Energetic Impact of Monohomoaromaticity[1]

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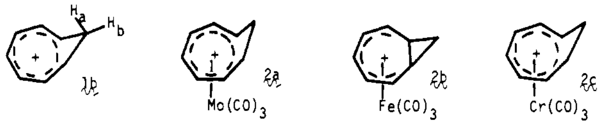
Abstract: The energetic importance of homoaromaticity is investigated theoretically for a series of potential monohomoaromatic molecules **5–14.** A lack of homoconjugate interactions is found between the cyclobutyl rings and the unsaturated bridges in **10–14.** In contrast, the cyclobutenyl (**4**) and homotropylium (**1**) cations are determined to benefit from homoaromatic delocalization to the extent of ca. 10–15 kcal/mol. However, the energetic effects of homoconjugation in the other cyclopropyl fused species (**6–8**) are comparatively small. The proposed designation of the bicyclo[3.1.0]hexenyl (**7**) cation as nonaromatic is in opposition to earlier assignments as homoantiaromatic. The theoretical results are compared with the available experimental data which is reviewed. The analyses employ extensive MINDO/3, EH, and PMO calculations. The discussion centers on the qualitative consideration of orbital interactions that are illustrated by drawings of key MO's.

The experimental support for homoaromaticity has relied predominantly on NMR data.[3] The large difference in chemical shift for the exo vs. endo methylene protons in the homotropylium cation (**1a**) is interpreted to result from the delocalization of the two electrons in the fusion bond to yield a six π-electron, homoaromatic molecule. The delocalized representation **1b** is, therefore, considered more appropriate and is anticipated to possess a ring current that deshields the exo proton (H_b) and shields the endo one (H_a).[4] This proposal was elegantly supported by Winstein, who showed that the delocalized metal complexes **2a** and **2c** have similar $\Delta\delta$'s as the homotropylium cation. Furthermore, he determined that the $\Delta\delta$ for the iron tricarbonyl complex (**2b**), which can only accommodate four additional electrons, was significantly attenuated.[5]

1a

$\Delta\delta = \delta(H_b) - \delta(H_a)$



Δδ 5.8 3.6 0.2 4.5

Using the same approach, Vogel found evidence for homoaromaticity in norcaradienes.[6] Additional support was provided by x-ray diffraction work.[3b,7] However, the degree of homoaromaticity is apparently diminished relative to the homotropylium cations.

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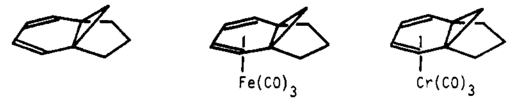
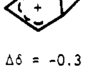


Δδ 1.7 0.2 1.6

Berson has also obtained NMR data on the potentially homoantiaromatic, bicyclo[3.1.0]hexenyl cation (**7**).[8a] Although the effect is small, the $\Delta\delta$ is in qualitative agreement with a paramagnetic ring current for this molecule. In addition, the relative ease of circumambulation in monodeuterio derivatives of **7**[8a] vs. **1**[8b] has been interpreted as a reflection of the difference in homoaromaticity for the compounds.[8c,11]



Δδ = -0.3

More recently, Olah has studied the lowest homologue of the monohomoaromatic series, homocyclopropenyl cation.[9] The species is best described as a puckered cyclobutenyl cation (**4**). Since the puckering is small relative to the other homoaromatics, the $\Delta\delta$ is reduced; however, the NMR results are still consistent with a highly delocalized structure. The importance of the 1,3-π overlap is emphasized by the substantial barrier to ring flipping (8.4 kcal/mol) that was observed.[9]

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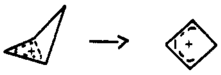
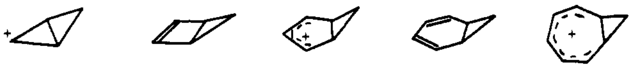
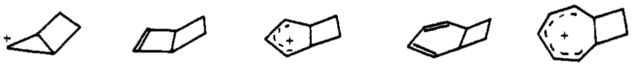


$\Delta G^{\ddagger}$ = 8.4 kcal/mole

Besides the numerous experimental investigations of homoaromaticity,[3] considerable theoretical effort has been expended in the area.[10-13] Nevertheless, with one exception,[11] there appears to be a total lack of sophisticated, quantitative estimates of the energetic importance of the phenomenon. In order to address this problem, the present paper describes theoretical studies using molecular orbital theory on the monohomoaromatic series **5–9**, For the purpose of comparison and in continuing our studies of cyclopropyl vs. cyclobutyl conjugation,[2,14] calculations and analyses are also reported for the cyclobutyl fused analogues **10–14.** Our findings indicate a lack of conjugative interactions between the cyclobutyl rings and unsaturated bridges in **10–14.** Although the homoaromaticities of **1** and **4** are verified, the energetic importance of homoconjugate interactions in the other cyclopropyl fused molecules (**6–8**) is also found to be comparatively small. The observation that the bicyclo[3.1.0]hexenyl cation is nonaromatic is of particular interest in view of the homoantiaromatic character that has previously been ascribed to it.[8c,11]



