

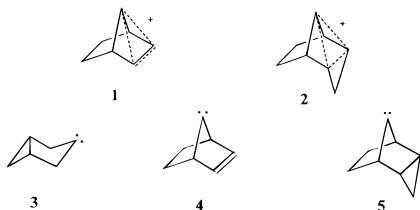
Homoaromaticity in Carbene Intermediates

Peter K. Freeman

Department of Chemistry, Oregon State University
Corvallis, Oregon 97331

Received November 17, 1997

Homoaromaticity in carbocations is well established, especially in the 7-norbornenyl (**1**) and 8-endotricyclo[3.2.1.0^{2,4}]octyl systems (**2**).¹ The related radicals have not provided convincing evidence to support homoaromaticity.² An intriguing question arises as a consequence: are carbene intermediates homoaromatic? Earlier, we have reported on the chemistry of 3-carbenabicyclohexane (**3**)³ and *endo*-8-carbenatricyclo[3.2.1.0^{2,4}]octane (**5**).⁴ Moss, Kirmse, and Brinker and their co-workers have described 7-carbenanorbornene (**4**),⁵ and Gleiter and Hoffmann have carried out an extended Hückel calculation on **4** which provides encouragement,⁶ but whether these species are homoaromatic was either not revealed or is in question.



Homoaromaticity for singlet state bivalent intermediates **3S**, **4S**, and **5S** should be revealed by enhanced stability, geometric changes relative to model systems, and changes in the singlet–triplet energy gap (ΔE_{ST}). The enhanced stabilities of singlet state carbenes **3S**, **4S**, and **5S** were evaluated at the B3LYP/6-31G*//B3LYP/6-31G* level,⁷ correcting for zero-point energy differ-

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Table 1. Stabilization Energies of Carbenabicyclohexane **3S**, 7-Carbenanorbornene (**4S**), *endo*-8-Carbenatricyclo[3.2.1.0^{2,4}]octane (**5S**), and 7-Norbornenyl Cation (**1**)^a

	carbene(i)	alkane(i)	alkene(f)	carbene(f)	SE ^b
3S	–233.169352	–235.709223	–234.483602	–234.389755	3.27
4S	–271.274917	–273.790526	–272.573762	–272.466886	15.56
5S	–310.541299	–273.790526	–311.842531	–272.466886	14.06
1	–271.693953	–273.790526	–272.573762	–272.877395	20.91

^a Energies of the individual species calculated at the B3LYP/6-31G*//B3LYP/6-31G* level + ZPE at B3LYP/6-31G* (Nimag = 0 in each case) in hartrees. ^b The stabilization energy SE = $E_{\text{alkene}(f)} + E_{\text{carbene}(f)} - E_{\text{carbene}(i)} - E_{\text{alkane}(i)}$ in kcal/mol. For the cation, the energies for the cationic intermediates replace the analogous carbene species.

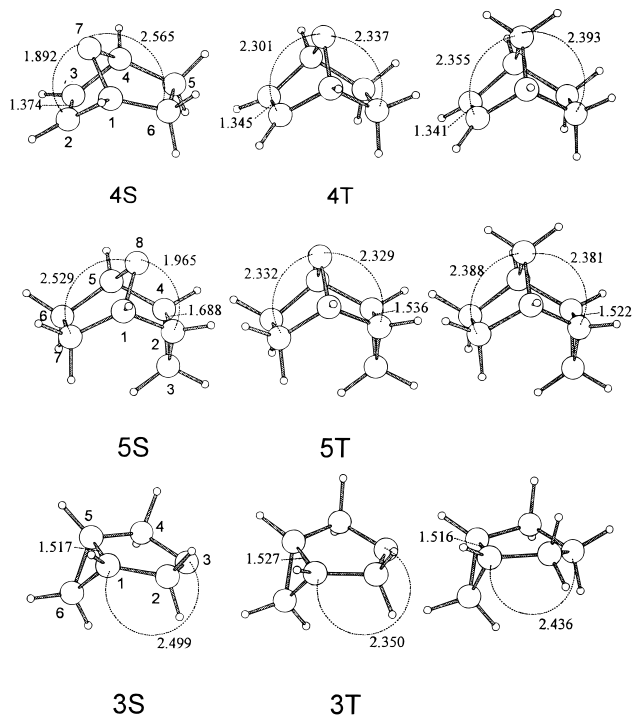
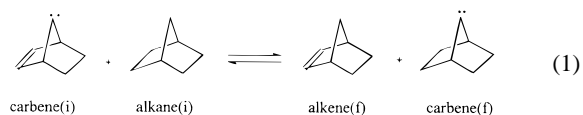


