

# Brother versus brother: competitive stabilization of carbocationic centers by flanking cyclopropanes and $\pi$ -systems

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**ABSTRACT:** B3LYP and MP2 quantum chemical calculations on cyclopropylcarbiny cations fused to various cyclic and polycyclic architectures are described. ‘Competition’ for delocalization between the cyclopropane and other cyclopropanes and/or  $\pi$ -systems incorporated into the (poly)cyclic framework to which it is fused was assessed, primarily through the use of characteristic geometric perturbations to the cyclopropane substructure. For example, a linear correlation between the orientation of the ‘empty p-orbital’ at the carbocationic center, which is affected by the nature of the (poly)cyclic framework, and the magnitude of bond elongation in the cyclopropane was observed. Possible bis- and trishomoaromaticity of some systems was also evaluated using nucleus independent chemical shift (NICS) and magnetic susceptibility exaltation calculations. Copyright © 2007 John Wiley & Sons, Ltd.

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**KEYWORDS:** cyclopropane; polycyclopropane; cyclopropylcarbiny; carbocation; polycyclic; homoaromatic; trishomoaromatic; substituent effects

## INTRODUCTION

It is well known that the C—C bonds in cyclopropanes have more  $\pi$ -character than those in less strained systems.<sup>1</sup> This begs the question: to what extent can such bonds behave like  $\pi$ -bonds and participate in the stabilization of adjacent cationic centers? This question has a long history,<sup>2,3</sup> and is of particular interest to us in that terpenoids can be both synthesized and biosynthesized via cationic rearrangement reactions that involve putative intermediates containing cyclopropane rings.<sup>4,5</sup> Although a great deal of studies – both experimental and theoretical – have explored the ability of cyclopropane rings to interact directly with carbocation centers,<sup>2,3</sup> it is the purpose of this study to (1) determine the effects of constraining cyclopropylcarbiny cation groups in bicyclic structures (Chart 1a), (2) to assess the relative donating abilities of two different cyclopropanes flanking a single carbocation center in polycyclic systems that constrain their relative orientations (Chart 1b), and (3) to define the geometric and electronic perturbations that are necessary to allow a cyclopropane ring to out-compete a C=C  $\pi$ -bond in stabilizing a carbocation center wedged

between them (Chart 1c). We address these issues using quantum chemical (B3LYP and MP2) calculations.

## COMPUTATIONAL METHODS

All calculations were performed with *GAUSSIAN03*.<sup>6</sup> Geometries were optimized without symmetry constraints at the B3LYP/6-31G(d)<sup>7</sup> and MP2/6-31G(d)<sup>8</sup> levels of theory. All structures were characterized by frequency analysis, and reported energies include zero-point energy corrections scaled by 0.9806 for the B3LYP/6-31G(d) level and by 0.9661 for the MP2/6-31G(d) level.<sup>9</sup> All of structures **1–8** and the structures in Schemes 2 and 3 are fully optimized minima except for structures **4a-H**, **4b-H**, **4c-H**, and **5c**. We have found that B3LYP and MP2 often produce similar results for structures of the sort described herein, although MP2 tends to slightly favor more delocalized geometries than does B3LYP, in accord with previous comparisons of the two methods.<sup>10</sup> GIAO-B3LYP/6-31G(d)//B3LYP/6-31G(d) and GIAO-B3LYP/6-31G(d)//MP2/6-31G(d) nucleus independent chemical shift (NICS(0)) and NICS(1) values were calculated for selected cations to assess their aromatic character.<sup>11,12</sup> For cations **4a–c**, isodesmic reactions allowed for evaluation of their aromatic nature based on both aromatic stabilization energies (ASE’s) and magnetic susceptibility exaltations ( $\Lambda$ ) calculated at the

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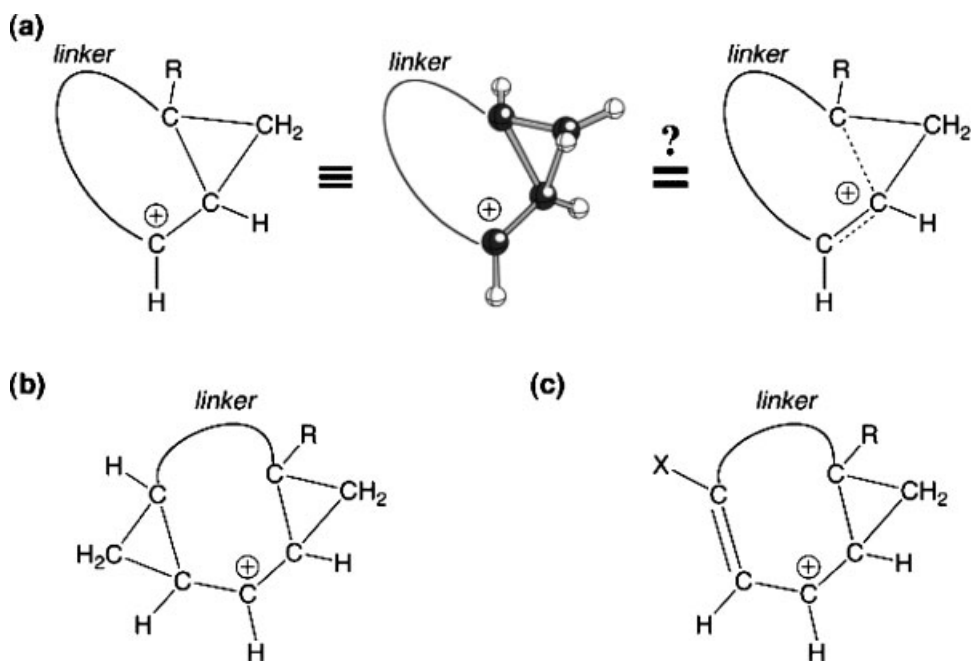


Chart 1.

