

A Study into the Possible Homoaromatic Nature of Some Related Carbene and Cationic Intermediates with the Potential for Transannular Interaction

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A comparison of the aromatic nature of the cations and carbenes centered at the 8-position of tricyclo[3.2.1.0^{2,4}]octane, the 9-position of pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane, the 6-position of tricyclo[3.1.1.0^{2,4}]heptane, and the 4-position of tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane has been undertaken. Hybrid density functional theory calculations have been used to examine the geometric, energetic, and magnetic characteristics of each cation, singlet carbene, and triplet carbene. The results shed light on the flexibility of the polycycles to achieve stable intermediates and on the breadth of homoaromaticity.

Homoaromaticity in which cyclic delocalization, typical of aromaticity, is exhibited by systems in which there is an insulating group interrupting the continuous adjacent overlap of orbitals has been revealed in cationic, anionic, and neutral polycyclic hydrocarbons. Illustrative parent systems are the 3-bicyclo[3.1.0]hexyl cation (**1**),^{1,2} the bicyclo[3.2.1]octadienyl anion (**2**),³ and barbaralane species **3**⁴ (Chart 1). In a recent study in this laboratory, homoaromatic properties of carbene intermediates **4–6** were explored using hybrid density functional theory methodology B3LYP/6-311+G(3df,2p)/(B3LYP/6-31G(d)).^{3a} In addition, calculations employing the B3LYP/6-311+G(3df,2p)/B3LYP/6-31G(d) method were used to analyze homoaromaticity or antihomoaromaticity in the cation, singlet carbene, and anion at the 2-position of bicyclo[3.2.1]octadiene, **7**^{3a} (Chart 2).

Is the homoaromaticity revealed for bivalent singlets **5** and **6** general, and will the analogy to homoaromaticity of carbocations hold across a larger range of structures? In this study, we compare the degree of homoaromaticity in cationic and neutral carbene intermediates for species centered at the 8-position of tricyclo[3.2.1.0^{2,4}]octane **8**, the 9-position of pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane **9**,

CHART 1

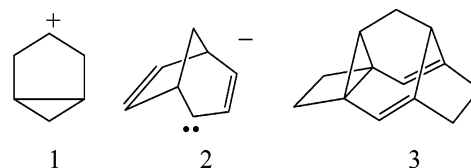
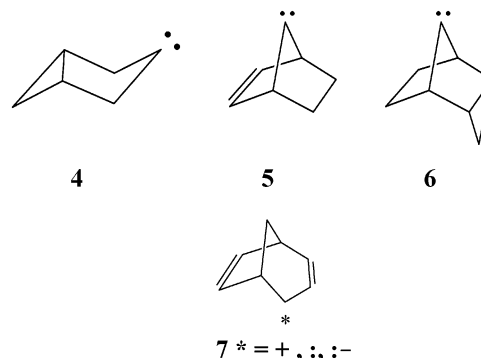


CHART 2

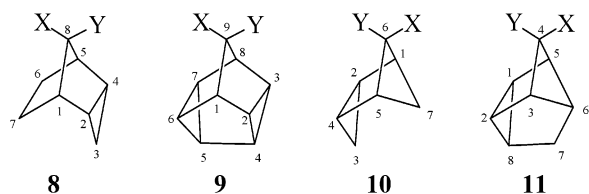


the 6-position of tricyclo[3.1.1.0^{2,4}]heptane **10**, and the 4-position of tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane **11** (Chart 3). The B3LYP/6-31G(d) method, as implemented in the Gaussian 98 suite of programs,⁵ is employed for geometric analysis of structural anomalies indicative of homoaro-

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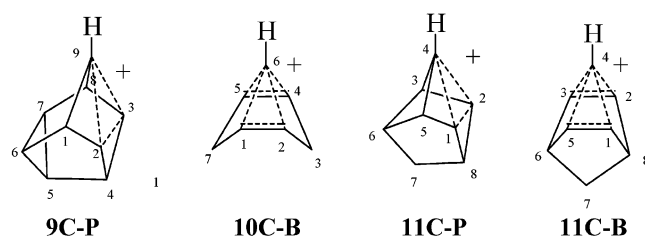
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CHART 3



- a: X=H, Y=H
 b: X=leaving group
 C-B: X=+, bishomo square pyramidal geometry
 C-P: X=+, trishomocyclopropenyl geometry
 Y=H
 S-B: XY=, singlet, bishomo square pyramidal geometry
 S-P: XY=, singlet, trishomocyclopropenylidene geometry
 T: XY=, triplet

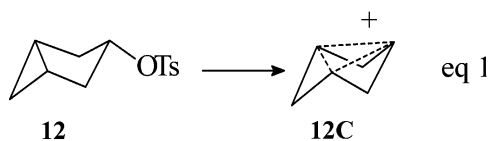
CHART 4



maticity. The B3LYP/6-31G(d) geometries paired with B3LYP/6-311+G(2d,p) and B3LYP/6-31+G(3df,2p) calculations are used to examine magnetic and energetic properties, respectively.