5 6 7 8 9



10 11 12 13 14

To begin, a qualitative description of the important orbital interactions between small rings and unsaturated bridges in the molecules is given. The discussion is supported by computer-generated drawings of key molecular orbitals. The geometrical and energetic results of extensive MINDO/3,[15,16] extended Hückel,[17] and perturbation theory calculations are then presented.

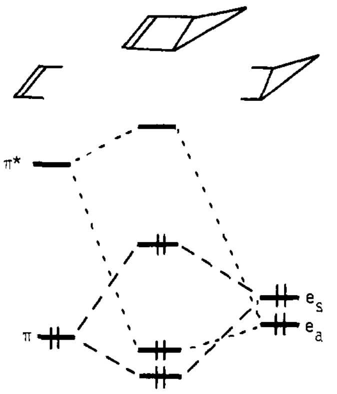
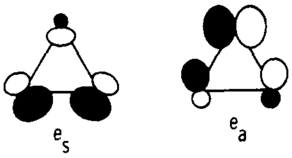


Figure 1. Frontier orbital interactions in bicyclo[2.1.0]pentene (**6**).

Qualitative Orbital Interactions

The homoaromatic characters of **5–9** are anticipated to be profoundly affected by the extent and types of interactions between the orbitals of the cyclopropane rings and the π orbitals of the unsaturated bridges.[2,11-14] In previous studies,[2,14] the important orbital interactions in **6** were shown to occur between the degenerate pair of cyclopropane HOMO's (e_s and e_a) and the π and π^* orbitals of the ethylene bridge. As schematized in Figure 1, there is a net destabilizing interaction between π and e_s, since four electrons are involved (overlap repulsion[14]). The two-electron stabilizing interaction between e_a and π^* does not offset the π–e_s repulsion because there is a substantial energy separation between e_a and π^* and because e_a is less localized on C1 and C4 in **6** than e_s, so it interacts less strongly with opposing π orbitals. Thus, the net interaction between the cyclopropyl orbitals and the π orbitals of the ethylene bridge in **6** is predicted and found to be destabilizing.[2,14] The molecule may, therefore, be termed homoantiaromatic.[18]



The same form of analysis can be applied to **7** by considering the interaction of an allylic and a cyclopropyl fragment as illustrated in Figure 2. In this case, the repulsive interaction between χ_1 and e_s will be mitigated through interaction with the low-lying, unoccupied π orbital of the same symmetry, χ_3^*. In addition, the e_a–χ_2 interaction is more stabilizing than the e_a–π^* interaction in **6** because χ_2 is at lower energy (nonbonding) than π^* (antibonding). Although **7** is a potential four π-electron homoantiaromatic species like **6**, the qualitative orbital interactions suggest that **7** is not significantly destabilized and may, in fact, be slightly stabilized by the interactions between the allylic and cyclopropyl orbitals.

Analogous interaction diagrams may be constructed for the other cyclopropyl fused species. The diagrams become increasingly complex as the size of the bridging π system increases. To simplify matters, some general observations may be made concerning the important frontier orbital interactions[19] (the interactions between the HOMO's and LUMO's of the bridge and cyclopropyl ring) in **5–9**. A key point pertains to the interaction of e_s with the unoccupied π orbitals of the bridges in **5–9**. Specifically, e_s has the wrong symmetry to interact with the LUMO's of the bridging π orbitals in the potential homoantiaromatics **6** and **7**. However, e_s has the same symmetry and can interact with the bridging LUMO's in the potential homoaromatics **5, 8,** and **9**. The interactions with e_s in **5** and **9** should be particularly strong, since the bridging LUMO's are nonbonding. These two-electron interactions will cause a transfer of electron density from e_s into the π orbitals. Since e_s is highly bonding for the fusion bonds, the loss of electron density is predicted to result in the lengthening of the fusion bonds in **5** and **9** consistent with structures **4** and **1b.** Concomitantly, the bonds between the bridges and the cyclopropyl rings are shortened due to the increase in constructive π-type interactions between e_s and the bridging LUMO's.

