

The Naphthylcarbene Potential Energy Hypersurface

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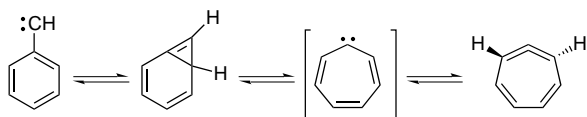
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Abstract: The naphthylcarbene potential energy surface (PES) was examined *ab initio*, employing self-consistent field (SCF), second-order perturbation theory (MP2), and density functional (Becke3LYP) methods in conjunction with 6-31G*, DZ, DZP, and 6-311+G* basis sets. All stationary structures were characterized by vibrational frequency analyses at the Becke3LYP/6-31G* level; final energies were evaluated at the Becke3LYP/6-311+G**//Becke3LYP/6-31G* + ZPVE level. Cyclobuta[*de*]naphthalene is the global minimum on this part of the C₁₁H₈ PES. Generally, seven-membered benzocarbenes are no minima as they converge to their corresponding allenes. Both 1- and 2-naphthylcarbene have triplet ground states, but the small S–T gaps (ca. 5 kcal mol⁻¹) allow facile rearrangements in the singlet manifold to take place. The triplet rotational barrier for the *exo*-methylene in 2-naphthylcarbene is relatively small (3.5 kcal mol⁻¹) due to weak π -bonding. At low temperatures, singlet 2-naphthylcarbene equilibrates with 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene and bicycloheptatetra-1,3,5,7-ene, but not with 4,5-benzocycloheptatrienyliene which is not a minimum; rearrangement to singlet 1-naphthylcarbene occurs only at higher temperatures via bicycloheptatetra-1,2,4,6-ene, the second lowest minimum. As the rearrangement barriers from 1- and 2-naphthylcarbene to bicycloheptatetra-1,2,4,6-ene are of similar magnitude ($\Delta\Delta E^\ddagger = 1.9$ kcal mol⁻¹), the latter species may be observed in small quantities only. The allenes bicycloheptatetra-1,2,4,6-ene, bicycloheptatetra-1,3,5,7-ene, and bicycloheptatetra-2,3,5,7-ene are thermodynamically remarkably stable and should be observable at low temperatures.

Introduction

Singlet aryl carbenes undergo fascinating rearrangements.¹ Phenylcarbene exhibits a series of degenerate ring expansion–ring contraction steps which lead to extensive label scrambling.^{2,3}



The reaction cascades of substituted phenylcarbenes, such as

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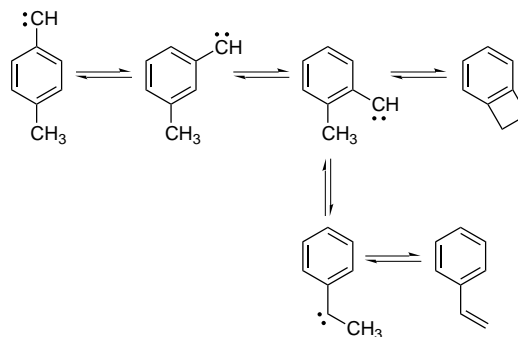
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p-tolylcarbene, often terminate by intramolecular reactions to give rearranged products.⁴



Highly strained benzocyclopropene and cyclic seven-membered-ring intermediates are implicated. These have energies similar to the aryl carbenes, but the mechanistic details of such reactions have been clarified only recently.^{3–5} These studies settle the controversy^{6,7} about the nature of the Hückel aromatic cycloheptatrienyliene, which is a transition structure for interconverting two enantiomeric 1,2,4,6-cycloheptatetraenes, the most stable C₇H₆ form (which is then trapped in subsequent reactions).^{3,7}

Although the naphthylcarbene rearrangements are expected to be analogous, the known situation is not straightforward (for

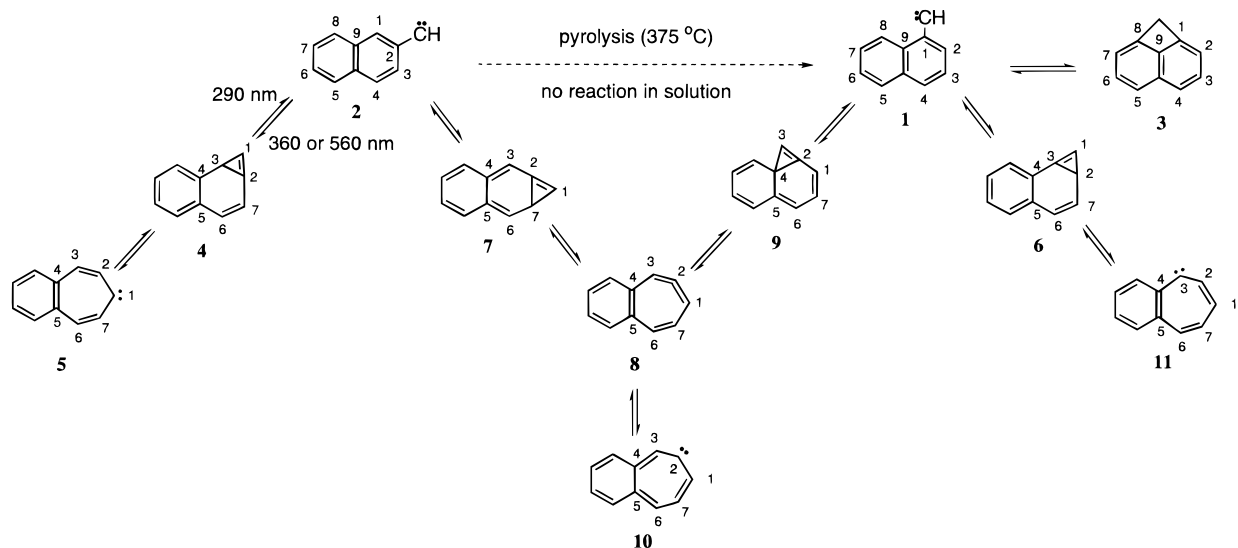
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Scheme 1