Background

Early proposals for homoaromatic intermediates were born from observations of the solvolysis of *cis*-3-bicyclo-[3.1.0]hexyl tosylate (**12**).¹ Winstein rationalized the solvolysis rate and deuterium scrambling in terms of the direct formation of trishomoaromatic cation **12C** in which a cyclopropane bond and the empty orbital at C3 form a three-center, two-electron aromatic system, eq 1. Fourteen years later the existence of stable ion intermediate **12C** was confirmed with ¹³C NMR by Masamune and co-workers.² The ethano-bridged derivative of cation **12C** is **8C-P** and is well established as a homoaromatic species.⁶



The Coates cation **9C-P**, Chart 4, was first proposed by Coates and Kirkpatrick to explain the solvolysis rate enhancement of **9b** (10^{10} to 10^{12} with X = *p*-nitrobenzoate) and the deuterium scrambling.⁷ This rationale was

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supported by NMR observation of delocalized cation **9C-P** in superacid solution.⁸ In addition, Saunders and Kates demonstrated using deuterium perturbation of ¹³C NMR that cation **9C-P** exists as a single static structure and not as a rapid equilibrium of equivalent classical forms.⁹

While the cations derived from ionization of **8b** and **9b** are trishomocyclopropenyl in nature, the cations generated by ionization of **10b** and **11b** enlarge the vista from that of the trishomocyclopropenyl species. A bis-homo square-pyramidal cation, **10C-B**, was observed in superacid solution at -110 °C by Masamune et al.¹⁰ Geometry optimization calculations at the MP2/6-31G(d) level by Prakash and co-workers¹¹ revealed the square-pyramidal cation as the only minimum on the potential energy surface. Similarly, studies of the carbocations derived from **11b** have focused on both the trishomocyclopropenyl and bishomo square-pyramidal ions.^{11,12} However, in contrast to the cationic intermediate derived from **10b**, where only the bishomo square-pyramidal cation is a minimum on the potential energy surface, both the trishomocyclopropenyl ion, **11C-P**, and the bishomo square-pyramidal ion, **11C-B** (Chart 4), are minima. Indeed, Møller–Plesset calculations as high as the MP4-(SDQ)/6-31G(d)//MP2/6-31G(d) level brought to light the fact that the two cations are practically isoenergetic.¹¹

This background raises the question of whether neutral carbene species, which will exhibit a reduced attraction for transannular sources of electron density relative to that of analogous carbocations, will provide structural, energetic, and magnetic characteristics similar to those of cations derived from **8b–11b**.

Results and Discussion

Key geometric features of the optimized structures (B3LYP/6-31G(d)) for polycyclic hydrocarbons **8a–11a** and the related cationic and carbene intermediates are displayed in Table 1. Indicators of aromaticity include lengthening of conjugative bonds compared to bonds in nonconjugated molecules, bond equilization, and planarity of the set of interacting atoms. Although many aromatic molecules are planar, allowing maximum cyclic delocalization of π -electrons, it has been recognized that other geometric shapes provide favorable conditions for cyclic electron delocalization.¹³ Included in those geometries is the bishomo square-pyramidal geometry possessed by several of the cations and carbenes in this study.

Hydrocarbons **8a**, **10a**, and **11a** possess C_s symmetry, while **9a** is C_{2v} , Table 1. In all cases, the cyclopropane bond fused with the larger ring is about 1.52 Å in length

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TABLE 1. Optimized Geometries of the Hydrocarbons, Cations, and Carbenes of the Series 8–11 (B3LYP/6-31G⁺; Nimag = 0 for All Species)

bond distance (Å) or dihedral angle (deg)	8a	8C-P	8T	8S-P		
C2–C4	1.522	1.929	1.537	1.688		
C7–C8	2.388	2.467	2.332	2.529		
C2–C8	2.381	1.812	2.329	1.964		
Φ ₈₁₅₄	122	82	123	90		
Φ ₈₅₁₇	121	166	121	150		
bond distance (Å) or dihedral angle (deg)	9a	9C-P	9T	9S-P		
C2–C3	1.520	1.849	1.530	1.637		
C2–C9	2.406	1.850	2.351	1.998		
C6–C9		2.438	2.351	2.528		
Φ ₉₁₈₃	125	82	125	93		
Φ ₉₈₁₆		166	125	155		
bond distance (Å) or dihedral angle (deg)	10a	10C-B	10T	10S-P	10S-B	
C1–C2		1.444			1.425	
C2–C4	1.522	2.123	1.540	1.710	2.114	
C2–C6	2.387	1.635	2.347	1.973	1.735	
C7–C6	2.113		2.037	2.222		
Φ ₆₁₅₄	113	54	113	83	59	
Φ ₆₅₁₇	128	175	127	151	170	
bond distance (Å) or dihedral angle (deg)	11a	11C-P	11C-B	11T	11S-P	11S-B
C1–C2	1.520	1.904	2.138	1.534	1.595	2.128
C1–C5			1.440			1.424
C2–C4	2.436	1.860	1.629	2.388	2.153	1.724
C6–C4	2.157	2.175		2.079	2.248	
Φ ₄₅₃₂	118	77	54	118	97	58
Φ ₄₃₅₆	133	173	167	132	153	171