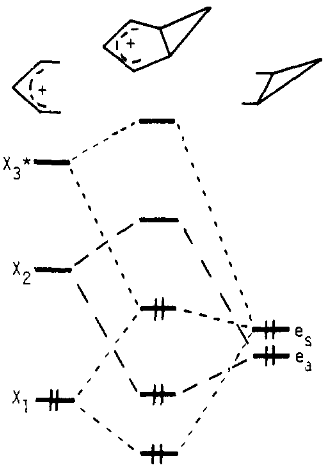
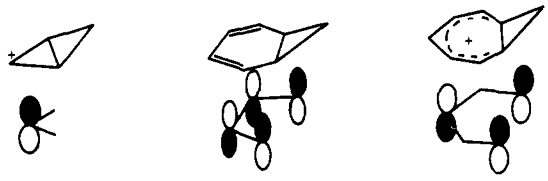
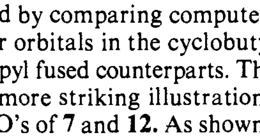


Figure 2. Frontier orbital interactions in bicyclo[3.1.0]hexenyl cation (**7**).



In a similar fashion, lengthening of the cyclopropyl bonds adjacent to the fusion bond in the cyclopropyl fused compounds is symptomatic of electron donation from e_a into the empty π orbitals of the bridge. This effect should be most pronounced for **7** due to the mixing of e_a with the nonbonding LUMO, χ_2.

Applying the same analysis to the cyclobutyl fused compounds, the important orbital interactions are anticipated to occur between the degenerate pair of cyclobutane HOMO's, e_s' and e_a',[2,20] and the π orbitals of the bridges in **10–14.** On the basis of electron density and orientational factors, e_s' has previously been rejected as a significant participant in π-type interactions.[2,13a] This assessment is fully supported by the geometrical data calculated using MINDO/3 that are presented in a following section. However, the lack of interaction is easily illustrated by comparing computer-generated drawings for molecular orbitals in the cyclobutyl fused molecules and their cyclopropyl fused counterparts. This was done earlier for **6** and **11.**[2] A more striking illustration is found on comparing the HOMO's of **7** and **12.** As shown in Figure 3,[21] the HOMO of **7** reveals a mixture of e_s and χ_1 in an antibonding manner as expected (Figure 2). The $2p_\pi$ coefficients at C2 and C4 in the HOMO of **7** have been annihilated by the mixing with χ_3^*. Thus, the HOMO of **7** is best described as $e_s - \chi_1 + \chi_3^*$. In contrast, mixing of e_s' with the allylic π orbitals is not revealed in the HOMO of **12.**



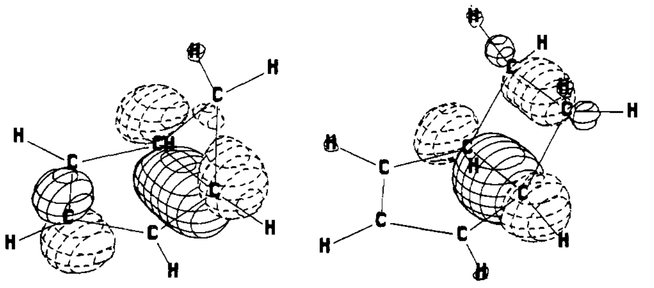


Figure 3. The HOMO's of bicyclo[3.1.0]hexenyl (**7**) and bicyclo[3.2.0]heptenyl (**12**) cations.

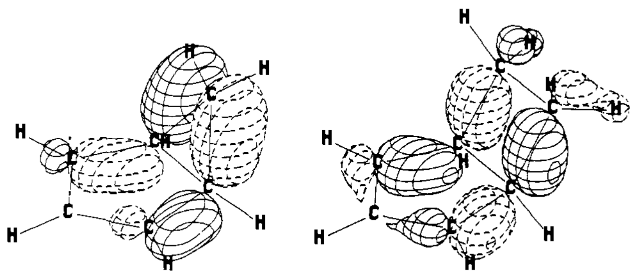


Figure 5. The NHOMO's of bicyclo[3.1.0]hexenyl (**7**) and bicyclo[3.2.0]heptenyl (**12**) cations.

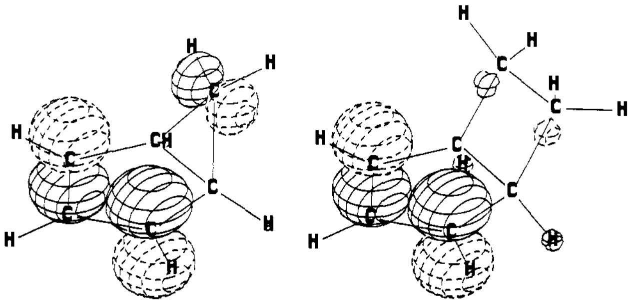


Figure 4. The LUMO's of bicyclo[3.1.0]hexenyl (**7**) and bicyclo[3.2.0]heptenyl (**12**) cations.