the following introduction see Scheme 1). Only parts of the possible naphthylcarbene PES have been examined experimentally. Albrecht and McMahon found "...no evidence for isomerization of 2-naphthylcarbene to 1-naphthylcarbene..." at 10 K in matrix isolation.⁶ Thus, in marked contrast to the degenerate phenylcarbene rearrangements, the interconversion of 1-naphthylcarbene (**1**) and 2-naphthylcarbene (**2**) is *not* facile. However, both precursors of **1** and **2** do give cyclobuta[de]naphthalene (**3**) at *high* temperatures (>360 °C, Scheme 1), and the intermediacy of **1** is assumed.^{2,8}

The detailed rearrangement pathways as well as the characterization of other important intermediates have remained experimentally elusive, and there is evidence for only a few of the structures on the singlet naphthylcarbene surface which can be proposed by analogy with the phenylcarbene PES. Of the many possible isomers, only six (**1**–**6**, see below) have been characterized nominally, but the electronic nature of **5** is not clearly established.^{9,10} All rearrangements are assumed to take place in the singlet state,^{11,12} although triplet **2** (*syn*, **2st**; *anti*, **2at**) was determined (via ESR spectroscopy) as early as 1965 to be the electronic ground state.¹³ Consequently, only the 2-naphthylcarbene triplet state is well characterized.¹³ Senthilnathan and Platz showed that the rotational barrier connecting **2st** and **2at** is at least 4.4 kcal mol⁻¹.¹⁴ There are also many reports on the trapping of triplet **2**, generated in various ways.^{15–18} The experimentally unknown singlet–triplet separation (ΔE_{ST}) is assumed to be small since the singlet rearrangements *via* singlet **2** (*syn*, **2ss**; *anti*, **2as**) are facile.

However, these rearrangements are not well understood and there are several possible interpretations. For instance, singlet **2** undergoes reversible ring closure to **4**^{7b–e} but *no* rearrangement into 1-naphthylcarbene (**1**) takes place in *solution*.^{6,19} Conversion of **2** into **1** was postulated to take place in the gas phase under high-energy conditions (pyrolysis of the diazo precursor, 360–375 °C).⁸ However, **1** could not be observed as an intermediate in the reactions of **2**, as further rearrangement to cyclobuta[de]naphthalene (**3**, discussed below) occurs readily.

Isomer **4** has been well characterized in the solution chemistry of naphthylcarbenes.^{4–7(b–e)} However, structures **7**–**10** were only postulated, but never characterized or even fleetingly observed. A complicating feature is that these C₁₁H₈ rearrangements led to a common stable product, cyclobuta[de]naphthalene (**3**), at high temperatures.^{8,20} However, "...a minor product common to the thermolysis of both diazo compounds... [of **1** and **2**]" was observed and tentatively identified as **8**.^{7b–e,11,19} Clearly, the structures on the naphthylcarbene PES are only partly known and characterized, and no unified description of the rearrangement pathways is possible from the available experimental reports. We therefore undertook a theoretical examination of the relevant stationary points. We wish to answer the following questions:

1. Which of the suggested C₁₁H₈ structures are minima? What are the magnitudes of the diamagnetic ring currents—indicative of aromaticity—in the closed-shell singlet states?
2. What is the C₁₁H₈ global minimum? Which structures are important chemically based on both their character and relative energies?
3. What are the electronic ground states of the various isomers? How large are the S–T energy separations (ΔE_{ST})?
4. Are there any structures which were not considered previously?
5. Why does 2-naphthylcarbene equilibrate with 1-naphthylcarbene only at high temperatures?
6. What is the nature of benzocycloheptatetraene (**8**)?
7. How does the behavior of naphthylcarbene compare with phenylcarbene?