and the distance between the bridge carbon and the closest carbon in the cyclopropane ring is about 2.4 Å. These distances are dramatically changed in cations **8C-P**, **9C-P**, **10C-B**, **11C-P**, and **11C-B**, Table 1. In trishomocyclopropenium ions **8C-P**, **9C-P**, and **11C-P** the bridge cationic carbon leans significantly toward the fused cyclopropane bond with the distance between the cationic carbon and a carbon in the fused cyclopropane bond shortening to an average of 1.84 Å. In both **8C-P** and **11C-P**, the fused cyclopropane bond lengthens by approximately 0.4 Å. In Coates's cation **9C-P** the fused cyclopropane bond only lengthens by 0.33 Å; however, the triangle of overlap (C9–C2–C3) is equal on all sides at 1.85 Å. Trishomocyclopropenyl ion **11C-P** was previously examined at MP2/6-31G(d); at that level, the triangle of overlap is equalized with a C4–C1 distance of 1.851 Å, and a C1–C2 distance of 1.859 Å.¹¹ In bishomo square-pyramidal cations **10C-B** and **11C-B** the C–C bonds from the center pentavalent carbon equalize to 1.63 Å at the B3LYP/6-31G(d) level. The base of the pyramid (carbons 1, 2, 4, and 5 in **10C-B** and carbons 1, 2, 3, and 5 in **11C-B**) aligns in a cyclobutadiene-like rectangle with

bond distances of ~1.44 and ~2.1 Å. Cations **10C-B** and **11C-B** were also examined using MP2/6-31G(d) methodology and gave structures very similar to those obtained at the B3LYP/6-31G(d) level. Prakash and co-workers reported C1–C2 and C4–C6 bond distances of 1.443 and 1.623 Å for **10C-B**, and C1–C5 and C2–C4 bond distances of 1.441 and 1.619 Å, respectively, for **11C-B**.¹¹ The geometries of cations **8C-P**, **9C-P**, **10C-B**, **11C-P**, and **11C-B** display bond lengthening and architectural changes which can be associated with homoaromaticity and which provide a basis for comparison with the related bivalent carbenes.

In contrast to the cationic intermediates, triplet carbene intermediates **8T**, **9T**, **10T**, and **11T**, Table 1, do not display the idiosyncrasies associated with cyclic electron delocalization, which is in harmony with the lack of homoaromaticity in related radical systems.¹⁴ The fused cyclopropane bond in these intermediates is increased by only 0.010–0.018 Å compared to that of their hydrocarbon parents. Because triplet carbenes ordinarily possess large bond angles at the bivalent carbon, the angle centered at the carbene carbon in **8T**, **9T**, **10T**, and **11T** is expected to increase with respect to that of the parent hydrocarbon; indeed in each case the carbene angle is about 5° larger than the same angle in the related hydrocarbon. This angular increase, and the necessary geometric changes required to accommodate it, can explain the increase in cyclopropane bond length as easily as conjugative interaction with the carbene center. In addition, the carbene carbon in each triplet carbene does not lean toward the cyclopropane bond, as would be expected to achieve delocalization. The lack of leaning can best be conveyed using the dihedral angle containing the carbene carbon, looking across the two bridgehead carbons, to either the cyclopropane carbon or the one- or two-carbon bridge on the opposite side. For example, the C8–C1–C5–C4 dihedral angle in **8a** is 122°, and the C8–C5–C1–C7 dihedral is 121°. The corresponding dihedral angles in **8T** are also 123° and 121°. The analogous dihedral angles in **9T**, **10T**, and **11T** also do not differ by more than a degree from those of their hydrocarbon parents.

The geometries of singlet carbenes **8S-P**, **9S-P**, **10S-P**, **10S-B**, **11S-P**, and **11S-B**, Table 1, exhibit varying degrees of delocalization. Carbenetricyclooctane **8S-P** displays both lengthening of the fused cyclopropane bond (C2–C4 = 1.688 Å) and leaning of the carbene carbon bridge toward the fused cyclopropane bond (C8–C2 = 1.964 Å), as previously observed,^{3a} and included here for completeness of comparison. However, there is not the degree of distortion and thus not the degree of delocalization in **8S-P** that is evident in **8C-P**, which possesses corresponding bond distances of 1.929 and 1.812 Å. Singlet carbene **9S-P** exhibits decreased bond distances connecting carbon 9 to carbons 2 and 3. The carbene carbon bridge in singlet **9S-P** leans noticeably; the C9–C1–C8–C3 dihedral angle is 93° in **9S-P** compared to 125° in **9T** and **9a**. Interestingly, both the trishomocyclopropenylidene and bishomo square-

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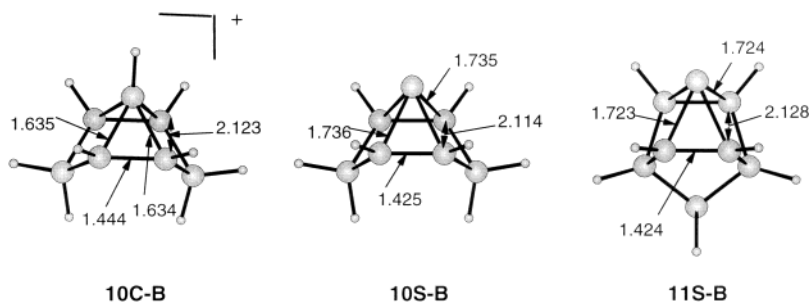


FIGURE 1. B3LYP/6-31G(d)-optimized geometries for cation **10C-B** and singlet carbenes **10S-B** and **11S-B**.