CSGT-B3LYP/6-31G(d)//B3LYP/6-31G(d) and CSGT-B3LYP/6-31G(d)//MP2/6-31G(d) levels of theory.<sup>13</sup> Intrinsic reaction coordinate (IRC)<sup>14</sup> calculations were performed to verify the identity of transition state structure **5c**. Structural drawings were produced using *Ball & Stick*.<sup>15</sup>

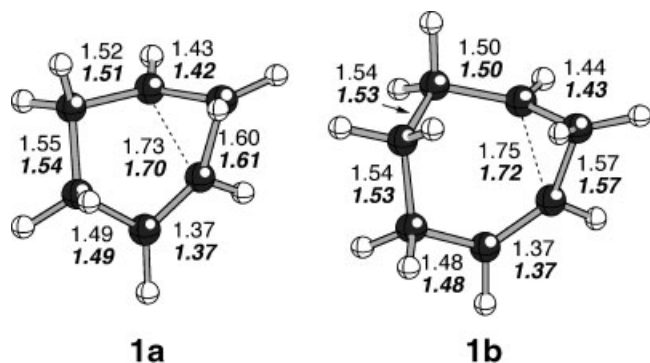
## RESULTS AND DISCUSSION

### Geometrically constrained cyclopropylcarbanyl cations

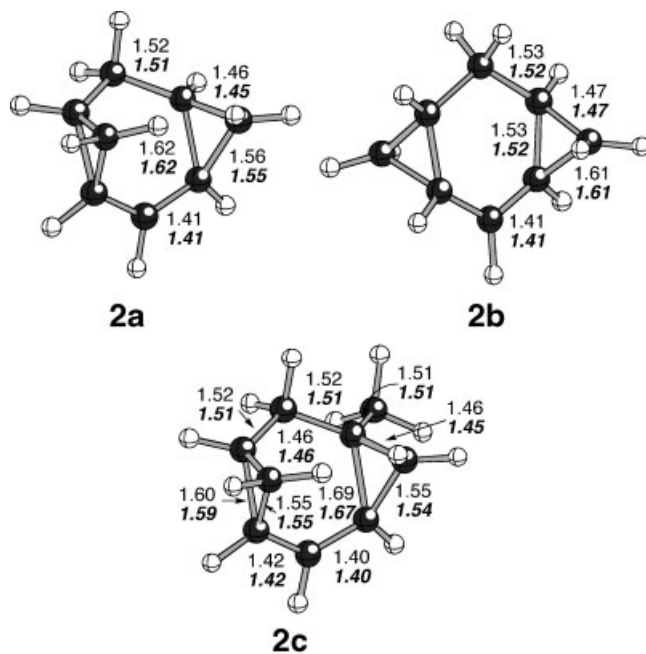
The simplest cation considered herein (**1a**<sup>21</sup>, Fig. 1) contains just an ethylene linker (Chart 1). In this system, the positive charge is highly delocalized through the interior bond of the cyclopropane ring, which is accompanied by extensive lengthening of the fused cyclopropane C—C bond (to  $\sim 1.7$  Å; for comparison, the internal bond in bicyclo[3.1.0]hexane is 1.52 Å with

B3LYP/6-31G(d) and 1.51 Å with MP2/6-31G(d)) and concomitant shortening of the attached C—C bond (to  $< 1.4$  Å). Extension of the linker by an additional methylene group results in carbocation **1b**<sup>2m</sup> (Fig. 1). In this case, the interior bond is even further lengthened, reflecting the delicate balance between strain in the cyclopropane substructure and in the linker.

Fusion of a second cyclopropane ring to **1b**, in either a *syn* or *anti* relationship with respect to the first cyclopropane, results in cations **2a** and **2b** (Fig. 2),

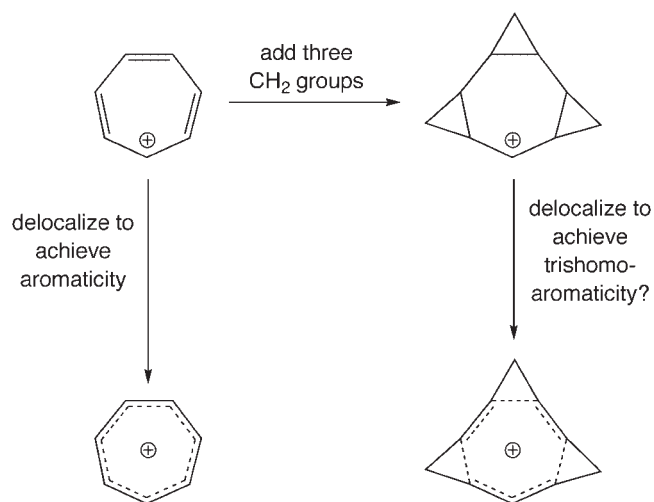


**Figure 1.** Geometries of carbocations **1**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in bold italics)



**Figure 2.** Geometries of carbocations **2**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in bold italics)

respectively. Note that changing the relative disposition of the two cyclopropane rings changes which of their bonds is elongated; in  $C_s$ -symmetric **2a**, the interior bond of each is lengthened, while in  $C_2$ -symmetric **2b**, the other C—C bond adjacent to the cationic center is lengthened, reflecting the geometric constraints imposed on the methine center (and its ‘empty p-orbital’) by the two different tricyclic frameworks. In both **1a** and **1b**, cyclopropane C—C bonds are lengthened dramatically, but in **2a** and **2b** the interaction is spread between two cyclopropanes, leading to less bond elongation for each.<sup>2</sup> Note also that one cyclopropane ring of **2b** can be preferentially elongated by simply adding a cation-stabilizing substituent such as a methyl group (**2c** Fig. 2), to one of the cyclopropane carbons distal to the cationic center.



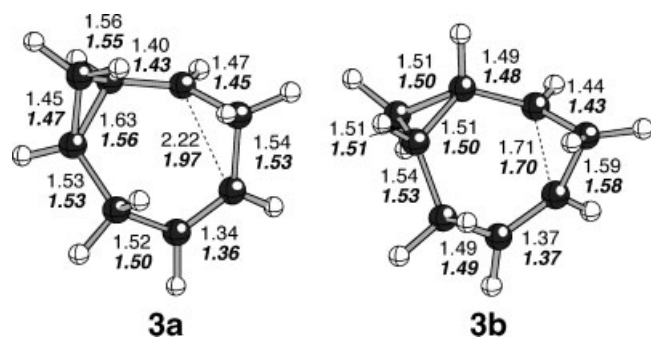
Scheme 1

### Extending the delocalization?

An alternative mode of fusing a second cyclopropane to **1b** is to place the two cyclopropanes adjacent to each other (rather than to the cationic center), leaving a methylene between one of them and the methine group. The resulting *syn* and *anti* isomers, **3a** and **3b**, are shown in Fig. 3. In the case of cation **3a**, the cyclopropane ring nearest to the methine group essentially opens to produce a C=C double bond and a new cyclopropylcarbanyl substructure. Thus, cation **3a** contains overlapping cyclopropylcarbanyl and homoallyl carbocation substructures. The geometric differences between the hydrocarbon frameworks of **3a** and **3b** result in a rather different situation for **3b**. In this system, the delocalization is restricted to the first cyclopropane ring, for which elongation of the interior C—C bond is comparable to that observed for cation **1b** (Fig. 1).

