Homoaromaticity in Carbene Intermediates

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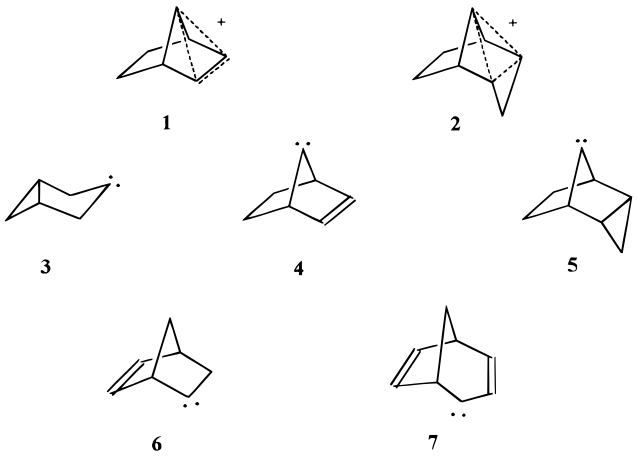
Analyses of isodesmic reactions for singlet 7-carbenanorbornene (**4S**), 8-carbena-*endo*-tricyclo-[3.2.1.0^{2,4}]octane (**5S**), 3-carbenabicyclo[3.1.0]hexane (**3S**), 2-carbenanorbornene **6S**, and 2-carbenabicyclooctadiene **7S** at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* level provide stabilization energies of 13.83, 13.50, 3.00, −2.22, and −3.01 kcal/mol, respectively. The C7 carbene in **4S** and the C8 carbene center in **5S** are strongly bent toward the double bond and cyclopropane ring, respectively, in contrast to their related triplets, **4T** and **5T** and parent hydrocarbons. The geometric change for **3S** compared to **3T** or to parent bicyclo[3.1.0]hexane is minimal. Comparison of the stability of **6S** with 2-carbenanorbornane and the geometry of **6S** with that of **6T** and also with the singlet and triplet 2-carbenanorbornane suggests very modest bridging. The stabilization energy and geometry of 2-carbenabicyclooctadiene **7** resemble antihomoaromatic bicyclooctadienyl cation **9** rather than the related homoaromatic bicyclooctadienyl anion **8**. The diamagnetic susceptibility exhaltations ($\Delta\chi$) of **3**, **4**, **5**, and **7**, calculated at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G* level, are −0.7, 22.7, 26.0, and −10.3 cgs-ppm, respectively. The singlet−triplet energy differences, ΔE_{TS}, for carbenacyclohexane, carbenacyclopentane, **3**, **4**, **5**, **6**, **7**, and 2-carbenabicyclo[3.2.1]oct-3-ene at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* level are 3.4, 10.3, 8.8, 27.1, 25.9, 12.7, −4.0, and −0.9 kcal/mol, respectively.

Homoaromaticity in the 7-norbornenyl (**1**) and 8-*endo*-tricyclo[3.2.1.0^{2,4}]octyl (**2**) cations has been a source of fascination and plays a dominant role in determining the chemistry.[1] The related radicals have not provided convincing evidence to support homoaromaticity.[2] This raises an intriguing question: where geometries are appropriate, are singlet carbenes also homoaromatic or perhaps, in some cases, antihomoaromatic? Earlier, we have reported on the chemistry of 3-carbenabicyclohexane (**3**),[3] *endo*-8-carbenatricyclo[3.2.1.0^{2,4}]octane (**5**),[4] and 2-carbenabicyclo[3.2.1]octadiene (**7**).[5] Moss, Kirmse, and Brinker and their co-workers have described 7-carbenanorbornene (**4**),[6] and Gleiter and Hoffmann have carried out an extended Hückel calculation on **4** that provides encouragement,[7] but whether these species are homoaromatic or antihomoaromatic was either not revealed or is in question.[8] Related homoallylic carbene 2-carbenanorbornene **6** is included and 2-carbenabicyclo[3.2.1]octa-3,6-diene **7** presents the potential for either homoaromaticity or antihomoaromaticity depending on the orbital occupancy of the nonbonding carbene electrons.