TABLE 2. Stabilization Energies (SEs) at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)^a Level for the Bridge Cation and Carbenes of **8** and **9** (B3LYP/6-31G(d)//B3LYP/6-31G(d)^a Stabilization Energies in Parentheses) Using Eq 2 (SE = $E_{\text{alkane}(f)} + E_{\text{intermediate}(f)} - E_{\text{intermediate}(i)} - E_{\text{alkane}(i)}$) (kcal/mol) and Diamagnetic Susceptibility Exaltations (Λ) Calculated at the CSGT-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) Level Using Eq 2 (cgs ppm)

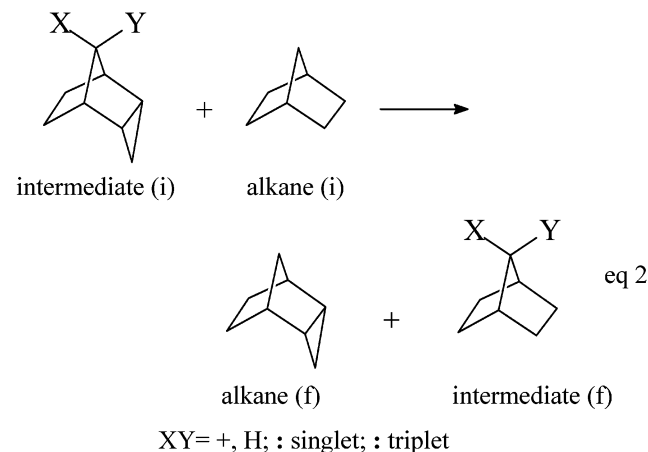
molecule	SE	Λ
8-tricyclo[3.2.1.0 ^{2,4}]octyl cation, 8C-P	29.4 (31.2)	14.6
8-carbenatrimethylcyclo[3.2.1.0 ^{2,4}]octane singlet, 8S-P	13.5 (14.1)	26.2
8-carbenatrimethylcyclo[3.2.1.0 ^{2,4}]octane triplet, 8T	0.6 (0.6)	2.3
9-pentacyclo[4.3.0.0 ^{2,4} .0 ^{3,8} .0 ^{5,7}]nonyl cation, 9C-P	22.9 (24.7)	15.7
9-carbenapentacyclo[4.3.0.0 ^{2,4} .0 ^{3,8} .0 ^{5,7}]nonane singlet, 9S-P	10.3 (11.4)	22.9
9-carbenapentacyclo[4.3.0.0 ^{2,4} .0 ^{3,8} .0 ^{5,7}]nonane triplet, 9T	1.1 (1.1)	4.2

^a Includes B3LYP/6-31G(d)//B3LYP/6-31G(d) zero-point energies uncorrected.

pyramidal structures are minima for the intermediate derived from 6-carbenatrimethylcycloheptane **10**, whereas only the bishomo square-pyramidal ion is a minimum-energy structure for the C6 cation derived from **10b**. The trishomocyclopropenylidene structure **10S-P** has bond distances in the triangle of overlap that are comparable to those of singlet carbene **8S-P**; i.e., the C2–C4 and C2–C6 bond distances in **10S-P** are 1.710 and 1.973 Å, respectively. The bishomo square-pyramidal singlet carbene **10S-B** is similar in overall structure to cation **10C-B** with the apical carbon to basal carbon distance (C6–C2) longer at 1.735 Å in **10S-B** relative to 1.635 Å in **10C-B** (Figure 1). The theme revealed for species derived from 6-carbenatrimethylcycloheptane **10** is extended to the related intermediates of 4-carbenatetracyclooctane **11**, where both the trishomocyclopropenylidene and bishomo square-pyramidal structures are minima. Although the C1–C2 cyclopropane bond of **11S-P** is only 1.595 Å, in contrast to 1.520 Å in **11a**, the C4 carbene carbon of **11S-P** leans toward the C1–C2 bond. The C4–C5–C3–C2 dihedral angle in **11S-P** is 97° compared to 118° in **11a** and **11T**. It is intriguing to note how similar in structure the bishomo square-pyramidal carbene **11S-B** is to the square-pyramidal carbene **10S-B** despite the additional carbon tying together the two halves of the molecule (Figure 1). The C2–C4, C1–C2, and C1–C5 bond distances in **11S-B** are 1.724, 2.128, and 1.424 Å, respectively, with a C8–C1–C5 angle of 106.4°. The analogous bond distances in **10S-B** are 1.735, 2.114, and 1.425 Å with a C3–C2–C1 angle of 117.9°. A clear difference between **10S-B** and **11S-B** lies in the angle of the cyclopropane-like wings relative to the base of the pyramid; that is, the C5–C4–C2–C3 dihedral angle in **10S-B** is 131°, while the comparative dihedral angle (C3–C2–C1–C8) in **11S-B** is 113°.

Stabilization energies were examined by the use of homodesmotic equations. In the case of the stabilization energies of the C8-centered cation and carbenes derived

from **8**, and the C9-centered cation and carbenes of **9**, homodesmotic eq 2 was employed with norbornane and