### Homoaromatic variants?

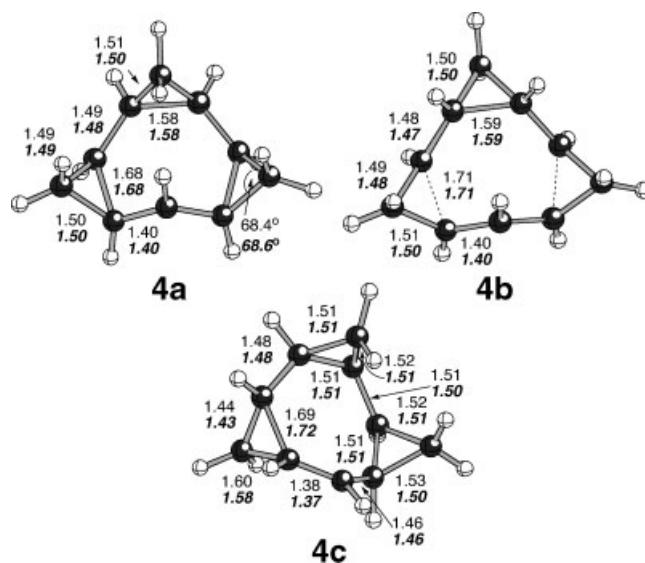
Larger systems with three cyclopropane rings surrounding a cationic methine group like a pair of calipers have



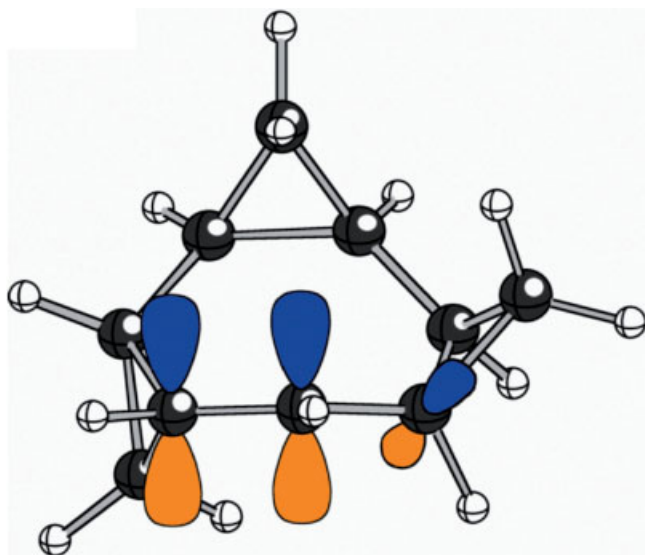
**Figure 3.** Geometries of carbocations **3**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in bold italics)

the potential for trishomoaromaticity. These systems are related to the cycloheptatrienyl (or tropylium) cation by the addition of three methylene groups (Scheme 1).<sup>16</sup> Several isomers differing in the relationships of their methylene groups (*syn* or *anti*) are possible; the computed geometries of these structures (**4a–c**) are shown in Fig. 4.

The extent of elongation of the interior cyclopropane C—C bonds that flank the methine groups in cations **4a** and **4b** is slightly greater than that observed for cation **2a**, and the delocalization appears to be extended through the distal cyclopropane whose interior C—C bond is elongated to almost 1.6 Å for both **4a** and **4b**. Cation **4c** is structurally related to cations **2b** (*anti* cyclopropanes flanking a methine group), **3a** (two *syn* cyclopropanes on



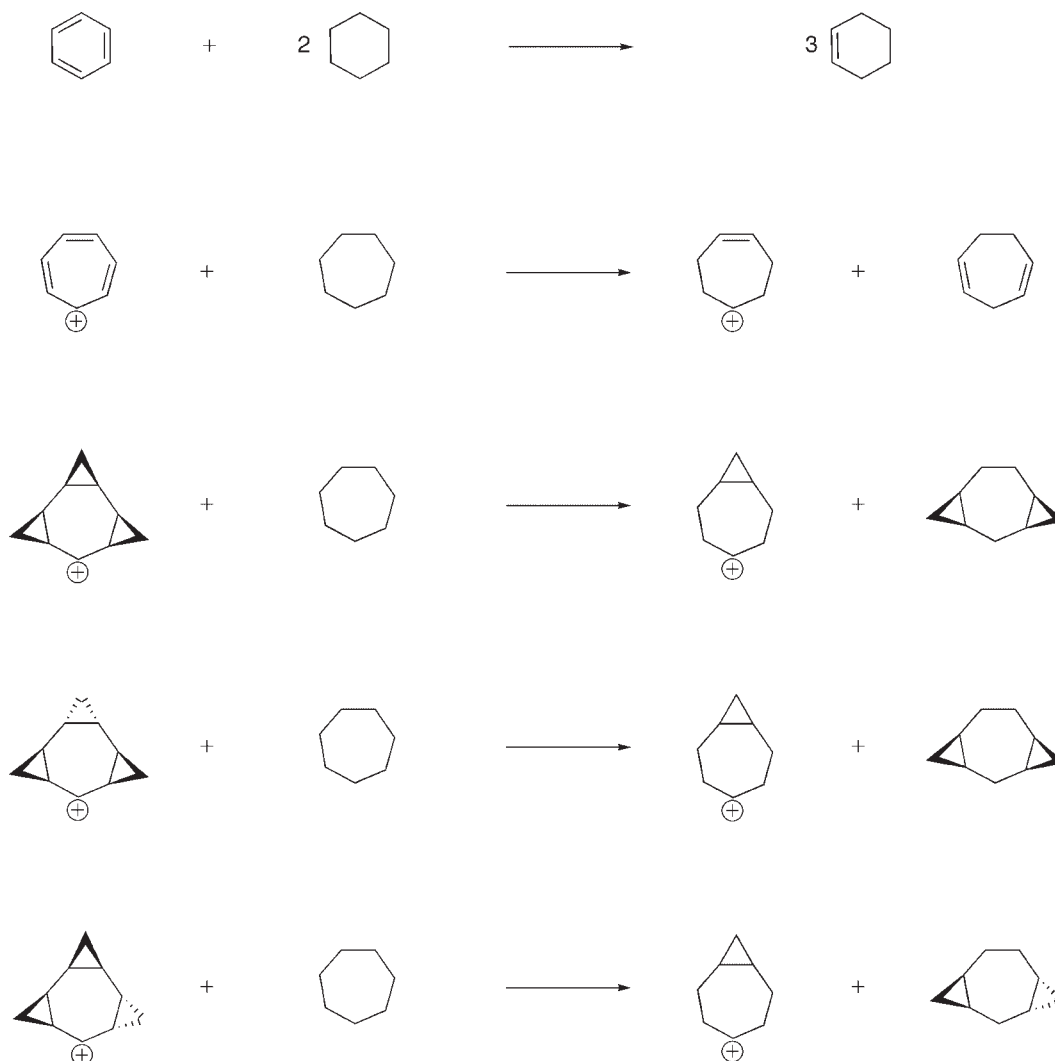
**Figure 4.** Geometries of carbocations **4**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in bold italics)