Figure 1. Structures for singlet carbenes **4S**, **5S**, and **3S**, triplet carbenes **4T**, **5T**, and **3T**, and the related parent hydrocarbons calculated at the B3LYP/6-31G*//B3LYP/6-31G* level.

ences, using isodesmic equations such as that illustrated for bivalent **4** (eq 1) (Table 1).



The stabilization energies determined for singlet carbenes **3S**, **4S**, and **5S** are 3.27, 15.56, and 14.06 kcal/mol and may be placed in perspective by comparison with that of the well-established homoaromatic 7-norbornenyl cation, which provides a stabilization energy of 20.91 kcal/mol (Table 1). The initial conclusion that carbenes **4S** and **5S** are strongly homoaromatic and carbenabicyclohexane only mildly so should be reflected in an altered architecture for each carbene. The C7 carbon of singlet 7-carbenanorbornene 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.⁸ for the 7-norbornadienyl moiety in (C₅Me₅)₂Sm(O₂C₇Me₅) (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** $\phi_{7412} = 127.8^\circ$ and $\phi_{7145} = 119.9^\circ$, while in norbornene $\phi_{7412} = 127.3^\circ$ and $\phi_{7145} = 120.8^\circ$. There is, in addition, a lengthening of the alkene double bond (1.374 Å) relative to the double bonds in triplet **4T** (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** ($\phi_{8154} = 122.7^\circ$, $\phi_{8517} = 121.1^\circ$) and *endo*-tricyclo[3.2.1.0^{2,4}]octane ($\phi_{8154} = 122.1^\circ$, $\phi_{8517} = 121.5^\circ$) 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.⁹ The much smaller stabilization energy of singlet carbene bicyclohexane **3S** (21% 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°.

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Table 2. Singlet–Triplet Energy Differences for Carbenacyclohexane and Bivalent Intermediates **3**, **4**, and **5**

	carbene	ΔE_{ST} (kcal/mol)	carbene	ΔE_{ST} (kcal/mol)
carbenacyclohexane		3.06	4	27.82
3		8.33	5	25.74

^a $\Delta E_{ST} = E_T - E_S + \Delta ZPE + 4.09$ at the B3LYP/6-31G**/B3LYP/6-31G* level (NImag = 0 for each species).

Our analysis of the singlet–triplet energy gap (ΔE_{ST}) for these potentially homoaromatic carbene species followed the approach used by Sulzbach *et al.*¹⁰ in their analysis of di-*tert*-butylcarbene. The overestimation of the ΔE_{ST} for methylene (4.09 kcal/mol at the B3LYP/6-31G**/B3LYP/6-31G* + ZPE level) was used to correct the ΔE_{ST} values for bivalent intermediates **3**, **4**, **5**, and standard carbenacyclohexane (Table 2). The positive numbers in the table correspond to a singlet level below the triplet. Thus, the picture for the energy gap ΔE_{ST} series is clear: stabilization for singlet carbenabicyclohexane **3** increases the gap only a modest amount, but substantial stabilization for singlet carbenes **4** and **5** provides a large energy gap. Overall an analysis of energies of stabilization, the geometries of related intermediates, and an analysis of ΔE_{ST} values all provide a clear basis for our conclusion that carbenes **3S**, **4S**, and **5S** are homoaromatic, **4S** and **5S** strongly so, while with **3** the effect is considerably diminished.

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

JA9739143