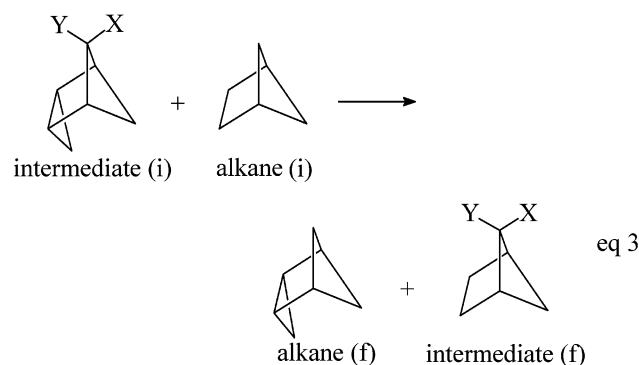
the 7-norbornyl cation and carbenes acting as the reference system. The results for B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) calculations are listed in Table 2. Homoaromatic cations **8C-P** and **9C-P** show large stabilization energies of 29.4 and 22.9 kcal/mol, respectively. Since both of these cations are known to be homoaromatic, the confirmation of their stabilization supports the use of eq 2 as a method for revealing homoconjugative interaction. Moreover, since the cations carry the added driving force of delocalizing charge, diminished overlap in the case of singlet carbenes **8S-P** and **9S-P** is to be expected. Both singlet carbenes **8S-P** and **9S-P** display about 45% of the homoconjugative stability exhibited by their cationic cousins. Although energetic stabilization in **8S-P** and **9S-P** is less than in their related cations, the stabilization energies are nevertheless significant, being greater than 10 kcal/mol in both singlet carbenes. Triplet carbenes **8T** and **9T** show no significant increase in stability relative to the 7-carbenanorbornane triplet.

TABLE 3. Stabilization Energies (SEs) Calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)^a Level for the Bridge Cations and Carbenes of **10, **11**, and Parent Carbene **13** (B3LYP/6-31G(d)//B3LYP/6-31G(d)^a Stabilization Energies in Parentheses) Using Eqs 3 and 4 (kcal/mol) and Diamagnetic Susceptibility Exaltations (Λ) Calculated at the CSGT-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) Level Using Eqs 3 and 4 (cgs ppm)**

molecule	SE	Λ
singlet pyramidal C ₅ H ₄ carbene, 13	25.3 (26.6)	38.8
6-tricyclo[3.1.1.0 ^{2,4}]heptyl cation, 10C-B	15.2 (16.7)	-2.4
trishomocyclopropenylidene 6-carbenatrimethylcyclo[3.1.1.0 ^{2,4}]heptane singlet, 10S-P	0.4 (0.8)	6.0
bishomo square-pyramidal 6-carbenatrimethylcyclo[3.1.1.0 ^{2,4}]heptane singlet, 10S-B	4.5 (3.6)	2.9
6-carbenatrimethylcyclo[3.1.1.0 ^{2,4}]heptane triplet, 10T	0.7 (0.7)	2.1
trishomocyclopropenium 4-tetracyclo[3.3.0.0 ^{2,8} .0 ^{3,6}]octyl cation, 11C-P	0.4 (1.9)	2.7
bishomo square-pyramidal 4-tetracyclo[3.3.0.0 ^{2,8} .0 ^{3,6}]octyl cation, 11C-B	0.5 (1.8)	-1.0
trishomocyclopropenium 4-carbenatetracyclo[3.3.0.0 ^{2,8} .0 ^{3,6}]octane singlet, 11S-P	-6.9 (-6.7)	-4.1
bishomo square-pyramidal 4-carbenatetracyclo[3.3.0.0 ^{2,8} .0 ^{3,6}]octane singlet, 11S-B	-12.0 (-12.8)	6.5
4-carbenatetracyclo[3.3.0.0 ^{2,8} .0 ^{3,6}]octane triplet, 11T	1.3 (1.2)	2.4

^a Includes B3LYP/6-31G(d)//B3LYP/6-31G(d) zero-point energies uncorrected.

Homodesmotic eq 3 was used to compare homoconjugative stabilization in the cations and carbenes centered at C6 in tricycloheptane **10** and C4 in tetracyclooctane



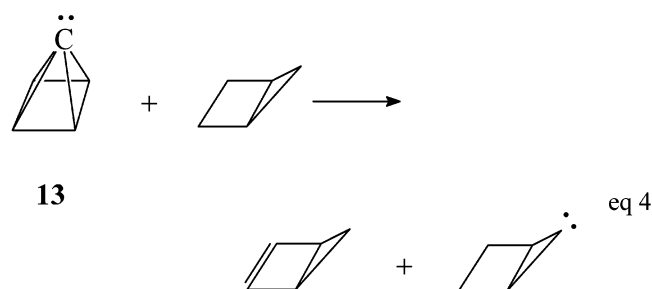
11, Table 3.¹⁵ This reaction takes advantage of the bicyclo[2.1.1]hexane skeleton common to both **10** and **11**. Bishomo square-pyramidal cation **10C-B** reveals good delocalization with a stabilization energy of 15.2 kcal/mol. Interestingly, both bishomo square-pyramidal cation **11C-B** and trishomocyclopropenyl cation **11C-P** reveal no significant stabilization energy. However, the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) energies are in excellent agreement with the MP2/6-31G(d) study by Prakash and co-workers, which revealed that **11C-P** and **11C-B** are isoenergetic.

Although both the trishomocyclopropenylidene and bishomo square-pyramidal structures are geometric minima for the C6-centered singlet carbenes of **10**, the bishomo square-pyramidal structure is clearly more stable. Bishomo square-pyramidal carbene **10S-B** is over 4 kcal/mol more stable than **10S-P**. This contrasts with the case for the C4-centered singlet carbenes of **11**, where square-pyramidal carbene **11S-B** is more than 5 kcal/mol less stable than **11S-P**. Both the trishomocyclopropenylidene, **11S-P**, and bishomo square-pyramidal, **11S-B**, structures are less stable than 6-carbena-bicyclo[2.1.1]hexane, Table 3. Neither triplet carbene **11T** nor triplet carbene **10T** is significantly stabilized relative to its bicyclo[2.1.1]hexane counterpart.