Homoaromaticity should be revealed in enhanced stability, geometric changes related to model systems, magnetic properties, and in the triplet−singlet energy gap (ΔE_{TS}). Enhanced stabilities for singlet species **3S**−

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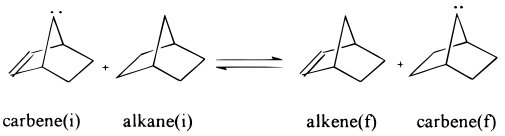
Table 1. Stabilization Energies of Carbenes 3S−7S, 7-Norbornenyl Cation (1), Bicyclooctadienyl Anion 8, and Bicyclooctadienyl Cation 9[a]

intermediate	carbene(i)	alkane(i)	alkene(f)	carbene(f)	SE[b]
carbenabicyclohexane **3**	−233.249575	−235.787256	−234.561349	−234.470700	3.00
	(−233.169352)	(−235.709223)	(−234.483602)	(−234.389755)	(3.27)
carbenanorbornene **4**	−271.364447	−273.878236	−272.662619	−272.558023	13.83
	(−271.274917)	(−273.790526)	(−272.573762)	(−272.466886)	(15.56)
carbenatricyclooctane **5**	−310.643238	−273.878236	−311.941938	−272.558023	13.50
	(−310.541299)	(−273.790526)	(−311.842531)	(−272.466886)	(14.06)
7-norbornenyl cation **1**	−271.773528	−273.878236	−272.662619	−272.960601	17.91
	(−271.693953)	(−273.790526)	(−272.573762)	(−272.877395)	(20.91)
2-carbenanorbornene **6**	−271.351798	−273.878236	−272.662619	−272.570947	−2.22
	(−271.261328)	(−273.790526)	(−272.573762)	(−272.480756)	(−1.67)
carbene **7**	−309.456260	−311.977920	−310.763235	−310.6757361	−3.01
	(−309.354000)	(−311.876808)	(−310.661542)	(−310.574241)	(−3.12)
anion **8**	−310.161702	−311.977920	−310.763235	−311.3616363	9.26
	(−310.033893)	(−311.876808)	(−310.661542)	(−311.233897)	(9.58)
cation **9**	−309.878431	−311.977920	−310.763235	−311.1041652	−6.93
	(−309.785466)	(−311.876808)	(−310.661542)	(−311.010355)	(−6.04)

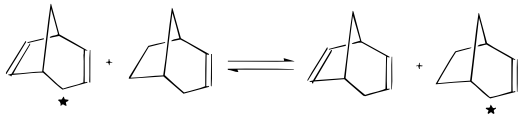
[a] Energies of the individual species calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* level + ZPE at B3LYP/6-31G* or in parentheses at the B3LYP/6-31G*//B3lYP/6-31G* + ZPE level (NImag = 0 in each case) in Hartrees. [b] The stabilization energy SE = $E_{alkene(f)} + E_{carbene(f)} - E_{carbene(i)} - E_{alkane(i)}$ in kcal/mol. Using isodesmic reactions of the type illustrated with eq 1 for intermediates **4**−**6** and **1**, norbornane is the standard reactant, alkane(i), whereas for carbene **3**, cyclohexane is the standard reactant. For intermediates **7**−**9**, eq 2 is employed. For the cations and anion, the energies for the cationic and anionic intermediates replace the analogous carbene species.

6S were evaluated using isodesmic equations of the type illustrated in eq 1 for **4** with calculations of the energies



(1)

of the individual species at the B3LYP/6-311+G(3df, 2p)// B3LYP/6-31G* and B3LYP/6-31G*//B3LYP/6-31G* levels,[9] correcting for zero point energy differences (at B3LYP/6-31G* geometries). Using the B3LYP/6-311+G-(3df, 2p)//B3LYP/6-31G* energies, the stabilization energies listed in Table 1 reveal that singlets 7-carbenanorbornene **4S** and 8-carbenatricyclooctane **5S** are strongly stabilized (13.8 and 13.5 kcal/mol), approaching that for the 7-norbornenyl cation **1** (17.9 kcal/mol), while that for singlet carbenabicyclohexane **3S** is considerably reduced (3.0 kcal/mol). The related 2-carbenanorbornene **6S** and 2-carbenabicyclooctadiene **7S** are destabilized (−2.2 and −3.0 kcal/mol), the latter evaluated using isodesmic eq 2. The initial impression is that bivalent singlet carbenes



(2)