Methods

For orientation as well as comparisons with older semiempirical and with experimental data, we first optimized all structures with the

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Table 1. Relative Energies (in kcal mol⁻¹) of Triplet *anti*- and *syn*-2-Naphthylcarbenes (**2at** and **2st**) and Related Triplet Isomers^a

state	structure	ZPVE	relative energies	
		Becke3LYP/6-31G*	Becke3LYP/6-31G*	Becke3LYP/6-311+G**/Becke3LYP/6-31G*
³ A''	1at	93.8	-0.7	-0.5
³ A''	1st	93.8	0.3	0.4
³ A	TS2t	92.7	3.9	3.5
³ A''	2at^b	93.6	0.0	0.0
³ A''	2st^c	93.6	0.0	0.0
³ B ₁	5t	94.1	6.2	6.0
³ A''	11t	94.2	4.8	4.5

^a Final energies are ZPVE (B3LYP/6-31G*, in kcal mol⁻¹) corrected ^b Absolute energies (in au): B3LYP/6-31G* = -423.87476; B3LYP/6-311+G**/B3LYP/6-31G* = -423.96517. ^c Absolute energies (in au): B3LYP/6-31G* = -423.87470; B3LYP/6-311+G**/B3LYP/6-31G* = -423.96515.

semiempirical AM1 algorithm.²¹ Geometries of all stationary points were then optimized using self-consistent-field (SCF) and density functional analytic gradient methods. We used Becke's three-parameter exchange-correlation functional²² including the nonlocal gradient corrections described by Lee-Yang-Parr (LYP),²³ as implemented in the Gaussian 94 program package.²⁴ Residual Cartesian and internal coordinate gradients for the stationary points were always less than 10⁻⁵ atomic units. Harmonic vibrational frequencies for the most critical structures were computed by analytic second derivative methods.²⁵ For comparisons, we also evaluated single-point energies at the MP2(fc)/DZP//HF/DZP level.²⁶

Four basis sets were employed: the standard 6-31G* and 6-311+G* bases²⁷ for DFT optimizations and single-point energies, a double- ζ (DZ) basis set, namely Dunning's C(9s5p/4s2p) and H(4s/2s) basis,^{28,29} and a DZP basis set which included one set of polarization functions on all the nuclei (d for carbon and p for hydrogen). The exponents of the polarization functions were $\alpha_p(\text{C}) = 0.75$, and $\alpha_p(\text{H}) = 0.75$. The computations were carried out using the ab initio programs PSI 2.0.8,³⁰ Turbomole 2.0,³¹ and Gaussian 94.²⁴ We only report here the results (Tables 1 and 2) at our reference level B3LYP/6-311+G**/B3LYP/6-31G* + ZPVE (unless noted otherwise); all HF and MP2 energies are available in the Supporting Information.

It was demonstrated in a very recent study^{3d} that the Becke3LYP/6-311+G**/Becke3LYP/6-31G* + ZPVE level gives rather good singlet-triplet energy separations (ΔE_{ST}) for methylene (computed 11.4 kcal mol⁻¹; expt³² 9.1 kcal mol⁻¹) and phenylcarbene (5.0 kcal mol⁻¹, experimentally not known) at reasonable computational costs. We therefore assume that this method will perform comparably well for naphthylcarbene. Note that AM1 gives a ΔE_{ST} for methylene of 30 kcal mol⁻¹.

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Table 2. Relative Energies (in kcal mol⁻¹) of Singlet *anti*- and *syn*-2-Naphthylcarbenes (**2as** and **2ss**) and Related Singlet Isomers Relative to Triplet *anti*-2-Naphthylcarbene (**2at**, see Table 1)^a

state	structure	ZPVE	relative energies	
		Becke3LYP/6-31G*	Becke3LYP/6-31G*	Becke3LYP/6-311+G**/Becke3LYP/6-31G*
¹ A'	1as	93.8	6.3	4.7
¹ A'	1ss	93.8	7.7	5.8
¹ A'	2ss	93.6	7.0	4.6
¹ A'	2as	93.6	7.6	5.1
¹ A ₁	3	94.2	-29.4	-27.7
¹ A	4	94.6	0.4	0.5
¹ A ₁	5s	94.2	14.1	11.5
¹ A	6	94.5	-0.3	-0.2
¹ A	8	94.9	-12.1	-13.4
¹ A	11s	94.3	11.9	9.4
¹ A	14	92.7	37.1	37.4
¹ A	15	95.0	38.6	37.9
¹ A	16	94.4	1.8	2.4
¹ A	17	94.5	2.9	1.4
¹ A	18	95.0	8.9	6.0
¹ A	TS1	91.2	37.0	36.9
¹ A	TS2s	92.7	19.7	29.6
¹ A	TS3	93.1	27.8	26.5
¹ A	TS4	92.9	28.7	29.1
¹ A	TS5	93.5	9.9	9.5
¹ A	TS6	93.6	8.6	8.0
¹ A	TS7	91.1	84.9	82.0
¹ A	TS8	91.7	59.0	57.6

^a Final energies are ZPVE (B3LYP/6-31G*, in kcal mol⁻¹) corrected.

In order to assess the aromatic/antiaromatic character of the various cyclic π -systems, we computed (at RHF/6-31G* using the GIAO approach)³³ the absolute magnetic shieldings, termed the "nucleus independent chemical shifts" (NICS), at selected points in space as a function of the electron density.³⁴ NICS are taken negative to conform with chemical convention. The geometrical center of the ring's heavy atoms served as the most easily defined reference point.