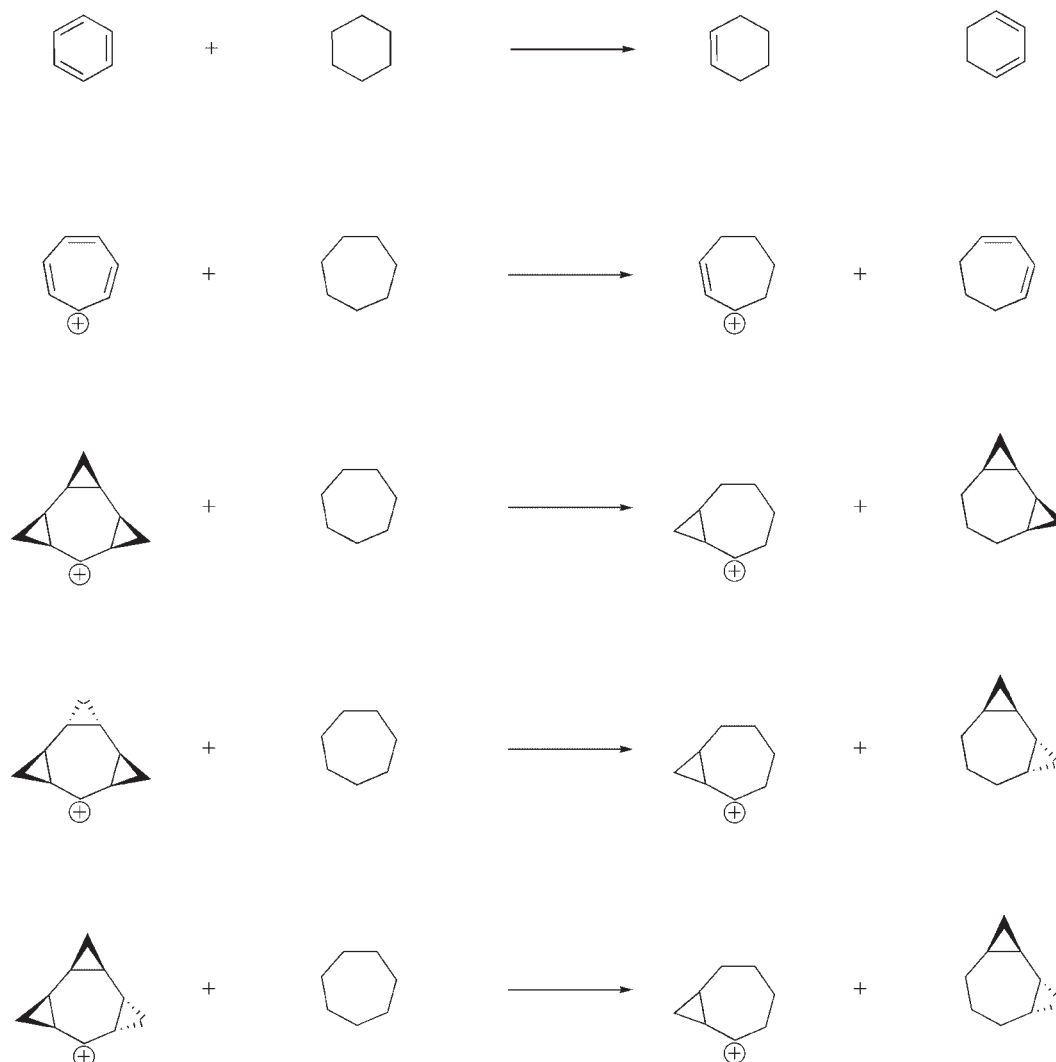
**Figure 5.** Orbital overlap in cation **4c** (cyclopropyl donor orbitals are approximated here by simple p-orbitals). Note that the p-orbital of the left cyclopropane ring is aligned with the empty p-orbital of the cation, while the right cyclopropane is out of alignment

one side of a methine group), and **3b** (two *anti* cyclopropanes on one side of a methine group). Cation **2b** displays symmetric elongation of the closest exterior cyclopropane bonds, cation **3a** displays severe elongation of the closest interior cyclopropane bond and moderate elongation of the next interior cyclopropane bond, and cation **3b** displays elongation of the interior cyclopropane bond of one ring, and no elongation in the other ring. Interestingly, cation **4c** exhibits characteristics of both **2b** and **3b**, as both the interior and closest exterior bonds of one (the *anti*-oriented) cyclopropane ring are elongated. Note that since the 'empty p-orbital' of the methine group in **4c** is roughly aligned with the two elongated bonds of the *anti*-oriented cyclopropane, it essentially bisects the other flanking cyclopropane ring, and therefore no significant delocalization involving this ring is observed (Fig. 5).

Since it is not entirely clear from the geometries of cations **4a–c** whether or not they might be aromatic, several standard methods for probing aromaticity were



**Scheme 2**



Scheme 3

applied. First, consider cations **4a** and **4b**. NICS(0) and NICS(1) values calculated at the GIAO-B3LYP/6-31G(d)//B3LYP/6-31G(d) and GIAO-B3LYP/6-31G(d)//MP2/6-31G(d) levels of theory for **4a** and **4b** are large and negative (Table 1, *cf.* benzene, tropylium), indicating a substantial ring current. Differences between NICS(1) values calculated on the  $\alpha$  and  $\beta$  faces of **4a** and **4b** are most likely due to the close proximity of some methylene groups to the points at which NICS(1) values were computed. For comparison, the NICS(0) values were also calculated after addition of a hydride to **4a** and **4b**.<sup>17</sup> NICS(0) values close to zero would be expected for these new structures (**4a-H** and **4b-H**) if the large NICS(0) values for **4a** and **4b** were the result of cyclic delocalization, and this is exactly what is observed (Table 1). The methylene hydrogens of the distal cyclopropane ring also have the possibility of being good reporters on the aromaticity of the ring; however, interpretation of the computed chemical shifts for these

hydrogens is not straightforward.<sup>18</sup> ASE's were also calculated (Table 1) based on the isodesmic reactions shown in Schemes 2 and 3, and the resulting stabilization energies for **4a** and **4b**, although smaller than those of benzene and tropylium, do indicate substantial stabilization. Further, magnetic susceptibility exaltations ( $\Lambda$ ) were calculated from the same isodesmic reactions at the CSGT-B3LYP/6-31G(d)//B3LYP/6-31G(d) and CSGT-B3LYP/6-31G(d)//MP2/6-31G(d) levels of theory,<sup>13</sup> and the resulting values (Table 1) again suggest that cations **4a** and **4b** are somewhat aromatic.