7 ★ = ·· ; **8** ★ = ·· ; **9** ★ = +

4S and **5S** are strongly homoaromatic, while stabilization or destabilization for potentially homoallylic species **6S** may be complicated by the comparison with 2-carbenanorbornane, which may be stabilized (vide infra). The stabilization energy for singlet carbene **7S** suggests antihomoaromaticity since its value contrasts with homoaromatic anion **8** (9.26 kcal/mol) and is similar, instead, to antihomoaromatic cation **9** (−6.9 kcal/mol) (eq 2), the latter two results anticipated on the basis of the results of Jiao and Schleyer.[10]

The initial impression concerning the nature of carbenes **4S** and **5S** should be reflected in an altered architecture for each carbene. The C7 carbon of singlet 7-carbenanorbornene (**4S**) clearly leans toward the double bond, with the C2−C7 distance (1.892 Å) much shorter than the C6−C7 distance (2.565 Å). The C2−C7 distance is close to that reported by Laube for the C2−C7 distance in 2,3-dimethyl-7-phenylnorbornen-7-yl ion (1.86 Å)[1b] and that reported by Evans et al.[11] for the 7-norbornadienyl moiety in $(C_5Me_5)_2Sm(O_2C_7Me_5)$ (C2−C7 = 1.876 Å). The dihedral angles ϕ_{7412} (90.0°) versus ϕ_{7145} (146.2°) are equally telling. The analogous distances in the triplet **4T** and in norbornene place the C7 symmetrically between the etheno and ethano wings (Figure 1); in **4T** ϕ_{7412} = 127.8° and ϕ_{7145} = 119.9°, while in norbornene ϕ_{7412} = 127.3° and ϕ_{7145} = 120.8°. There is, in addition, a lengthening of the alkene double bond (1.374 Å) relative to the double bonds in triplet 4**T** (1.345 Å) and norbornene (1.341 Å) as one would expect. Similar features are observed for singlet *endo*-8-carbenatricyclooctane. The C8 carbene carbon leans strongly toward the endo fused cyclopropane unit; the C8−C2 distance is 1.965 Å, shorter than the C8−C7 distance (2.529 Å), and dihedral ϕ_{8154} is 89.5°, much smaller than dihedral ϕ_{8517} (150.1°). Comparisons with the analogous distances and dihedral angles for triplet **5T** (ϕ_{8154} = 122.7°, ϕ_{8517} = 121.1°) and *endo*-tricyclo[3.2.1.$0^{2,4}$]octane (ϕ_{8154} = 122.1°, ϕ_{8517} =

(9) The density functional theory calculations employed Becke's three parameter hybrid method (Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652) and the correlation functional of Lee, Yang, and Parr (Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 785−789) within the Gaussian 94 program. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision B.2; Gaussian, Inc.: Pittsburgh, PA, 1995. The singlet carbenes were calculated using the restricted B3LYP, and the triplets at the unrestricted UB3LYP method; however, the singlet carbenes in this study were all UB3LYP stable, calculations using B3LYP or UB3LYP providing the same energy.

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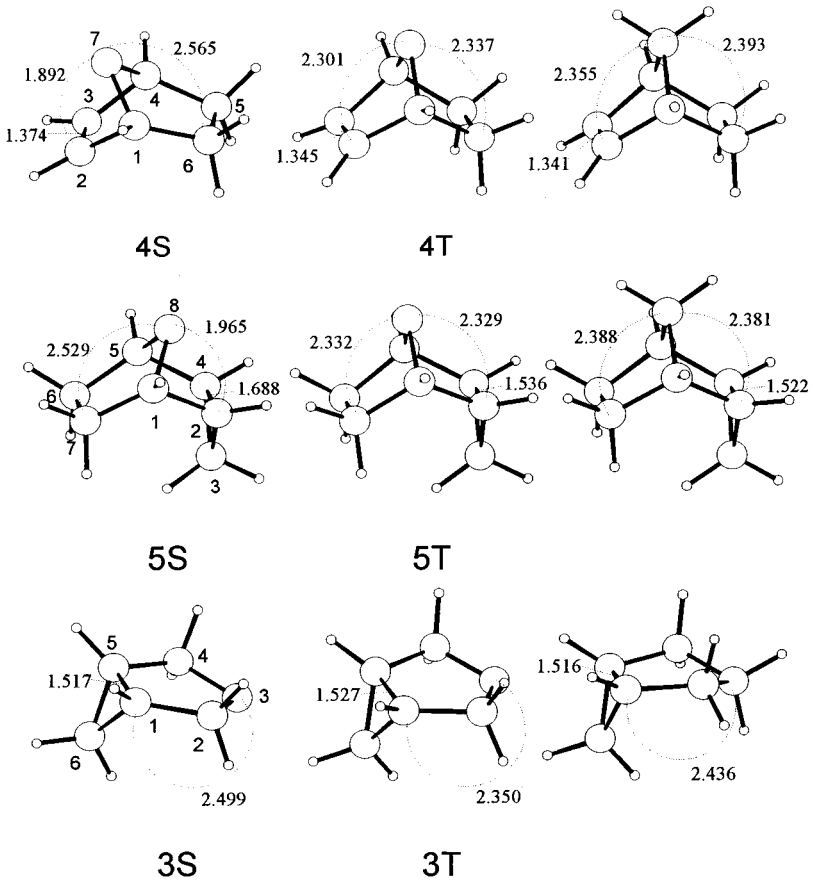
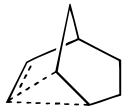