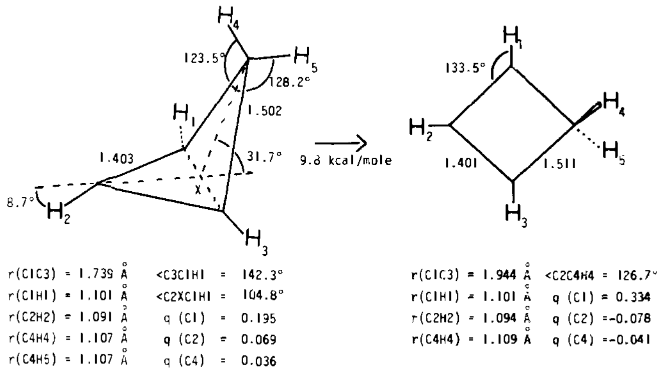


Figure 6. MINDO/3 geometries, charges, and bridge flipping barrier for C_s and C_{2v} cyclobutenyl cations.

The e_a and e_a' orbitals are suitably oriented for interaction with bridging π orbitals. The LUMO's of **7** and **12**, which are presented in Figure 4, are interesting in this regard. For **7**, the LUMO reveals mixing of the allylic χ_2 with e_a in an antibonding fashion, in agreement with the scheme in Figure 2. Again, the antibonding interaction and the coefficients at C1 and C5 have been reduced by mixings with higher lying unoccupied orbitals, in this case, σ^* orbitals of the cyclopropyl fragment.[23] The interaction between χ_2 and e_a' in the LUMO of **12** (Figure 4) is comparatively small. The reason for the reduction in the mixing of χ_2 with e_a' relative to e_a is not immediately obvious. Arguments could be made that the greater e_a-χ_2 interaction is due to greater strain in the σ framework of **7** over **12** yielding a higher energy for e_a than e_a'.[24] In fact, the calculated geometrical data indicate that neither e_a nor e_a' mixes extensively with the bridging π orbitals for most of the molecules studied.

Another significant observation is that in contrast to e_s, e_a and e_a' mix extensively with the σ orbitals of the bridges in **5–14**. This is illustrated by the next highest occupied MO's (NHOMO's) for **7** and **12** that are displayed in Figure 5.[25] One factor that is consistent with the greater interaction of e_s and the π systems is that the strain on the fusion bond in **5–9** places e_s at higher energy than e_a and e_a'. e_s then becomes more associated with the π manifold, while e_a and e_a' mix with the higher-lying, filled σ levels. A final factor which may be important is that e_a and e_a' are predominantly localized on one side of the π nodal plane, while e_s is more uniformly distributed on both sides of the plane like a π orbital.[26] In any event, it appears that for the cyclopropyl fragment, e_s is the primary participant in π-type interactions in molecules such as **5–9**. There has previously been some debate on this last point.[11,13b] Furthermore, π-type interactions between the cyclobutyl rings and bridges in **10–14** are apparently very minor. Thus, barring significant differences in the σ interactions between the cyclobutyl fused compounds and their cyclopropyl fused counterparts, the cyclobutyl fused compounds may provide a reference for homoconjugate interactions in the cyclopropyl fused series.

Results of Calculations

Due to the lack of structural data on **5–14** except **6**,[27] MINDO/3 calculations[15,16] have been performed on these compounds with complete optimization of geometries in C_s symmetry.[28] For comparison and to help gauge the effect of including overlap in the computations, extended Hückel (EH) calculations[17] were also performed on **5–14** and any reference compounds using the geometries calculated by MINDO/3. In the following description of the results, comparisons are frequently drawn between the cyclopropyl fused compounds and their cyclobutyl fused relatives. As discussed in the next section, this is not possible for **5** and **10**, so they are treated separately.

Bicyclo[1.1.0]butyl and Bicyclo[2.1.0]pentyl Cations. The geometry calculated for **5** is shown in Figure 6. The molecule is found to correspond to a puckered cyclobutenyl cation (**4**). This agrees with Olah's results[9] and with the strong interaction predicted for e_s and the empty 2p orbital in **5**. The calculated ring flipping barrier through a planar cyclobutenyl cation (9.8 kcal/mol) also compares well with the experimental value determined in solution (8.4 kcal/mol[9]). The ab initio results of Devaquet and Hehre are in poorer accord with experiment as they predict little puckering (10°) and consequently a small barrier (0.4 kcal/mol).[12] It is worth noting that the calculated charge distribution for **4** (Figure 6) is still essentially allylic, though the 1,3-interaction and puckering in **4** have shifted electron density from C2 to C1 and C3 as compared to the planar form. This is consistent with a contribution to **4** from **5** as a resonance structure. The NMR data of Olah et al.[9] are interesting in this regard. The ^{13}C chemical shifts for methyl- and phenyl-substituted homocyclopropenyl and allyl cations are found to be qualitatively similar. However, for **4** the ordering of the shifts for C1 and C2 is reversed. Though it is tempting to interpret the reversal as an indication of a large contribution from **5**,[9] the charge distributions calculated by both MINDO/3 and ab initio[12] methods are in agreement that **4** is fundamentally allylic.