These isotropic chemical shifts yield information about ring currents and aromatic properties of molecules. Following the convention, aromatic molecules have negative isotropic NICS, while antiaromatic molecules have positive values. The absolute magnitude of a negative NICS is approximately proportional to the aromatic stabilization energy.³⁴

Results

1-Naphthylcarbene (1) and 2-Naphthylcarbene (2). There are ten structures to be discussed (energies and geometries are summarized in Tables 1–3): the *syn* and *anti* conformers of singlet and triplet 1-naphthylcarbene (**1ss**, **1as**, **1st**, and **1at**, respectively), as well as the analogous isomers for 2-naphth-

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Table 3. Selected Geometrical Parameters (Standard Numbering) for 1- and 2-Naphthylcarbenes and Related Structures at the B3LYP/6-31G* Optimization Level^a

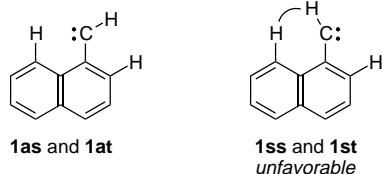
species	$r(\text{C}-\text{C}_{\text{exo}})$	$r(\text{C}1-\text{C}2)$	$r(\text{C}2-\text{C}3)$	$r(\text{C}1-\text{C}9)$	$r(\text{C}8-\text{C}9)$	$\angle(\text{C}-\text{C}_{\text{exo}}-\text{H})$
1as	1.435	1.409	1.402	1.455	1.415	106.5
1at	1.380	1.423	1.398	1.461	1.412	134.4
1ss	1.436	1.408	1.404	1.461	1.414	108.9
1st	1.378	1.422	1.397	1.469	1.412	137.8
2as	1.442	1.405	1.439	1.411	1.424	106.1
2at	1.388	1.416	1.447	1.413	1.423	134.7
2ss	1.441	1.403	1.442	1.411	1.423	106.5
2st	1.387	1.413	1.451	1.412	1.412	134.6
TS1s	1.440	1.390	1.438	1.418	1.422	109.5
TS1t	1.405	1.407	1.445	1.414	1.423	143.6
TS2	1.474	1.383	1.427	1.411	1.395	2.218 ^b
TS3	1.360	1.407	1.468	1.394	1.435	1.881 ^c
TS4	1.335	1.416	1.381	1.495	1.441	1.854 ^d
12		1.377	1.417	1.421	1.434	
13	1.510	1.379	1.424	1.422	1.432	

^a Bond lengths (r) in Å, angles (\angle) in deg. ^b $r(\text{C}_{\text{exo}}-\text{C}8)$. ^c $r(\text{C}_{\text{exo}}-\text{C}3)$ ^d $r(\text{C}_{\text{exo}}-\text{C}9)$.

ylcarbene (**2ss**, **2as**, **2st**, and **2at**, respectively), and the transition structures [**TS1s** (singlet) and **TS1t** (triplet)] for the interconversion of the *syn* and *anti* configurations of 2-naphthylcarbene (**2st** → **TS1** → **2at**). The latter isomerization has been studied experimentally for the triplet state;¹⁴ the results provide calibration with theory.

The S–T energy separations (ΔE_{ST} derived from the relative energies given in Tables 1 and 2) of **1** and **2** are around 5 kcal mol⁻¹. The assumption is that the singlet state (in which the rearrangements take place) is energetically close to the triplet state thus is justified.¹ Our reference level is 2.3 kcal mol⁻¹ in error for the ΔE_{ST} of methylene. Thus, the ΔE_{ST} of 5 kcal mol⁻¹ for **1** and **2** is probably an upper limit, and the true value is expected to be somewhat smaller.^{3d}

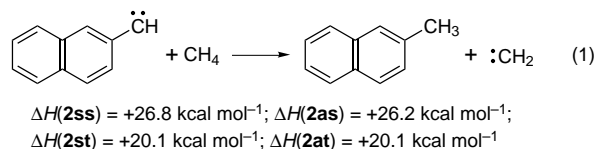
The π -electron systems of the *syn* and *anti* forms are quite similar, but the *anti* isomers (**1as** and **1at**) are more stable (by 1.1 and 0.9 kcal mol⁻¹, respectively) due to the greater steric repulsions in the *syn* forms (**1ss** and **1st**), as exemplified by the two conformers of **1** (C_s , singlet or triplet).



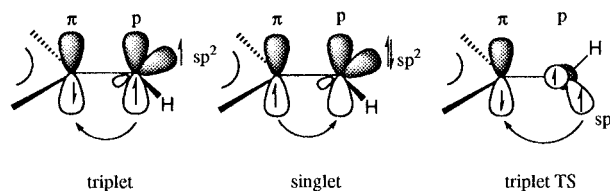
Despite the larger H–C–naphthyl (carbon-2) triplet angles (around 135°; singlets are around 107°), the differences in energies for *syn* and *anti* conformers, **1st** and **1at**, also are around 1 kcal mol⁻¹.