Figure 1. The structures for singlet carbenes **4S**, **5S**, **3S**; triplet carbenes **4T**, **5T**, **3T**; and the related parent hydrocarbons calculated at the B3LYP/6-31G* level.

121.5°) demonstrate that the leaning C8 carbene carbon is a singlet characteristic. In addition, there is a rather striking increase in the C2−C4 transannular cyclopropane bond in singlet **5S** (1.688 Å) that may be compared with the record breaking C−C bond distances of slightly greater than 1.7 Å described by Kammermeier et al.[12] The much smaller stabilization energy of singlet carbenabicyclohexane **3S** (22% of singlet **4S** and 17% of 7-norbornenyl cation) is reflected in geometries for singlet **3S**, triplet **3T**, and bicyclo[3.1.0]hexane, which are quite similar. All three are very slightly boat shaped. The dihedral angles ϕ_{1543} for **3S**, **3T**, and bicyclohexane are 6.7°, 18.1°, and 7.2°.

In contrast to the stabilization for **3S**, **4S**, and **5S**, 2-carbenanorbornene **6S** appears to be slightly destabilized relative to singlet 2-carbenanorbornane (Table 1); however, there is some evidence of bridging in singlet 2-carbenanorbornane. The C2−C6 distance is 2.244 Å while the C3−C5 distance is 2.464 Å and the C1−C6 bond is lengthened to 1.601 Å at the B3LYP/6-31G* level. This view is reinforced by a consideration of the triplet geometry in 2-carbenanorbornane, which exhibits a C2−C6 bond distance of 2.456 Å, a C3−C5 distance of 2.519 Å, and a C6−C1 distance of 1.546 Å. Perhaps both 2-carbenanorbornene **6** and singlet 2-carbenanorbornane are bridged and stabilized. An indication of the degree of bridging in carbenanorbornene **6S** is revealed by comparing the C2−C6 distance (2.263 Å) with the C3−C5 distance (2.424 Å) and noting that the C1−C6 bond (1.543 Å) is only slightly longer than the C4−C5 bond (1.529 Å). A comparison with the related triplet 2-carbenanorbornene bonds (C2−C6 = 2.397 Å, C3−C5 = 2.492 Å, C6−C1 = 1.536 Å) and noting that the double bonds in **6T** and **6S** are equal at 1.342 suggests that bridging is muted relative to 2-carbenanorbornane (Figure 2).

A comparison of the geometries of singlet carbene **7S** with **7T** is not as revealing as that for the related carbenes **4** and **5**; however the normal C6−C7 double bond distance in singlet **7S** is much shorter (1.331 Å) than the analogous C6−C7 distance in homoaromatic anion **8** (1.362 Å) and similar to the antihomoaromatic cation **9** (1.326 Å). A telling comparison revealing the nature of singlet **7S** is with the analogous 2-carbenabicyclo[3.2.1]oct-6-ene (**7H**). The linkage C3−C4 is now saturated and the carbene species homoallylic as in representation **7R**. A double bond at C3−C4 thus confers antihomoaromaticity character on **7S** increasing the transannular distances C2−C7 (1.5701 Å to 2.293 Å) and C4−C6 (2.480 Å to 2.521 Å), counteracting the bonding that would be normal for the homoallylic placement of carbene center and C6−C7 double bond in model carbene **7H**.