In contrast, **10** does not represent an energy minimum ac-

Table I. Calculated Bond Lengths and Deviations[a,b]

Compd	r_{fb}	Δr_{fb}	r_α	Δr_α	r_{12}	Δr_{12}
6	1.558	0.064	1.506	0.012	1.519	0.011
7	1.563	0.069	1.514	0.020	1.483	-0.010
8	1.565	0.071	1.503	0.009	1.485	-0.014
9	1.621	0.127	1.498	0.004	1.449	-0.034
11	1.582	0.056	1.538	0.012	1.519	0.011
12	1.580	0.054	1.552	0.026	1.493	0.000
13	1.580	0.054	1.541	0.015	1.505	0.006
14	1.575	0.049	1.547	0.021	1.488	0.005

[a] MINDO/3 results from complete geometry optimization in C_s symmetry. Bond lengths in angstroms. [b] r_{fb} is r (fusion bond); r_{12} is r (C1–C2); r_α is the length of the bond in the cyclopropyl or cyclobutyl ring adjacent to the fusion bond. For Δr_{fb} and Δr_α the reference bond length is for cyclopropane (1.492 Å) or cyclobutane (1.526 Å). For Δr_{12} the reference bond is the corresponding bond in the isolated, unsaturated ring.

cording to MINDO/3. **10** is computed to open in a disrotatory fashion without activation energy to the essentially planar, cyclopentenyl cation. This latter species is calculated to have a C1–C3 distance of 2.253 Å and insignificant 1,3-π overlap.

The nonexistence of **10** prohibits its use as a reference for the homoaromatic character of **4.** Probably the most reasonable estimate of the energetic importance of homoconjugate interactions in **4** is given by the ring flipping barrier.

Geometrical Results

Several important, calculated bond lengths for the remaining molecules are recorded in Table I. The three bond lengths r_{fb}, r_{12}, and r_α correspond, respectively, to the lengths of the fusion bond, the C1–C2 bond, and the bond in the cyclopropyl or cyclobutyl ring adjacent to the fusion bond. The changes in these bond lengths as compared with reference compounds are also recorded. For r_{fb} and r_α the reference bond length is for cyclopropane (calculated, 1.492 Å) or cyclobutane (calculated, 1.526 Å) as appropriate. For r_{12} the reference bond is the corresponding bond in the isolated, unsaturated ring, e.g., for **8** and **13,** the calculated reference bond length is the C1–C6 bond length in 1,3-cyclohexadiene.

The constancy of r_{fb} for the cyclobutyl fused compounds **11–14** is remarkable. This is consistent with the anticipated lack of interaction between e_s' and the bridging π orbitals. The uniform lengthening of r_{fb} relative to cyclobutane is, no doubt, a result of increased strain on the fusion bond in the bicyclic molecules. The data indicate a trend towards lessening of this effect in going to larger, less strained bicyclic systems.

The calculated r_α's for **11–14** show somewhat greater variation. The slight lengthening of r_α for **12** and **14** could be explained by interactions between e_a' and χ_2 (Figure 4) and χ_4*, respectively. Alternatively, an inductive effect through the σ framework might be invoked. The constancy of the r_{12}'s for **11–14** reinforces the conclusion that the π-type interactions between the cyclobutyl rings and unsaturated bridges in these compounds have little impact.

The data for the homotropylium cation (**9**) stand out in Table I. The lengthening of r_{fb} to 1.621 Å is in accord with the anticipated interaction of χ_3 and e_s and with Winstein's delocalized, homoaromatic structure **1b.** The reductions in the r_{12} values for **7–9** also reflect favorable interactions between the cyclopropyl orbitals and the π orbitals of the bridges and/or increased s character for the bonds exo to a cyclopropyl ring. Extension of r_α in **7** reflects the mixing of e_a and χ_2 (Figure 4). The r_α for **7** is, however, much smaller than the ab initio (STO-3G) value (1.617 Å) determined by Hehre[11] with partial geometry optimization. This suggests, as discussed above, that the e_a-χ_2 mixing may not be as substantial as proposed previously.[11] Significant differences in the MINDO/3 and STO-3G[11] geometries for **9** that become accentuated when the basal ring is allowed to distort from planarity have been discussed by Haddon.[13b] For **4** and **9,** the MINDO/3 geometries seem more reasonable than the STO-3G ones in view of the available experimental facts.[3-5,9]

