80997-23-5; **7**, 80997-24-6; **8**, 81026-58-6; **9**, 81026-59-7; **10**, 80997-25-7; **11**, 80997-26-8; **12**, 80997-27-9; **13**, 27761-35-9; **14**, 27861-45-6; **16**, 25681-56-5; **20**, 78607-00-8; **21**, 80997-28-0; **23**, 80997-29-1; **24**, 80997-30-4; 1,1,2-trimethylpropylium, 17603-18-8; 1,1-dimethylethylium, 14804-25-2; 1-methylethylium, 19252-53-0; 2-methylpropylium, 19252-54-1; ethylium, 14936-94-8; cyclopropane, 75-19-4; 1,2-dimethylpropylium, 25453-96-7; 1,1,2,2-tetramethylcyclopropane, 4127-47-3; (1α,2α,3α)-1,2,3-trimethylcyclopropane, 4806-58-0; *cis*-1,2-dimethylcyclopropane, 930-18-7.

Supplementary Material Available: MNDO-optimized geometries for cations **2–16** and **20–24** (12 pages). Ordering information is given on any current masterhead page.

---

(22) For reviews, see: (a) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41. (b) Sargent, G. D. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, **1972**; Vol. III, p 1099.

(23) The bridged 2-norbornyl cation is a *reference* compound in our calculations, and it does not matter whether this is a hypothetical or real species. We assume of course that cation **22** is symmetrical.