7R

(12) Kammermeier, S.; Jones, P. G.; Herges, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1757−1759.

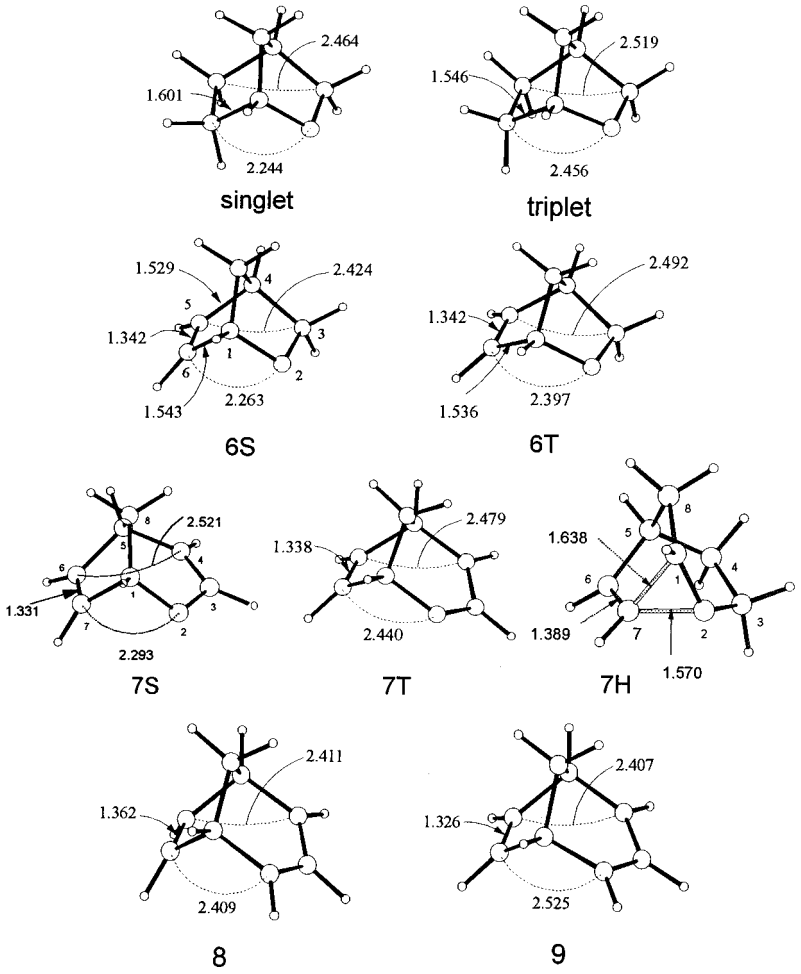


Figure 2. The structures for singlet and triplet 2-carbenanorbornane, 2-carbenanorbornene (**6S** and **6T**), 2-carbenabicyclo[3.2.1]-octa-3,6-diene (**7S** and **7T**), 2-carbenabicyclo[3.2.1]oct-6-ene (**7H**), and 2-bicyclo[3.2.1]octadienyl anion (**8**) and cation (**9**) at the B3LYP/6-31G* level.

Evaluation of magnetic properties provides evidence for aromaticity or, in the present case, homoaromaticity. A ring current emanating from an interacting cyclic array of atomic orbitals with $4n + 2$ electrons should be revealed in an enhanced diamagnetic susceptibility.[13] Using the isodesmic eqs 1 and 2 and the NMR=CSGT method included in Gaussian,[9] diamagnetic susceptibility exhaltations ($\Delta\chi$) were evaluated for bivalent intermediates **3**, **4**, **5**, and **7** at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G* level (Table 2). A positive sign for the change in diamagnetic susceptibility for the relevant isodesmic equation indicates diamagnetic susceptibility exhaltation and aromaticity, whereas a negative sign for $\Delta\chi$ supports antiaromaticity. We find, therefore, that singlet 3-carbenabicyclo[3.1.0]hexane (**3**) ($\Delta\chi = -0.7$ cgs-ppm) is nonaromatic, whereas singlets 7-carbenanorbornene (**4**) and 8-carbena-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**5**) are homoaromatic ($\Delta\chi = 22.7$ and 26.0 cgs-ppm) (Table 2). However, singlet carbenabicyclo[3.2.1]octadiene **7** is antihomoaromatic ($\Delta\chi = -10.3$ cgs-ppm) in contrast to the homoaromatic anion **8** ($\Delta\chi = 15.3$ cgs-ppm) but in harmony with the antihomoaromatic cation **9** ($\Delta\chi = -11.0$ cgs-ppm) (Table 2).