Table II. Calculated Cyclopropyl vs. Cyclobutyl Conjugation Energies[a]

Compd	MINDO/3 ΔH_c	Extended Hückel ΔH_c
6	-5.5	-14.1
7	1.4	-5.5
8	6.8	4.2
9	14.4	16.3

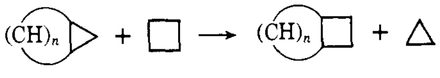
[a] ΔH_c's in kcal/mol. ΔH_c corresponds to the ΔH for the reaction shown in eq 1.

Finally, the equality of r_{12} for **6** and **11** is disturbing considering the homoantiaromatic character ascribed to **6.**[2] However, as previously discussed,[2,14] the net destabilization caused by the mixing of two filled orbitals, e.g., π and e_s in **6,** is proportional to their overlap. As a result the destabilization is not explicitly taken into account in MO methods that neglect differential overlap (NDO). Thus, it is possible that the MINDO/3 calculations are underestimating the e_s-π repulsion and, therefore, r_{12} in **6.**[29] Alternatively, increased s character may contribute to shortening r_{12} in **6.**

Energetic Results

Several approaches to calculating the energetic importance of the homoconjugate interactions in **6–9** have been considered. The results from the most promising methods are presented here.

In the first approach, the cyclopropyl fused compounds are related to their cyclobutyl fused relatives via the isodesmic reaction given by eq 1. In the equation, n equals 2, 3, 4, or 5 and



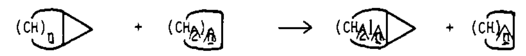
(1)

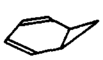
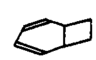
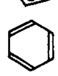
for n odd the bicyclic compounds are the cations. In the absence of variations in the aromatic characters of the bicyclic compounds, the two sides of eq 1 would be expected to be nearly isoenergetic due to the similarity of ring systems.[30] Furthermore, on the basis of the data described above, the homoconjugate interactions in the cyclobutyl fused compounds **11–14** are small, if present at all. Therefore, the ΔH for eq 1 (ΔH_c) should provide a fair estimate of the energetic impact of the orbital interactions between the cyclopropyl ring and unsaturated bridges in **6–9.** The calculated values are shown in Table II.

The MINDO/3 results suggest an assignment of **6** as homoantiaromatic, **7** as nonaromatic, and **8** and **9** as homoaromatic with the energetic benefit of homoconjugation in **9** being substantially greater than in **8.** These qualitative conclusions are in accord with the theoretical and experimental information discussed above. The extended Hückel results closely parallel the MINDO/3 data, though **6** and **7** are calculated to be more destabilized. The increased homoantiaromatic characters for **6** and **7** are probably due to the inclusion of overlap in the EH calculations. Thus, the EH results might provide a better description of the e_s-π and e_s-χ_1 repulsions in **6** and **7,** respectively. However, the effects of overlap repulsion may now be somewhat overestimated, since the geometries for the EH results are derived from the MINDO/3 computations (neglecting overlap).[33]

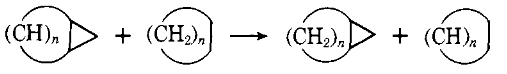
The second approach relates the bicyclic compounds **6–9** and **11–14** to their saturated analogues according to the isodesmic reactions in eq 2 and 3 (n = 2–5). Again, an approxi-

Table III. Calculated Reductive Stabilization Energies[a,b]



Compd	ΔH_H	Compd	ΔH_H	Compd	ΔH_H
	-6.1		-0.7		-20.3
	2.0		4.2		-20.9
	2.3		2.0[c]		26.6[d]

[a] MINDO/3 results. ΔH_H's in kcal/mol. [b] ΔH_H for the cyclopropyl bridged compounds corresponds to the ΔH for the reaction shown above. Analogous equations apply for the cyclobutyl and ethylene bridged compounds. [c] The experimental value is 3.9 from ref 31, 35, and 36. [d] The experimental value is 34.6 from ref 36.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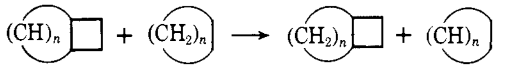
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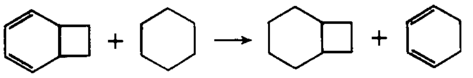
mate equality of ring strain is expected on both sides of the equations.[30] The advantage to this method is that estimates of the homoconjugate stabilizations in both the cyclopropyl and cyclobutyl fused compounds are obtained. The significant disadvantage is that the method requires calculating the geometries and energies for four sizable molecules in each case. The computation time for the saturated bicyclics becomes substantial for $n > 3$.[34]

As a consequence, the ΔH's for eq 2 and 3 (ΔH_H) have only been computed for $n = 2$-4. The MINDO/3 results are shown in Table III. The data in Tables I and II clearly indicate that **9** is homoaromatic with a homoconjugation energy of roughly 15 kcal/mol. It is unlikely that calculating the ΔH_H's for **9** and **14** would provide any new insight.