When the same measures of aromaticity are applied to cation **4c**, the situation is less clear. First, the geometry of **4c** (Fig. 4) does not show any lengthening of the C—C bonds in its distal cyclopropane ring. The NICS(0) and NICS(1) values computed for **4c** (Table 1) are also considerably smaller than those computed for **4a** and **4b**, and the NICS(0) value computed for **4c-H** is not very different than that for **4c**. In addition, the magnetic

**Table 1.** Magnetic and energetic measures of aromaticity for cations **4a–c** including aromatic stabilization energies (ASE's) and magnetic susceptibility exaltations ( $\Lambda$ ) calculated from Schemes 2 and 3

	NICS(0) <sup>a</sup>	NICS(1) <sup>a<math>\alpha</math></sup> face	NICS(1) <sup>a<math>\beta</math></sup> face	Scheme 2		Scheme 3	
				ASE <sup>b</sup> (kcal mol <sup>-1</sup> )	$\Lambda^c$ (cgs-ppm)	ASE <sup>b</sup> (kcal mol <sup>-1</sup> )	$\Lambda^c$ (cgs-ppm)
Benzene	-9.7	-11.2	—	-39.4	-10.6	-37.6	-12.6
	<b>-9.7</b>	<b>-11.3</b>	—	<b>-42.3</b>	<b>-10.9</b>	<b>-40.2</b>	<b>-12.4</b>
Tropylium	-6.7	-9.8	—	-56.5	-7.4	-33.8	-16.3
	<b>-6.7</b>	<b>-9.7</b>	—	<b>-60.8</b>	<b>-6.8</b>	<b>-42.1</b>	<b>-16.0</b>
Cation <b>4a</b>	-18.4	-8.2	-13.6	-22.5	-10.0	-2.2	-11.1
	<b>-18.7</b>	<b>-8.0</b>	<b>-13.0</b>	<b>-25.2</b>	<b>-9.7</b>	<b>-4.4</b>	<b>-11.3</b>
Cation <b>4b</b>	-14.6	-7.5	-9.2	-25.3	-6.1	-2.9	-8.8
	<b>-14.6</b>	<b>-7.6</b>	<b>-13.4</b>	<b>-28.6</b>	<b>-5.6</b>	<b>-5.2</b>	<b>-8.8</b>
Cation <b>4c</b>	-6.4	-2.5	-8.0	-23.5	0.3	-0.9	-2.7
	<b>-6.5</b>	<b>-2.5</b>	<b>-9.8</b>	<b>-24.4</b>	<b>1.4</b>	<b>-1.0</b>	<b>-2.1</b>
<b>4a-H</b>	-0.2	—	—	—	—	—	—
	<b>-0.1</b>	—	—	—	—	—	—
<b>4b-H</b>	-1.3	—	—	—	—	—	—
	<b>-1.3</b>	—	—	—	—	—	—
<b>4c-H</b>	-4.4	—	—	—	—	—	—
	<b>-3.7</b>	—	—	—	—	—	—

<sup>a</sup> GIAO-B3LYP/6-31G(d)//B3LYP/6-31G(d) in normal text; GIAO-B3LYP/6-31G(d)//MP2/6-31G(d) in bold italics.

<sup>b</sup> B3LYP/6-31G(d) in normal text; MP2/6-31G(d) in bold italics.

<sup>c</sup> CSGT-B3LYP/6-31G(d)//B3LYP/6-31G(d) in normal text; CSGT-B3LYP/6-31G(d)//MP2/6-31G(d) in bold italics.

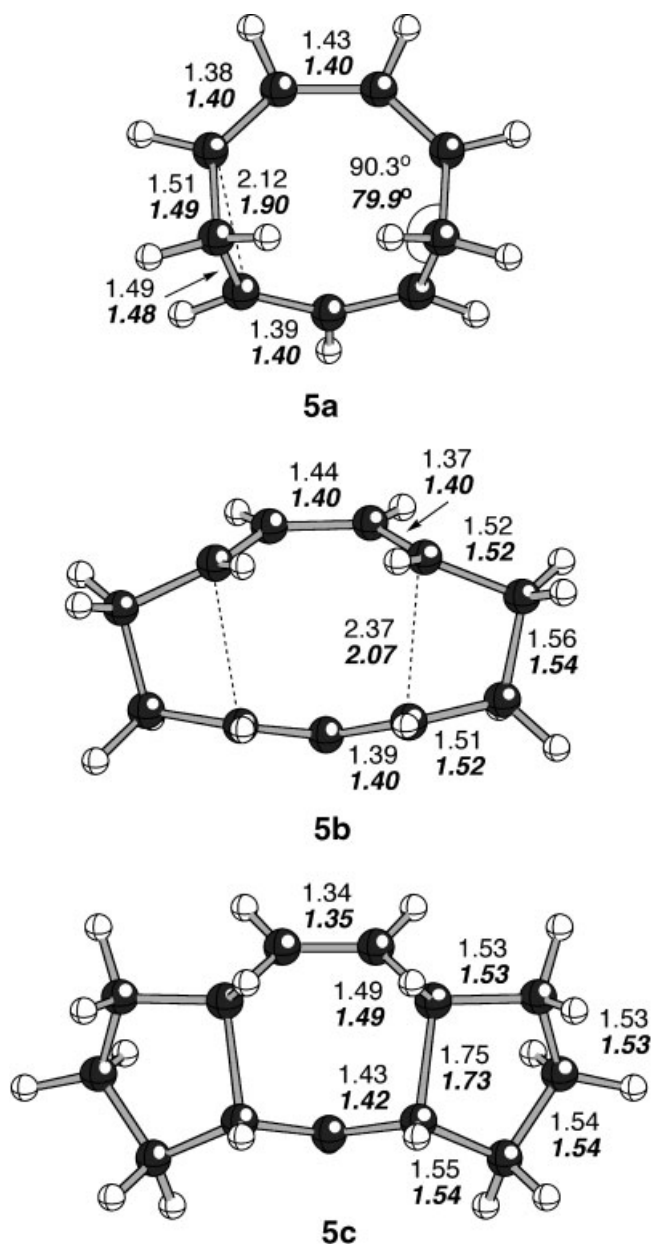
susceptibility exaltation calculated for **4c** (Table 1) is close to zero. These considerations point to a lack of aromatic character for **4c**, but the computed ASE for this cation is very close to those computed for **4a** and **4b** (Table 1), likely reflecting the fact that cyclic delocalization through multiple cyclopropyl groups and acyclic delocalization involving a single cyclopropyl group can both be substantial.<sup>18</sup> Although we cannot rule out some aromatic character for **4c**, we can say that if it is at all aromatic, then it is less so than cations **4a** and **4b**.