Since the characteristics of 1-naphthylcarbene (**1**) and 2-naphthylcarbene (**2**) are quite similar, the following discussion concentrates on the nature of the isomers of **2** (which is also somewhat better characterized experimentally). The similarity in the geometries of the isomers of **2** (Table 3) with the parent hydrocarbons naphthalene (**12**, Table 3) and 2-methylnaphthalene (**13**, Table 3) is obvious, but the interaction of the carbene CH group lengthens the adjacent ring CC bonds by about 0.03 Å both in the singlets and in the triplets. The C(ring)–CH bond length depends upon the electronic state, i.e., on the overlap between the p-orbital on the *exo*-methylene and the π -electron system of the naphthalene moiety as well as on the σ -repulsion resulting from the occupied in-plane orbitals. The C(ring)–CH bond length in the triplets, 1.388 Å (**2at**) and 1.387 Å (**2st**), is elongated to 1.405 Å in the rotation transition structure (**TS1t**, Table 3). In contrast, the corresponding bonds are longer in

the singlets, and do not change at the rotation TS (C–CH = 1.441 ± 0.001 Å for **2as**, **2ss**, and **TS1s**). These distances may be compared with the values for the central CC bond in *trans*-butadiene [C–C(sp²–sp²) = 1.46 Å (Becke3LYP/6-31G*, 1.48 Å expt)], with the benzene distances (1.40 Å), and with that in ethylene [C=C(sp²–sp²) = 1.33 Å (Becke3LYP/6-31G*, 1.34 Å expt)].³⁵ These differences in the singlet and triplet C(ring)–CH lengths are only partly due to the p– π interaction, as the Weinhold bond indices (1.13 for **2at**, 1.06 for **2as**, and 1.09 for **TS1t**) indicate only weak π -bonding. Moreover, according to eq 1, the singlets are stabilized *more* (by about 6–7 kcal mol⁻¹ with respect to singlet methylene) by the naphthyl fragment than the triplets. Consequently, the longer C(ring)–CH bond in the singlets must be due to σ -repulsion: the doubly occupied in-plane sp² orbital interacts unfavorably with the adjacent C–C bond. The stabilization energies (defined by eq 1, ΔH_{R} , Table 6) of 2-naphthylcarbenes are comparable to those of the phenylcarbenes (singlet, 25.9 kcal mol⁻¹; triplet, 19.4 kcal mol⁻¹).



These conclusions are readily confirmed by the small triplet rotational barrier between **2st** and **2at** (theory, 3.5 kcal mol⁻¹; experiment,¹⁴ >4.4 kcal mol⁻¹; singlet barrier (theory), 29.6 kcal mol⁻¹). The MO's depicting the most important orbital interactions of the naphthyl fragment and the *exo*-methylene clarify the situation.



The singlet and triplet states as well as the triplet transition structure benefit from p– π interactions. The energy difference between the ground state triplet and the triplet transition structure thus arises from the less favorable overlap of an sp² (**TS1t**) vs. a p (**2st**) orbital. As the *exo*-methylene bond angle widens more

(35) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons, Inc.: New York, 1992; p 21.

in the transition structure (from 135° to 144°), the activation energy is relatively small. This interpretation is consistent with the earlier analysis of the rotational barrier of triplet phenylcarbene.³⁶ Similar arguments explain why the singlet barrier via **TS1s** (29.6 kcal mol⁻¹ vs. **2as**) is much higher than the triplet barrier. While the π -system reacts favorably with the empty p-orbital in the ground states (**2ss** and **2as**), the interaction of the π -HOMO with the doubly occupied sp² orbital is unfavorable in **TS1s**. Even though the S–T gap is of similar magnitude as the activation energy for the *exo*-methylene rotation, we confirm that the triplet *exo*-methylene rotation (**2at** → **TS1t** → **2st**) is far more favorable than the singlet rotation (**2as** → **TS1s** → **2ss**), as suggested by Senthilnathan and Platz.¹⁴

Does an in-plane triplet transition structure (**TS1tip**) also exist corresponding to the least-motion pathway (linearization) for moving the *exo*-hydrogen? Indeed, we did locate such a stationary point with an almost perfectly linear *exo*-CH group, but it has Hessian index two: 792i and 443i cm⁻¹; one of the imaginary modes (443i cm⁻¹, a'') leads to **TS1t**. However, **TS1tip** is not much higher in energy (1.3 kcal mol⁻¹) than **TS1t**. If higher levels of correlation were to decrease this difference even more, the in-plane mode might be a viable alternative to the out-of-plane *exo* rotation. By analogy, linear triplet methylene (relative energy = 5.9 kcal mol⁻¹, Becke3LYP/6-31G*) is the transition structure (with a doubly degenerate imaginary mode of 987i cm⁻¹) for linearization of bent methylene.

To facilitate comparisons with experiment, we computed the harmonic vibrational frequencies of triplet *anti*-2-naphthylcarbene (**2at**) (Table 7) at Becke3LYP/6-31G*. The C–H stretching modes are tightly clustered. An average of the most intense vibrational frequencies in this range is in good agreement with experimental data (mean error = 2.4%).⁸