The homoantiaromatic character of **6** is again revealed in the calculated ΔH_H (Table III). For **7** and **12**, the ΔH_H's suggest that **12** is now the energetically favored species in contrast to the MINDO/3 result in Table II. The energy differences are small (1.4 vs. -2.2 kcal/mol) and little significance can be attached to the results. The qualitative conclusion is, however, obvious: the homoconjugate interactions between cyclopropyl ring and allylic bridge in **7** have essentially neutral energetic impact, i.e., **7** is nonaromatic.

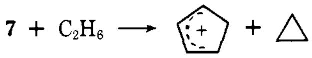
The calculated ΔH_H for **13** (2.0 kcal/mol) is in excellent agreement with the experimental value (3.9 kcal/mol).[31,35,36] At first the experimental value might seem to indicate that **13** is stabilized by delocalization. When the equation for the ΔH_H of **13** (eq 4) is further scrutinized, the more reasonable ex-


(4)

planation is a conformational one. Specifically, the cyclohexane ring in bicyclo[4.2.0]octane cannot be in a chair conformation while the cyclohexane on the left side of eq 4 is chair. Therefore, the endothermicity of eq 4 is partly due to the higher relative energy of bicyclo[4.2.0]octane rather than unusually low energy for **13**. Strain differences between the cyclohexadienes in eq 4 are not expected to be as significant, since cyclohexadiene is less conformationally flexible than cyclohexane.

The most unsettling result in Table III is the ΔH_H for norcaradiene (**8**). The stabilization of norcaradiene revealed in its ΔH_c (Table II) is no longer obvious. It could well be that the energy differences are again below the sensitivity of MINDO/3. The EH results for the ΔH_H's are reassuring in this regard. The results are qualitatively similar to the MINDO/3 data except for norcaradiene. The EH value for the ΔH_H of norcaradiene is found to be 7.3 kcal/mol greater than the ΔH_H for **13**, consistent with a homoaromatic designation for **8**. It is unwarranted to assign quantitative significance to EH calculations; however, in this and numerous other cases the qualitative results are gratifying. A simple second-order perturbation theory calculation also suggests that **8** is homoaromatic.[37] However, it is clear that the energetic benefit of homoconjugation in **8** is substantially less than in **9**.

Another approach to estimating the energetic importance of homoconjugate interactions in **6–9** and **11–14** is to consider isodesmic reactions such as eq 5 and 6 for **7** and **9**. However, a lack of cancellation of ring strain distorts the results for the smallest bicyclic molecules. For **7** and **9**, the results seem reasonable: the ΔH's calculated by MINDO/3 for eq 5 and 6 are -2.1 and 11.4 kcal/mol, respectively.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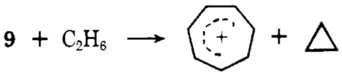
(6)

Hehre has implied that the difference in bond separation energies for **7** and **9**, the ΔH's for eq 7 and 8, is a measure of the difference in homoaromatic character for **7** and **9**.[11] This is clearly a rough estimate because in the difference of eq 7 and 8, there has been no effort to take into account the inequality

$$\mathbf{7} + 4CH_4 + CH_3^+ \longrightarrow \triangle + C_2H_6 + 2C_2H_5^+ + C_2H_4 \quad (7)$$

$$\mathbf{9} + 6CH_4 + CH_3^+ \longrightarrow \triangle + 2C_2H_6 + 2C_2H_5^+ + 2C_2H_4 \quad (8)$$

of strain energies on the two sides of the equation. In addition, the ΔH for eq 9 contains a significant term that represents the variation in stabilization energies for pentadienyl and allylic cations.[41] This term has no relationship to the energetic effect of homoconjugation, i.e., for **7** and **9**, the energetic stabilization or destabilization associated with the conjugative interactions between the cyclopropane ring and the allylic and pentadienylic bridges in **7** and **9**. The STO-3G[11] and MINDO/3 values for the ΔH of eq 9 are 29 and 56 kcal/mol,[39] respectively. The two

$$\mathbf{9} + 2CH_4 \longrightarrow \mathbf{7} + C_2H_6 + C_2H_4 \quad (9)$$

numbers are not strictly comparable due to incomplete optimization of the STO-3G geometries.[11] Nevertheless, it is obvious that these are rather high estimates for the homoconjugate stabilization of **9**, if the stabilization of **7** is assumed to be roughly zero. For the MINDO/3 results, the implication would be that **9** has about twice the resonance energy of benzene (Table III).[37]

The investigations described here propose that the best estimates of the energetic impact of homoaromaticity in molecules like **6–9** and **11–14** are obtained from the ΔH's of reactions such as eq 1-3, and 5 and 6.