(15) The C_s symmetric structure of singlet 5-carbenabicyclo[2.1.1]hexane used in this reaction possesses one imaginary frequency at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level. However, since all the singlet carbenes are C_s in structure, the symmetry is maintained as C_s to provide the best comparison.

The relative instability of bishomo square-pyramidal carbene **11S-B** is especially intriguing when compared to that of **10S-B** considering their geometric similarities. It is apparent that while the pyramid portions of **11S-B** and **11C-B** are very similar to those in **10S-B** and **10C-B**, the energetic stability of the bishomo square-pyramidal structure is highly dependent on strain in the molecule as a whole. This was proposed by Prakash and co-workers in their MP2 study,¹¹ where the instability of **11C-B** relative to **10C-B** was ascribed to poor orbital overlap between the apical carbon and the basal carbons of the pyramid. A similar rationale is tempting for the relative stabilities of **10S-B** and **11S-B**.

The singlet bivalent species **10S-B** and **11S-B** may be viewed as singlet carbon complexes of 1,4-cyclohexadiene and norbornadiene. Since these diene moieties are bis-homo analogues of cyclobutadiene, it is of interest to compare the stabilization energies of **10S-B** and **11S-B** with that of the singlet carbon complex of cyclobutadiene (**13**), which serves as the parent system. Singlet species **13** has previously been evaluated at the HF/3-21G, HF/4-31G, and MP2/6-31G* levels.¹⁶ The architecture we derive from B3LYP/6-31G* calculations is in good agreement (apical to basal 1.659 Å, basal to basal 1.449 Å, corresponding to 1.645 and 1.445 Å at MP2/6-31G*).^{16c} The stabilization energy as calculated at the B3LYP/6-311+G(3df, 2p)//B3LYP/6-31G* level, using homodesmotic eq 4, is substantial at 25.3 kcal/mol. Homodesmotic



eq 4 might be improved if the dihedral angle $\phi(2,1,4,5)$ in bicyclo[2.1.0]pentane and the analogous angles in bicyclo[2.1.0]pentene and 5-carbenabicyclo[2.1.0]pentane

(16) (a) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781–4788. (b) Minkin, V. I.; Minyaev, R. M.; Orlova, G. V. *J. Mol. Struct.: THEOCHEM* **1984**, *110*, 241. (c) Bataji, V.; Michl, J. *Pure Appl. Chem.* **1988**, *60*, 189–194.

TABLE 4. B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) Singlet–Triplet Energy Gap for the Bridge Carbenes of Norbornane, Bicyclo[2.1.1]hexane, and 8–11

molecule	$\Delta E_{T-S}^{a,b}$
7-carbenanorbornane	13.0
8-carbenatricyclo[3.2.1.0 ^{2,4}]octane, 8	26.0
9-carbenapentacyclo[4.3.0.0 ^{2,4} .0 ^{3,8} .0 ^{5,7}]nonane, 9	22.2
5-carbenabicyclo[2.1.1]hexane	25.4
trishomocyclopropenylidene 6-carbenatricyclo[3.1.1.0 ^{2,4}]heptane 10	25.1
bishomo square-pyramidal 6-carbenatricyclo[3.1.1.0 ^{2,4}]heptane 10	29.2
trishomocyclopropenylidene 4-carbenatetracyclo[3.3.0.0 ^{2,8} .0 ^{3,6}]octane 11	17.2
bishomo square-pyramidal 4-carbenatetracyclo[3.3.0.0 ^{2,8} .0 ^{3,6}]octane 11	12.2

^a $\Delta E_{T-S} = (E_{\text{triplet}} - E_{\text{singlet}}) * 627.5095 + 1.75$ kcal/mol, where 1.75 kcal/mol is the calculation difference (B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)), from the experimental value, for the singlet–triplet gap of methylene. ^b Reported energies include B3LYP/6-31G(d)//B3LYP/6-31G(d) zero-point energies.






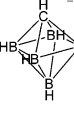


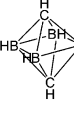
were closer to that of a resonance structure of carbon complex **13**. Adjustments in this direction would clearly raise the stabilization energy of **12** above the 25.3 kcal/mol level.

Since the triplets are insensitive to homoaromatic interaction, it is possible to probe for homoaromaticity in the corresponding singlet species through evaluation of the singlet–triplet carbene energy gap (ΔE_{S-T}), Table 4. All the singlet carbenes are more stable than the triplet carbenes, which was expected. However, when compared to structural standards 7-carbenanorbornane and 5-carbenabicyclo[2.1.1]hexane, a new picture emerges. The singlet–triplet carbene energy gaps for both **8** and **9** are greater than that for 7-carbenanorbornane. However, comparing the ring systems containing the bicyclo[2.1.1]hexane ring system (**10** and **11**), only the bishomo square-pyramidal structure for **10** has a larger singlet–triplet carbene energy gap than 5-carbenabicyclo[2.1.1]hexane. Both singlet–triplet carbene energy gaps for carbenes derived from 4-carbenatetracyclooctane **11** are at least 7 kcal/mol less than the singlet–triplet carbene energy gap for 5-carbenabicyclo[2.1.1]hexane.