Table 2. Diamagnetic Susceptibility Exhaltations of Singlet Carbenes 3−5 and 7 and Related Intermediates

carbene	$\Delta\chi^a$ (cgs-ppm)
3	−0.7
4	22.7
5	26.0
1	10.8
7	−10.3
8	15.3
9	−11.0

[a] $\Delta\chi$ determined using eqs 1 or 2 and CSGT-B3LYP/6-311+G(2d,p)//B3LYP/6-31G* calculations.

Our analysis of the singlet−triplet energy gap (ΔE_{ST}) for these potentially homoaromatic or antihomoaromatic carbene species followed the approach used by Sulzbach et al.[14] in their analysis of di-*tert*-butylcarbene. The B3LYP/6-31G* level for calculations on carbene species is recommended,[15] but our calculations on the singlet−triplet energy gap (ΔE_{ST}) for methylene using B3LYP/6-

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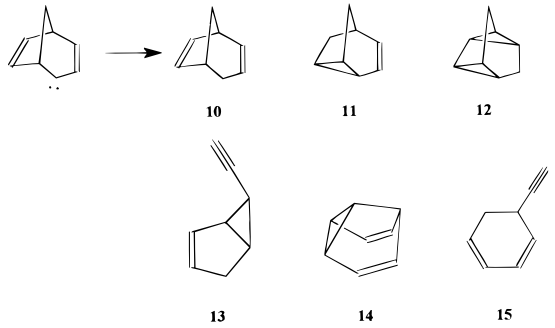
Table 3. Triplet−Singlet Energy Differences for Carbenacyclohexane and Bivalent Intermediates 3−7

carbene	ΔE_{TS}[a] (kcal/mol)	ΔE_{TS}[b] (kcal/mol)	ΔE_{TS}[c] (kcal/mol)
methylcarbene	−2.5	−2.3	−2.8
dimethylcarbene	2.8	2.5	2.7
carbenacyclohexane	3.4		
carbenacyclopentane (C_S)	10.3		
3	8.8		
4	27.1		
5	25.9		
6	12.7		
7	−4.0		
2-carbenabicyclo[3.2.1]oct-3-ene	−0.9		

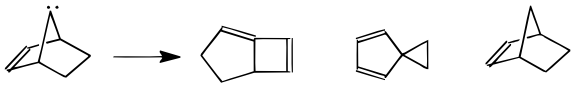
[a] $\Delta E_{TS} = E_T - E_S + \Delta ZPE$ +1.75 kcal/mol at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* level with the ΔZPE calculation at the B3LYP/6-31G* level (NImag = 0 for each species). [b] Triplet−singlet energy difference at B3LYP/TZ2P corrected for overestimation of ΔE_{ST} for methylene.[14] [c] Triplet−singlet energy difference at CCSD(T)/cc-pVTZ + ΔZPE at B3LYP/cc-pVTZ corrected for overestimation of ΔE_{ST} for methylene.[17]

311+G(3df,2p)//B3LYP/6-31G* yield $\Delta E_{ST} = 10.80$ kcal/mol (experimental value = 9.05 kcal/mol) providing a superior value to a variety of multiconfiguration methods using DZP or 6-31G* basis sets.[15] Thus the overestimation of the ΔE_{ST} for methylene (1.75 kcal/mol at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* + ZPE level) was used to correct the ΔE_{TS} values for bivalent intermediates **3**−**7**, carbenacyclopentane, carbenacyclohexane, and 2-carbenabicyclo[3.2.1]oct-3-ene, and for reassurance ΔE_{TS} values for methylcarbene and dimethylcarbene[16] (Table 3).[17] The positive numbers in the table correspond to a singlet level below the triplet. Thus, the picture for the energy gap ΔE_{TS} series is clear: there is no stabilization for singlet carbenabicyclohexane **3** relative to carbenacyclopentane, but substantial stabilization for singlet carbenes **4** and **5** provides an enhanced energy gap. Stabilization for 2-carbenanorbornene is minimal, and the singlet level for **7S**, in contrast to intermediates **3**−**6**, is above the triplet. This is not unusual for a vinyl carbene,[18] but the related carbene species lacking the transannular bond, 2-carbenabicyclo[3.2.1]oct-3-ene, exhibits $\Delta E_{TS} = -0.9$ kcal/mol, which suggests that there may be some destabilization of the singlet state in 2-carbenabicyclo[3.2.1]octa-3,6-diene **7**.