Conclusion

The calculations and analyses in this work have been aimed at estimating the energetic importance of homoaromaticity in the potential, monohomoaromatic species **5–14**. The homoconjugate interactions in the cyclobutyl fused compounds **10–14** were shown to be negligible. Three of the cyclopropyl fused compounds were found to be homoaromatic, **5** (**4**), **9** (**1b**), and, to a lesser extent, **8**. Bicyclo[2.1.0]pentene (**6**) may be classified as homoantiaromatic, while bicyclo[3.1.0]hexenyl cation is essentially nonaromatic. However, for the compounds in this study, the overall conclusion must be made that the energetic impact of monohomoaromaticity is only profound for the cyclobutenyl (**4**) and homotropylium (**1b**) cations. It seems that this issue should have been addressed earlier, considering the research effort that homoaromaticity has provoked.

Note Added in Proof. The recent NMR work of Olah et al.[43] supports the designation of **7** as nonaromatic.

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(24) The ionization potentials of unsubstituted cyclopropane and cyclobutane are very similar: see ref 20b, footnote 28.
(25) The interaction between e_a and the σ orbitals of the cyclobutene ring in **6** is revealed in the 6A″ MO on p 230 of ref 22.
(26) For accurate drawings of e_s and e_a, see ref 22, p 154.
(27) S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, and J. E. Baldwin, *J. Am. Chem. Soc.*, **92**, 5250 (1970).
(28) We have investigated distortions from C_s symmetry in several of the compounds and found them to be negligible. Haddon's experience with **9** was similar.[13b]
(29) An analogous concern could be expressed concerning the description by NDO calculations of all interactions between filled orbitals. However, it should be noted that the effects of overlap repulsion are most severe for high-lying filled orbitals that interact strongly, *e.g.*, e_s and π in **6**. See ref 14, footnote 20 for details.
(30) In support of the proposed cancellation of ring strains for the two sides of eq 1, the data compiled by Schleyer[31] are important. The data reveal that the mean deviation of the strain energies for the bicyclo[*n*.1.0]alkanes (n = 2–5) from the additivity of the strain energies of the component rings is 2.2 kcal/mol. It is well known that the additivity scheme breaks down for bicyclo[1.1.0]butane, which is ca. 10 kcal/mol more strained than two cyclopropanes.[31,32] Little thermodynamic data exists for the bicyclo-[*n*.2.0]alkanes except for $n = 4$, in which case the deviation of the strain energy from the additive value is 0.75 kcal/mol.
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(33) We previously calculated ΔH_c for **6** using its experimental geometry.[27] The results in this case were −9.7 kcal/mol via EH and −3.9 kcal/mol using MINDO/2.[2]
(34) The MINDO/3 calculation on bicyclo[4.2.0]octane required over an hour of CPU time for optimization of the geometry in C_s symmetry on our computer (CDC 6500), even after a careful choice of starting geometry.
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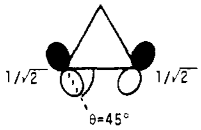

Second-order PMO calculations for the interaction of the model e_s with the π orbitals of a butadienyl or pentadienyl fragment then yield stabilization energies of 0.46β and 0.74β for **8** and **9**, respectively. The calculations assume an orbital energy of $\alpha + \beta$ for e_s, which is reasonable considering the experimental difference of only 0.4 eV for the ionization potentials of ethylene and cyclopropane.[38] Though these calculations are very crude, they predict **8** and **9** to exhibit roughly 25 and 40% of the homoconjugate stabilization of benzene, respectively. The agreement with the MINDO/3 results (Table II) is surprisingly good.
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(39) For the MINDO/3 results to be meaningful, it is necessary to use the experimental ΔH_f^{298} (g) for methane in determining the ΔH for eq 9. The reason is that the error in the ΔH_f for methane is three times the mean error for MINDO/3 results (6 kcal/mol).[15] This one correction accounts to a large extent for the discrepancies noted by Pople[40] between experimental ΔH's and MINDO/3 results.