2,3-Benzobicyclo[4.1.0]hepta-2,4,6-triene (4) and Related Fused Three Membered-Ring Isomers: 6, 7, 9, 14, and 15 (see Schemes 1 and 2). Of the six C₁₁H₈ isomers (for structural details see Table 4) containing a three-membered ring, only **4** and **6** have been observed and characterized to some extent experimentally.^{4–10} Structures **7** and **9** were suggested² to take part in the assumed interconversion of **1** to **2** but have remained experimentally elusive. Not surprisingly, neither 2,7-benzobicyclo[4.1.0]hepta-1,3,5-triene (**7**) nor 2,4-benzobicyclo[4.1.0]hepta-2,5,7-triene (**9**) are minima at levels of theory which attempt to include electron correlation. While we were able to obtain stationary structures at the HF/DZP level, both **7** and **9** optimize to **8** (Becke3LYP/6-31G*) when searching for ground states. Therefore, neither **7** nor **9** appear to be minima. The instability of these molecules is understandable because of their loss of aromaticity in *both* rings (with respect to a naphthylcarbene, see discussion below). After tedious searches, we were able to optimize **7** and **9** to transition structures (named hereafter **TS3** and **TS4**), interconnecting the allene **8** with 1- and 2-naphthylcarbene (**1ss** and **2ss**).

Isomer **14** is an intriguing minimum because two butadiene subunits are joined by a highly strained cyclopropene ring, despite the loss of all benzenoid character. The carbon-5 environment is far from tetrahedral: the C6–C5–C4 angle is 124°.

The three-membered-ring moieties in **4** and **6** are not coplanar with the naphthyl fragment; hence, the attached six-membered rings also deviate significantly from planarity. The other six-membered-ring geometry is closer to benzene (with CC bond lengths close to 1.39 Å) than to the more alternating bond lengths in naphthalene (**12**, Table 3). As found for **2**, the

Scheme 2

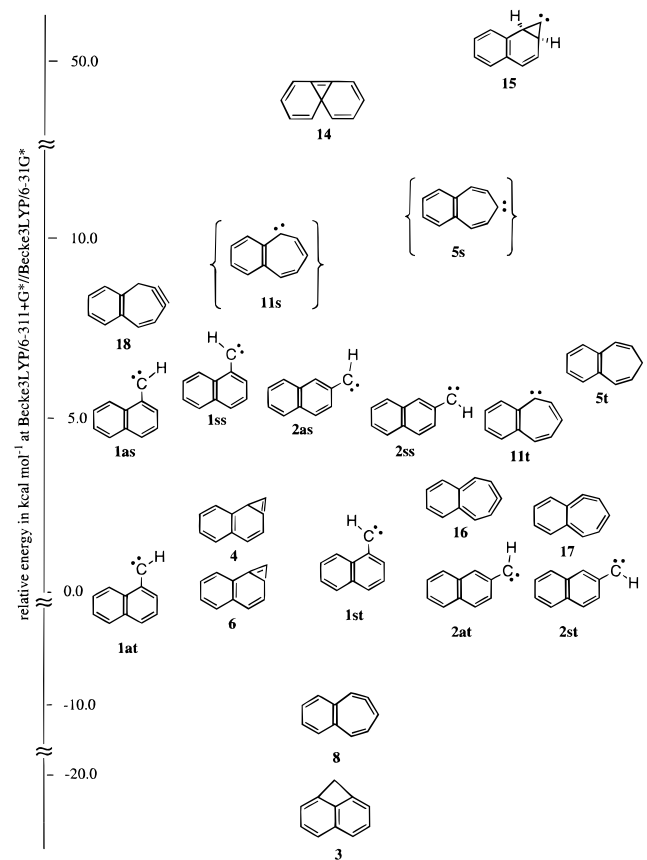


Table 4. Selected Geometrical Parameters (See Text for Numbering) of Benzobicyclo[4.1.0]heptatrienes and Related Structures at the B3LYP/6-31G* Optimization Level^a

species	<i>r</i> (C1–C2)	<i>r</i> (C1–C3)	<i>r</i> (C2–C3)	<i>r</i> (C4–C5)
4	1.303	1.511	1.521	1.428
6	1.512	1.302	1.525	1.426
14	1.362	1.433	1.303 ^a	1.563
15	1.508	1.525	1.509	1.413
TS5	1.299	1.461	1.951	1.449
TS6	1.468	1.295	1.943	1.439

^a Bond lengths (*r*) in Å, angles (∠) in deg. ^b *r*(C3–C4).

Table 5. Selected Geometrical Parameters (See Text for Numbering) of Benzocycloheptatrienylenes, Benzocycloheptetraenes, and Benzocycloheptyne at the B3LYP/6-31G* Optimization Level^a

species	<i>r</i> (C1–C2)	<i>r</i> (C2–C3)	<i>r</i> (C3–C4)	<i>r</i> (C4–C5)	∠(C2–C1–C7)
5s	1.434	1.383	1.428	1.434	118.6
5t	1.388	1.379	1.461	1.439	134.8
8	1.325	1.322	1.475	1.431	146.5 ^b
11s	1.386	1.426	1.445	1.452	122.1 ^c
11t	1.418	1.354	1.428	1.437	139.8 ^c
16	1.342	1.432	1.396	1.478	144.0
17	1.448	1.334	1.367	1.464	141.9 ^c
18	1.215	1.458	1.556	1.438	139.9
TS7	1.376	1.491	1.399	1.501	1.176 ^d

^a Bond lengths (*r*) in Å, angles (∠) in deg. ^b ∠(C1–C2–C3). ^c ∠C2–C3–C4). ^d *r*(C1–H).

computed Becke3LYP/6-31G* IR frequencies for **4** compare fairly well with experiment (Table 8).

cis-2,3-Benzobicyclo[4.1.0]hepta-6-ene-1-carbene (**15**) is a true minimum not considered previously. The *trans* isomer is not a stationary structure; all optimizations converged to **4** or **6**, depending upon the starting geometry. The three-membered-ring geometry is very close to that of the parent cyclopropylidene

(36) Dorigo, A. E.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 6942.