In 1980 Ohkata and Paquette<sup>2n</sup> described the methanolyses of trishomocycloheptatrienyl 3,5-dinitrobenzoates, which presumably involve cations **4b** and **4c**. Cation **4b** was trapped directly as the alcohol and was deemed to be too short lived to undergo rearrangement.<sup>2n</sup> Cation **4c** on the other hand was observed to rearrange and was trapped as a homocyclononatrienyl alcohol in which two of the three cyclopropane rings had opened.<sup>2n</sup> This observed difference in reactivity may speak to the difference in aromaticity between cations **4b** and **4c**. Cation **4b** appears to have more 'aromatic character' based on our calculations, and would therefore be less prone to rearrange, which would result in loss of its aromatic stabilization. Alternatively, cation **4c** appears to have less 'aromatic character' and would therefore incur less of a penalty for rearranging.

If the distal cyclopropane ring in  $C_s$ -symmetric cations **4a–b** is replaced by a double bond, cation **5a** results (Fig. 6). In this structure, both cyclopropane rings have essentially fully opened upon geometry optimization to

produce a butadiene-like substructure in close proximity to an allyl cation-like substructure. If these two substructures interact strongly, then bishomoaromaticity may be observed. With a NICS(0) value of -11.6 with B3LYP/6-31G(d) (-17.7 with B3LYP/6-31G(d)//MP2/6-31G(d)), **5a** does appear to possess substantial aromatic character. Note that the core of structure **5a** resembles a transition state structure for an orbital-symmetry allowed cycloaddition (although **5a** is a minimum).<sup>19</sup>

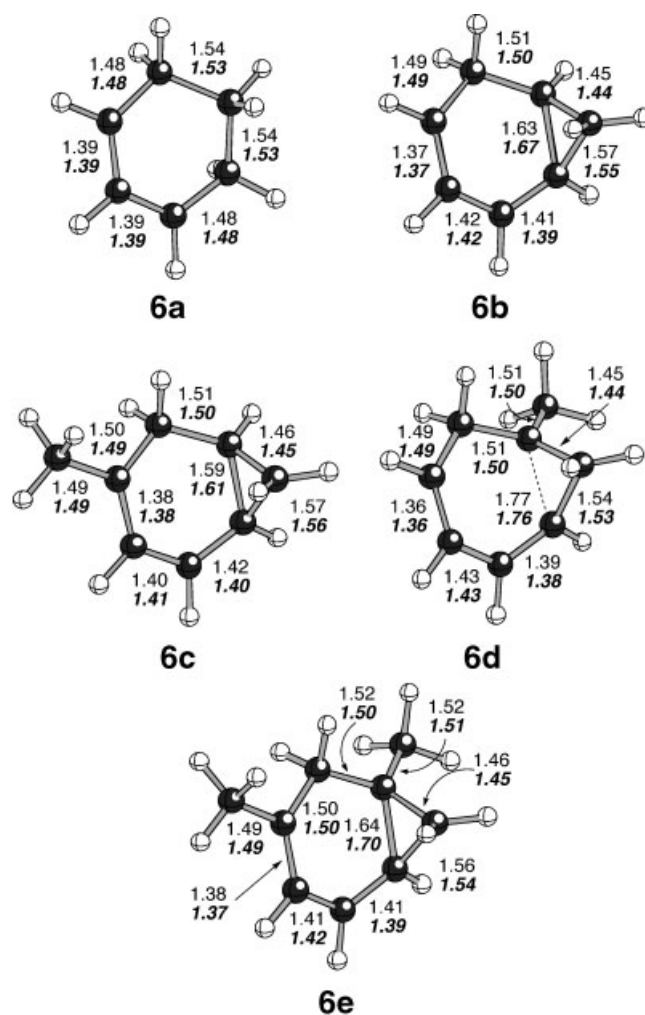
The effect of ring size on the propensity for **5a** to delocalize was probed by replacing the two cyclopropane rings with cyclobutane and then cyclopentane rings (**5b** and **5c**, respectively, Fig. 6). Addition of a single methylene to each linker increases the distance between the butadiene and allyl cation substructures (**5b**) and correspondingly decreases the magnitude of the NICS(0) (-8.7 with B3LYP/6-31G(d) [-14.2 with B3LYP/6-31G(d)//MP2/6-31G(d)]). The addition of a second methylene results in more dramatic changes, however. The symmetrical structure now becomes a transition state structure for an orbital-symmetry allowed [3,4] sigmatropic shift (**5c**).<sup>20</sup> The distance between the butadiene and allyl cation substructures is smaller here, but the magnitude of the NICS(0) again decreases (-6.5 with B3LYP/6-31G(d) [-6.5 with B3LYP/6-31G(d)//MP2/6-31G(d)]); although one might expect this geometric change to improve the cyclic delocalization, it actually serves to create a more localized C=C double bond in the butadiene substructure (Fig. 6).