A fourth method to characterize homoaromaticity involves an evaluation of magnetic properties.¹⁷ As it pertains to cyclic electron delocalization, magnetic susceptibility exaltation (Λ) can be defined as the difference between the molar susceptibilities (χ) of a cyclic conjugated compound and a model compound which possesses no ring current.^{13b,17b–e,h–j} To analyze the magnetic susceptibility exaltation of the cations and carbenes of **8–11**, homodesmotic eqs^{17k–m} 2–4 were used.¹⁸ The sign convention here is based on these homodesmotic equations, with Λ referring to $(\chi_{\text{alkane}(i)} + \chi_{\text{intermediate}(i)} - \chi_{\text{intermediate}(i)})$,

(17) (a) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465–2468. (b) Krygowski, T. M.; Cyranski, M. K.; Czarnocki, Z.; Häfelinger, G. Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783–1796. (c) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318. (d) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209. (e) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337. (f) Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 407. (g) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1763. (h) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811. (i) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 1991. (j) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1971; Vol. II, p 187. (k) Verevkin, S. P.; Beckhaus, H.-D.; Rüdhardt, C.; Haag, R.; Kozhushkov, S. I.; Zywiets, T.; de Meijere, A.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 11130–11135. (l) Jiao, H.; van E. Hommes, N. J. R.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1996**, *61* 2826–2828. (m) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2383–2386.

TABLE 5. Nucleus-Independent Chemical Shifts of Species Related to the Singlet Carbon Atom Complex of Cyclobutadiene

NICS ^a		NICS ^a		NICS ^b	
	-27.2 (-22.9)		-33.1 (-29.2)		-33.8
	-20.4 (-18.0)		-21.4 (-19.2)		-34.6
	-21.8 (-19.6)		-22.4 (20.6)		-36.0

^a GIAO-HF/6-31G**/B3LYP/6-31G* with GIAO-B3LYP/6-31G**/B3LYP/6-31G* values in parentheses. ^b GIAO-HF/6-31G**/MP2(fc)/6-31G* (ref 20).

– $\chi_{\text{alkane}(i)}$), Tables 2 and 3. A molecule is considered aromatic when $\Lambda > 0$, antiaromatic when $\Lambda < 0$, and nonaromatic when $\Lambda \approx 0$. The diamagnetic susceptibility exaltation of benzene is about 16 cgs ppm.¹⁹












The positive magnetic susceptibility exaltations of the studied cations and singlet carbenes of **8** and **9** indicate strong cyclic electronic delocalization in these molecules. Interestingly, the singlet carbenes of **8** and **9** display larger magnetic susceptibility exaltations than the related cations of **8** and **9** display. This is due in large part to the fact that the bridge cation of norbornane has a greater absolute value of magnetic susceptibility than the 7-carbenanorbornane singlet. The triplet carbenes of **8** and **9** reveal such small values of magnetic susceptibility exaltation that they are consistent with nonaromaticity.

In light of magnetic susceptibility exaltation, the bridge cations and carbenes of **10** and **11** exhibit mostly nonaromatic qualities. Since both bishomo square-pyramidal

(18) Without restriction, optimizations of 5-carbenabicyclo[2.1.0]pentane relax to planar 1,2-cyclopentadiene, so for the purposes of homodesmotic reaction 4, the interplanar angle of 5-carbenabicyclo[2.1.0]pentane was fixed at the angle ($\Phi = 113.32^\circ$) of the parent hydrocarbon.

(19) Jiao, H.; Schleyer, P. v. R.; Beno, B. R.; Houk, K. N.; Warmuth, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2761.

TABLE 6. Analysis of Aromaticity Criteria for Cations **8C-P**, **9C-P**, **10C-B**, **11C-P**, and **11C-B** and Singlet Carbenes **8S-P**, **9S-P**, **10S-B**, **11S-P**, and **11S-B**

	structural criteria	stabilization energy	$\Delta\Delta E_{T-S}^a$	Λ	NICS ^b
	positive	positive	n/a	positive	
8C-P					
	positive	positive	n/a	positive	
9C-P					
	positive	positive	n/a	~0	positive
10C-B					
	positive	~0	n/a	~0	
11C-P					
	positive	~0	n/a	~0	positive
11C-B					
	positive	positive	positive	positive	
8S-P					
	positive	positive	positive	positive	
9S-P					
	positive	~0	~0	positive (small)	
10S-P					
	positive	positive	positive (small)	Positive (small)	positive
10S-B					
	positive	negative	negative	negative (small)	
11S-P					
	positive	negative	negative	positive (small)	positive
11S-B					

^a $\Delta\Delta E_{T-S} = \Delta E_{T-S}(\text{molecule}) - \Delta E_{T-S}(\text{structural standard})$. ^b If the NICS value indicates aromaticity, the term positive is used.

cations **10C-B** and **11C-B** display only slightly negative magnetic susceptibility exaltation, they fall under the umbrella of nonaromaticity. Similarly, trishomocyclopropenyl cation **11C-P** shows only a slightly positive magnetic susceptibility exaltation and could be considered equally nonaromatic. Singlet carbene **10S-P**, however, manifests a respectable ~6 cgs ppm magnetic susceptibility exaltation which may place it in the modestly aromatic category. Conversely, in the case of the singlet carbenes of **11**, it is bishomo square-pyramidal carbene **11S-B** that exhibits aromatic magnetic susceptibility exaltation ($\Lambda = 6.5$ cgs ppm), while trishomocyclopropenium carbene **11S-P** displays slightly antiaromatic characteristics ($\Lambda = -4.1$ cgs ppm). Both triplet carbenes **10T**

and **11T** are nonaromatic with respect to magnetic susceptibility exaltation. Although there is weak or some aromaticity indicated by the diamagnetic susceptibility exaltation of **10S-B** and **11S-B**, the values are considerably less than that of the standard apical singlet carbon complex **13**, which at 38.8 cgs ppm is close to the values for *closo*-borane $B_6H_6^{2-}$ (40.02), *closo*-monocarborane $CB_5H_6^-$ (C_{4v}) (50.00), and *closo*-dicarborane (52.49)^{20,21} (structures **14–16** in Table 5).