Table 6. Comparison between Phenyl- and Naphthylcarbene at B3LYP/6-311+G*/B3LYP/6-31G*^a

	1as	1at	2as	2at	phenylcarbene singlet	phenylcarbene triplet
$r(\text{C}-\text{CH})$, Å	1.435	1.380	1.442	1.388	1.443	1.393
ΔE_{ST}	5.2		5.1		5.0	
ΔH_{R} (eq 1)	27.7	21.0	26.2	20.1	26.0	19.4
ΔE_{rot}^c	n.a.	n.a.	14.5	3.5	12.7	4.4

^a Energies in kcal mol⁻¹. ^b Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F. *J. Org. Chem.* **1996**, *61*, 7030. ^c Rotation of the *exo*-methylene group.

Table 7. The Most Intense Harmonic Vibrational Frequencies (Unscaled, in cm⁻¹) and IR Intensities (in Parentheses, in km/mol) for Triplet (³A'') *anti*-2-Naphthylcarbene (**2at**)

symmetry	Becke3LYP/6-31G*	exptl freq ^b	description
a'	3203 (34)	3076	C-H stretching
	averaged: ^a		C-H stretching
a'	3180 (10)	3053	C-H stretching
a'	1469 (2)	1492	
a'	1217 (6)	1185	
a''	976 (10)	1022	
a''	846 (50)	836	C-H wagging
a''	826 (14)	809	
a''	757 (20)	741	C-H wagging
a''	474 (17)	463	ring torsion

^a This refers to the 3180-cm⁻¹ frequency; there are several intense CH absorptions, which seem to have been observed as one broad band experimentally. ^b Note that the experimental values represent mixtures of the *syn* and *anti* isomers.

Table 8. The Most Intense Harmonic Vibrational Frequencies (Unscaled, in cm⁻¹) and IR Intensities (in Parentheses, in km/mol) for 2,3-Benzobicyclo[4.1.0]hepta-2,4,6-triene (**4**; ¹A') at Becke3LYP/6-31G*

Becke3LYP/6-31G*	exptl freq	description
3207 (34)		
3194 (33)	2985	C-H stretching
3070 (58)	2968	C-H stretching
1839 (25)	1755	C-H wagging
1042 (12)	1008	
814 (16)	794	C-H wagging and ring torsion
799 (39)	781	C-H wagging and ring torsion
765 (7)	747	C-H wagging and ring torsion
675 (25)	662	C-H wagging and ring torsion
428 (6)	415	

(C_{2v}, C1-C2 = 1.507 Å; C2-C3 = 1.486 Å, C1-C2-C3 = 60.4°; C2-C1-C3 = 59.1° at B3LYP/6-31G*; same numbering as for **15**).³⁷

Benzocycloheptatrienylidene and Benzocycloheptatetraene-like Structures 5, 8, 10, 11, 16, 17 and the Benzocycloheptyne 18 (see Schemes 1 and 2). Initially to our surprise, all attempted optimizations of the carbenes **5**, **10**, and **11** led directly to their allenic counterparts: singlet **5** (**5s**) converges to singlet **16**; singlet **10** to singlet **8**; singlet **11** (**11s**) to singlet **17**!

The singlet carbene **5s** was proposed by Jones and co-workers as an intermediate in the carbene-carbene rearrangement of naphthylcarbene.¹⁹ As found for **1** and **2**, **5** has a triplet ground state with a ΔE_{ST} of 5.5 kcal mol⁻¹. This seems to agree well with the experimental ΔE_{ST} estimate (only from the characterization of the triplet)³⁸ for **5** of 3.5 to 4.0 kcal mol⁻¹.¹⁸

However, vibrational frequency analysis shows that **5s** has two imaginary modes (B₁ 297.8i cm⁻¹ and A₂ 234.3i cm⁻¹); the A₂ mode points toward **16**! This is in complete analogy to the phenylcarbene PES, where cycloheptatrienylidene also is a

(37) For the latest detailed study on the cyclopropylidene PES see: Bettinger, H.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F. *J. Phys. Chem.* **1996**, *100*, 16147.

(38) The correlation between ΔE_{ST} and the ESR zero-field parameter $|E|/hc$ has been described in: Largan, J. G.; Sitzmann, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1984**, *110*, 521.