**Figure 6.** Geometries of carbocations **5**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in bold italics)

### Cyclopropane versus alkene

In cations **6b–e** (Fig. 7), a C=C double bond is in competition with a cyclopropane for the opportunity to delocalize a positive charge.<sup>21</sup> The geometry of cation **6b** not only shows clear signs that both moieties interact with the cationic center, but also that they mitigate each other's influence. Compared to the corresponding bond in the cyclohexenyl cation (**6a**, Fig. 7), the C=C double bond in **6b** is more localized, and compared to the interior cyclopropane C—C bond in **1b**, the corresponding bond in **6b** is shortened. The balance between these two

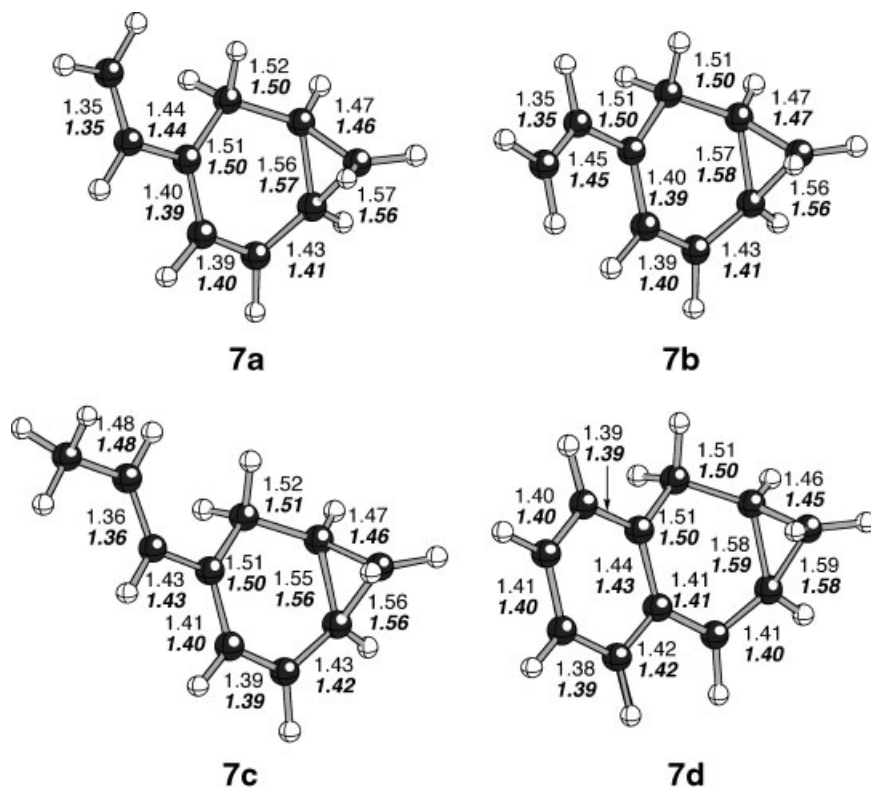


**Figure 7.** Geometries of cations **6**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in bold italic)

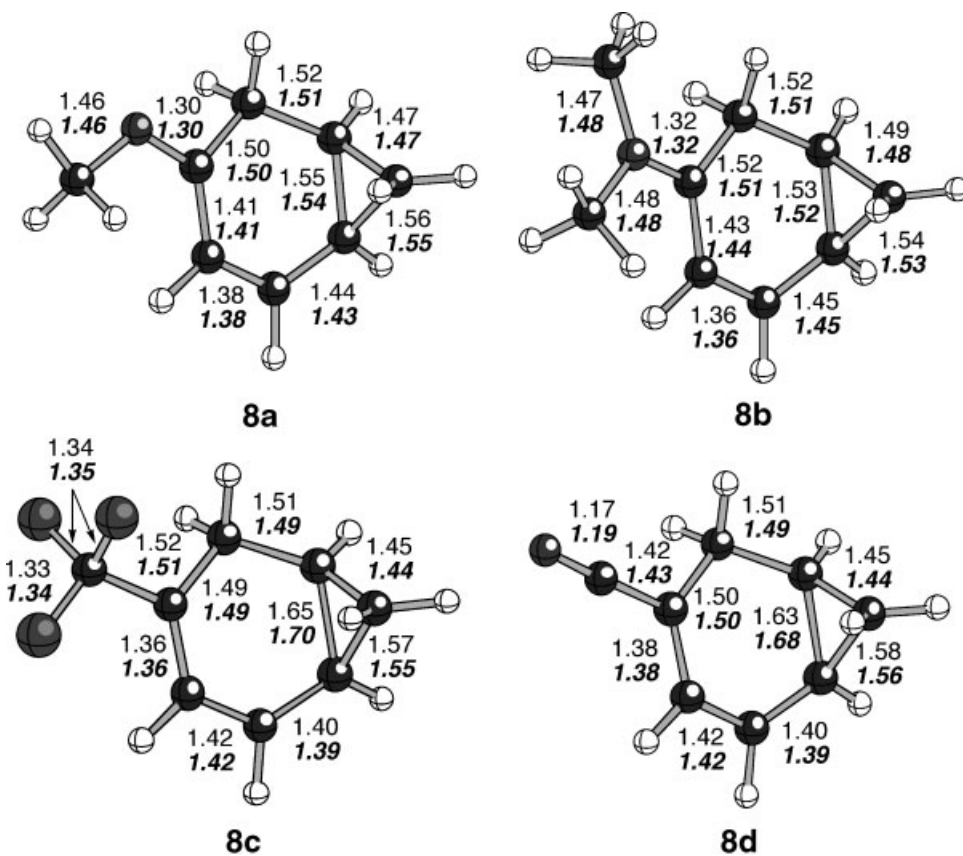
cation-stabilizing groups can be tipped in either direction by adding a methyl group to the alkene or cyclopropane (**6c–d**). Note that the methyl group appears to affect the cyclopropane and alkene to approximately the same degree, since placing methyl groups on both (see **6e**) leads to a core substructure that resembles that of **6b**.

Extending the alkene  $\pi$ -system in structures such as **7a–d** (Fig. 8) relieves the burden on the cyclopropane ring to participate in delocalization.<sup>21</sup> This is clear in the geometries of these structures, all of which have only slightly elongated interior cyclopropane C—C bonds.

Electron-donating and -withdrawing substituents can also be used to modulate the involvement of the cyclopropane ring. Donor substituents (e.g., OCH<sub>3</sub> and N(CH<sub>3</sub>)<sub>2</sub> as in **8a** and **8b**, Fig. 9) discourage cyclopropane involvement, while acceptor substituents encourage it (e.g., CF<sub>3</sub> and CN as in **8c** and **8d**). Thus, the cyclopropane's interior C—C distance provides a measure of the electron-donating ability of the substituents.