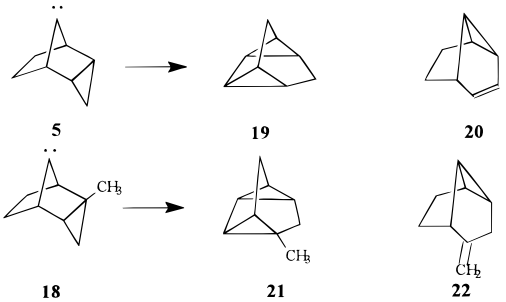
Overall, an analysis of energies of stabilization, the geometries of related intermediates, the magnetic properties, and an analysis of ΔE_{TS} values all provide a clear basis for our conclusion that carbenes **4S** and **5S** are homoaromatic, while with **6** and **3** there is little or no effect and in the case of carbenabicyclooctadiene **7** we may have a switch to antihomoaromaticity. These conclusions are consistent with the chemistry previously observed for these species. Carbenabicyclooctadiene **7** is the only species that exhibits substantial triplet characteristics. Generation of **7** by pyrolysis of the lithium or potassium salt of the precursor tosylhydrazone produces triplet products resulting from hydrogen abstraction (**10**−**12**) and singlet products formed by insertion or rearrangement (**13**−**15**).[5]



Carbenacyclohexane,[19] carbenacyclopentane,[19] carbenabicyclohexane **3**,[3] and the related 2-carbena-6,6-dimethylnorbornane[20] produce solely alkenes resulting from a 1,2 hydride shift, a singlet process. It is noteworthy that in the case of 2-carbena-6,6-dimethylnorbornane there is a preference for *exo*-C3 to *exo*-C2 over *endo*-C3 to *endo*-C2 hydride migration of 20:1, which may be the consequence of the bridging of 2-carbenanorbornane described above. 7-Carbenanorbornene **4** formed by pyrolysis of the lithium salt of the tosylhydrazone of the corresponding ketone produces rearrangement products (**16** (67%) and **17** (6.9%)) (singlet products) with a trace of triplet product norbornene (0.9%).[6a]



The carbenoid products formed from carbene **5** and analogous carbene **18** generated by decomposition of the precursor tosylhydrazones in $NaOCH_3$/diglime are singlet rearrangement products (**19**−**22**).[4]



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(16) The geometries obtained for methylcarbene and dimethylcarbene are in satisfactory agreement with higher level calculations, with methylcarbene singlet (C_1) exhibiting an angle at the carbene carbon ($\angle C_\alpha$) of 105.4°, C1−C2 = 1.467 Å, ∠H3−C2−C1 (H3−C2 close to coplanar with p-orbital at C1) = 94.1° (104.9°, 1.470 Å, 95.4° at CCSD/TZ2P(f,d), Ma, B.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1994**, *116*, 3539−3542; methylcarbene triplet (C_S), $\angle C_\alpha = 133.4°$, C1−C2 = 1.469 Å (131.2°, 1.490 Å at CISD/DZP), Gallo, M. M.; Schaefer, H. F., III. *J. Phys. Chem.* **1992**, *96*, 1515−1517. Dimethylcarbene singlet (C_2) provides an $\angle C_\alpha = 111.8°$, C1−C2 = 1.478 Å (111.5°, 1.473 Å at CISD/TZ2P +f); dimethylcarbene triplet (C_{2V}) exhibits $\angle C_\alpha = 133.5°$, C1−C2 = 1.472 Å (130.7°, 1.475 Å at CISD/TZ2P+f), the reference values for dimethylcarbene taken from Richards, C. A., Jr.; Kim, S.-J.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 10104−10107.

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