(20) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem.* **1998**, *37*, 3454–3470.

(21) The signs for the diamagnetic susceptibility exaltation values cited from ref 20 have been reversed to achieve consistency with the scheme used in the present discussion.

A second magnetic property which represents a relatively new and versatile method for characterization of aromaticity is that of the evaluation of the NICS (nucleus-independent chemical shift) calculated at the center of the molecule. If the chemical shift indicates shielding (a negative value) and thus a diatropic ring current, the species is aromatic. If deshielding (a positive value) is revealed, and thus a paratropic ring current, the structure is antiaromatic.^{17ac,20} The NICS values of the apical singlet carbon atom and :CH^+ complexes of cyclobutadiene, 1,4-cyclohexadiene, norbornadiene, and related *closo*-borane and -carborane species, evaluated at the center of the four-carbon diene equator in the cationic and carbene systems, are listed in Table 5. We have a clear indication of aromaticity for the cations and singlet carbenes, which, with comparison with the NICS values for the related *closo*-borane and -carboranes, suggests that these cations and carbenes are also good examples of three-dimensional aromaticity.

Conclusions

Characterization of the aromaticity of molecules is a multidimensional problem.²² Comparisons reveal that not all molecular entities will display aromaticities to the same degree across the same set of criteria.²² In this study, we have examined structural, energetic, and magnetic criteria for the bridged cations and carbenes of polycyclic structures **8–11**. The results of the aromatic gauges for the bridged cations and singlet carbenes of **8–11** are summarized in Table 6. No formal weighting of criteria is attempted; instead the overall picture is used to provide guidance and characterization. The triplet carbenes in this series do not display any significant stabilization with regard to these criteria and are therefore classified as nonaromatic. According to the criteria employed, trishomocyclopropenyl cations **8C-P** and **9C-P** are clearly homoaromatic, giving positive results to each test. The homoaromaticity of bishomo square-pyramidal cation **10C-B** is not quite as clearly defined. While **10C-B** gave a stabilization energy which may be grouped with those of **8C-P** and **9C-P**, and a substantial NICS (-20.4 ppm), **10C-B** failed to show aromatic magnetic susceptibility exaltation. On balance, it seems reasonable to classify **10C-B** as aromatic. While the structures for isoenergetic cations **11C-P** and **11C-B** are energetic minima, they do not present as persuasive a case for homoaromaticity, although the NICS value (-21.8) for

11C-B tempts one to suggest homoaromaticity, especially since the stabilization energy reflects an increase in both strain and homoaromaticity that may balance out. Drawing a similar picture to that of the analogous cations, trishomocyclopropenylidene carbenes **8S-P** and **9S-P** meet all the criteria for homoaromaticity. As observed for the related cation, the homoaromaticity for the singlet carbenes of **10** is not as clearly defined as that for the singlet carbenes of **8** and **9**. Trishomocyclopropenylidene carbene **10S-P** displays a small amount of diamagnetic susceptibility exaltation, but essentially no stabilization energy or $\Delta\Delta E_{T-S}$ relative to the model carbene. In contrast, bishomo square-pyramidal carbene **10S-B** displays a modest amount of energetic stabilization, a small amount of diamagnetic susceptibility exaltation, and a substantial NICS value (-21.4 ppm). We view the homoaromaticity of **10S-P** as borderline and designate isomeric **10S-B** as homoaromatic. Trishomocyclopropenylidene carbene **11S-P** is classified as non- to antiaromatic due to its negative stabilization energy and magnetic susceptibility exaltation. Finally, bishomo square-pyramidal carbene **11S-B** displays conflicting values for homoaromaticity. The structure is one that allows for cyclic electron delocalization, a small amount of positive magnetic susceptibility exaltation, and a substantial negative NICS value (-22.4 ppm); however, the stabilization energy again reflects both strain and potential homoaromaticity, but is substantially negative, and $\Delta\Delta E_{T-S}$ is negative. Intuitively, one would anticipate that the cationic species, with the potential for charge delocalization, would exhibit greater evidence of homoaromaticity. This is true for structure and stabilization energies. In every case the cations exhibit greater geometric change and greater stabilization energy relative to those of the corresponding carbene. In contrast, it is notable that with the exception of the **11C-P/11S-P** pair the carbenes provide a greater magnetic susceptibility exaltation, and the NICS values for the related cations and carbenes are very close in value.

Acknowledgment. Support from the Oregon State University Research Council, the MRF fund, and the NIEHS is gratefully acknowledged.

Supporting Information Available: Figures displaying structures, tables providing the energies and diamagnetic susceptibilities used to calculate stabilization energies (SEs) and diamagnetic susceptibility exaltations (Λ), and the Cartesian coordinates for all optimizations described. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(22) Katritzky, A. R.; Jug, K.; Oniciu, D. C. *Chem. Rev.* **2001**, *101*, 1421–1449.