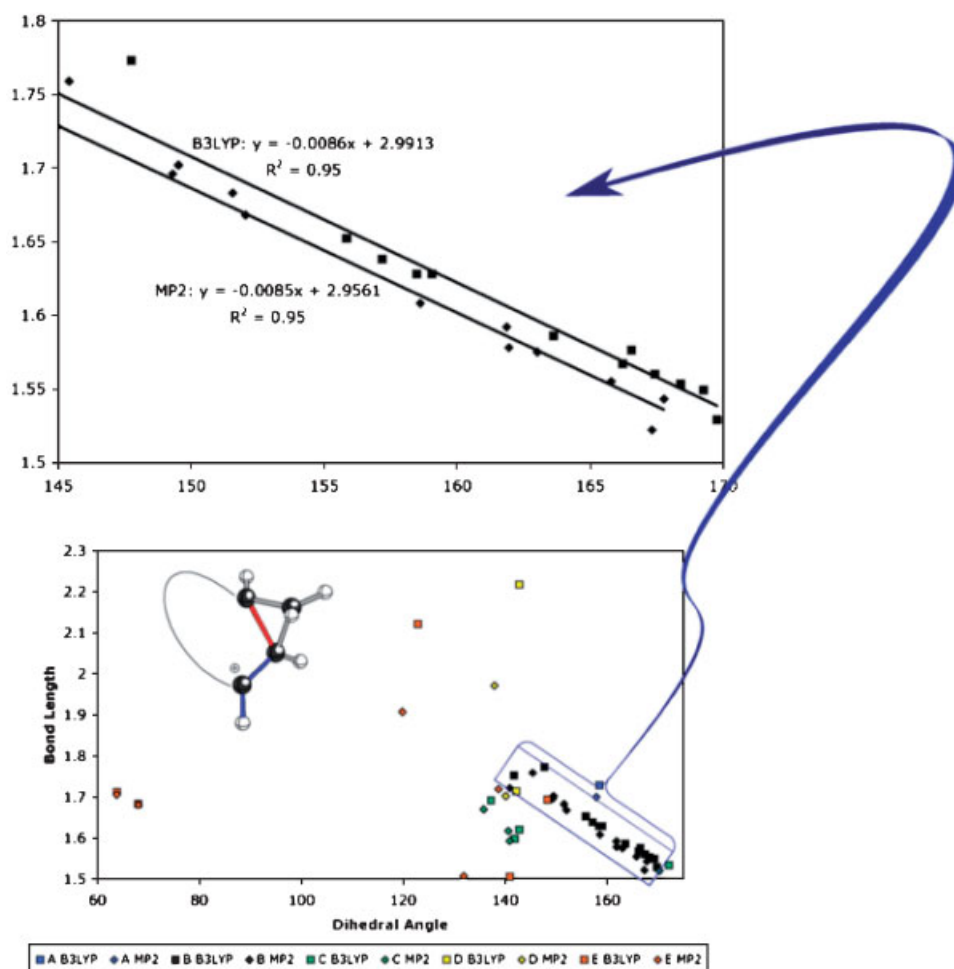


**Figure 8.** Geometries of carbocations **7**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in bold italics)



**Figure 9.** Geometries of carbocations **8**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in bold italics)





**Figure 10.** Plot of the dihedral angle (blue and red, above) versus the interior cyclopropane C—C bond length (red, above) for cations discussed herein (bottom plot). A = Cation **1a**; B = **1b**, **6b–e**, **7a–d**, and **8a–d**; C = **2a–c**; D = **3a–b**; E = **4a–c**, **5a**; Box = B3LYP value; Diamond = MP2 value

## Overall trends

One predictor of the extent of delocalization in the systems we have examined herein is the dihedral angle between the interior C—C bond of the cyclopropane and the methine C—H, which is implicitly related to the angle of the ‘empty p-orbital’ at the cationic center (see blue and red bonds in Fig. 10). A plot of this dihedral angle versus interior C—C bond length for all of the cyclopropane-containing carbocations described herein (Fig. 10, bottom) shows considerable scatter. However, these cations sport a variety of different architectures, which can be divided into families of related structures (A–E, Fig. 10). For example, families A and E contain cations with five- and seven-membered rings, respectively, while the remainder of the cations described herein have central six-membered rings. Family B contains cations with one cyclopropane fused to a six-membered ring (**1b**, **6b–e**, **7a–d**, and **8a–d**) and families C and D contain cations with two cyclopropane rings. If only cations B are considered (Fig. 10, top), then a linear

relationship is observed. One interpretation of this trend is that within series B (which contains some structures without alkenes, some with, and some with electron-donating or -withdrawing substituents), the group competing with the cyclopropane for interaction with the cationic center modulates involvement of the cyclopropane by orienting the methine C—H and its accompanying p-orbital. Although it is not surprising that the C—H orientation is directly related to the involvement of the cyclopropane and the competing C=C  $\pi$ -bond, it is not obvious that both groups cannot each, simultaneously, achieve ideal overlap.

## CONCLUSIONS

The calculations described herein show that ring-opening of cyclopropylcarbanyl cations to homoallyl cations (or conversion to bicyclobutonium cations<sup>22</sup>) can be hindered by the geometric limitations imposed upon simple fusion to carbocycles. Substantial evidence (geometric, ener-

getic, and magnetic; Table 1) shows that cyclic delocalization can be achieved not only through two cyclopropane rings (bishomoaromaticity), but also through three cyclopropane rings (trishomoaromaticity). Further, involvement of the cyclopropane ring in stabilizing an adjacent cation can be modulated by various ('competing') cation stabilizers.

## SUPPORTING INFORMATION AVAILABLE

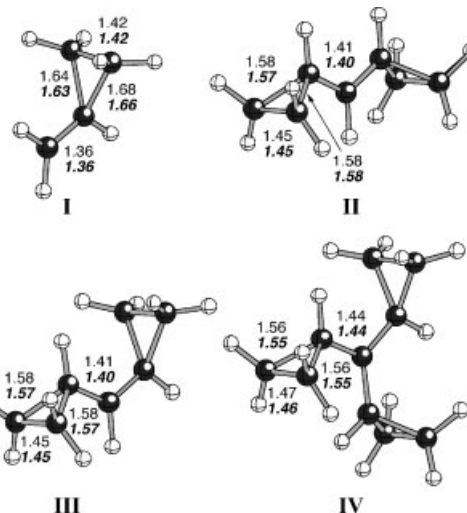
Coordinates and energies for all computed structures, NMR data, and an IRC plot for **5c**.

## Acknowledgements

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  - Hydride ions were added manually to make approximately tetrahedral methylene groups and NMR data were calculated on the resulting unoptimized molecules.
  - The difference in chemical shift of the distal methylene H's of all three cations (**4a–c**) was approximately 2 ppm, possibly indicating the presence of a weak ring current. Upon addition of a hydride<sup>17</sup> the difference was reduced to less than 0.5 ppm in all three structures. If the structures of cations **4a** and **4c** are truncated so as to eliminate any cyclic delocalization of electrons while preserving any transannular interactions, then differences in chemical shifts of the distal cyclopropane H's are reduced. See the Supporting Information for additional details on these and other related computational experiments.
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