Table 9. The Most Intense (>15 km/mol) Harmonic Vibrational Frequencies (Unscaled, in cm⁻¹) and IR Intensities (in Parentheses, in km/mol) of the Allenes Benzocycloheptatetra-1,2,4,6-ene (**8**), Benzocycloheptatetra-1,3,5,7-ene (**16**), and Benzocycloheptatetra-2,3,5,7-ene (**17**) at Becke3LYP/6-31G*

8	16	17
3290 (28)	3212 (27)	3211 (29)
3198 (30)	3200 (34)	3198 (27)
3168 (41)	3148 (58)	3164 (32)
3160 (36)	3127 (38)	3149 (42)
827 (28)	1390 (40)	3135 (41)
815 (23)	882 (39)	1356 (25)
775 (28)	790 (43)	821 (53)
716 (20)	545 (42)	775 (38)
639 (27)	354 (46)	545 (20)

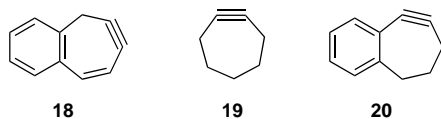
transition structure for interconverting two enantiomeric cycloheptatetraenes.³ Thus, allene **16** rather than carbene **5s** should be the observable species in singlet naphthylcarbene rearrangements. To stimulate the experimental identification of **16**, the most intense vibrational frequencies are summarized in Table 9. Note that **5t** (³B₁) is a minimum which is 3.4 kcal mol⁻¹ higher in energy than **16**. Thus, **16** and **5t** may well be the species for which the 3.5–4.0 kcal mol⁻¹ ΔE_{ST} was estimated.^{18,38} Structure **11** has been proposed in the literature twice^{20,39} as an intermediate resulting from rapid ring expansion of **1**. However, the rearrangement to the more stable isomer (**3**) predominates under the reaction conditions (600 °C, 10⁻³ Torr), and **11** remained experimentally elusive. Since **16** (incorrectly assigned to structure **5s**) is involved in the rearrangements of 2-naphthylcarbene (**2s**), we assumed that the participation of **11s** in the rearrangements of 1-naphthylcarbene (**1s**) is quite conceivable. Moreover, the ΔE_{ST} for **11** (4.9 kcal mol⁻¹) is even smaller than that for **5** (5.5 kcal mol⁻¹). However, as found for **5s**, **11s** is not a minimum (NIMAG=1) either! Removal of the C_s symmetry constraints for **11s** leads to allene **17** (C₁). Note that the energy difference between triplet **11t** and allene **17** is 3.1 kcal mol⁻¹.

Although **8** has been prepared and characterized via other routes,^{2,11} it has received the least attention in the context of naphthylcarbene rearrangements. We find **8** to be the second lowest minimum with a relative energy of 14.3 kcal mol⁻¹ above the global C₁₁H₈ minimum **3**! This finding is not surprising as cycloheptatetraene is the global minimum on the phenylcarbene PES, and the annelated benzene ring in **8** provides additional stabilization. It is quite conceivable that West *et al.* indeed observed **8** as a minor product in the rearrangements of **1** and **2**.¹⁰ We will explain below why **8** is only formed in small quantities. The most important vibrational frequencies for **8** are given in Table 9 to aid future experimental work.

To our knowledge, the unsaturated cycloheptyne (**18**) has not been reported in the literature before. The saturated parent

(39) (a) Balci, M.; Winchester, W. R.; Jones, W. M. *J. Org. Chem.* **1982**, *47*, 5180. (b) Tyner, R. L.; Jones, W. M.; Ohrn, Y.; Sabin, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 3765.

cycloheptyne⁴⁰ (**19**) and benzocycloheptyne⁴¹ (**20**) have been identified via trapping and labeling experiments.



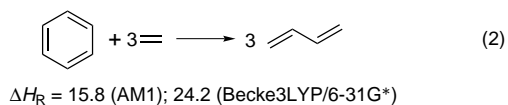
Although **18** is in the relevant energy regime (33.7 kcal mol⁻¹ relative to the global minimum **3**), it seems unlikely to be an important species on the naphthylcarbene rearrangement hypersurface (see Scheme 2), also due to its likely very low barriers for rearrangement into **16**.

Cyclobuta[de]naphthalene (3). Cyclobuta[de]naphthalene (**3**) is commonly found to be the final product of both **1** and **2** at high temperatures; **3** can be prepared in this way on a preparative scale.⁸ Consistent with these experimental observations, we find **3** to be the global minimum on the naphthylcarbene PES which contains an intact naphthyl moiety.⁴² Despite the highly strained four-membered-ring bridging the *peri* position of naphthalene **3** is the only non-carbenoid structure which retains the aromaticity in *both* rings and has no additional unsaturation.

Discussion

Rearrangements. Only part of the naphthylcarbene potential hypersurface has been explored experimentally (cf. Introduction and Scheme 1). Our theoretical data allow the remainder of this region of the PES to be analyzed. Several experimental facts require explanation.

Initially, we gained a first impression of the energies of the structures reported in the earlier literature at the semiempirical AM1 level. A few years ago, such approaches were the only practicable way to study a system of this size and complexity. Indeed, some of the species were studied earlier using the INDO formalism.⁴³ AM1 predicts the singlet–triplet gaps generally much too large, and sometimes even gives the wrong energetic order (e.g., for **5**). Three non-benzenoid structures (**7**, **9**, and **10**) could be located as minima only with AM1 due to its underestimation of the aromatic stabilization (a simple evaluation is given in eq 2). At correlated *ab initio* levels, the non-benzenoid structures (the cyclic allenes are exceptions) converge to their aromatic counterparts.



The AM1 relative energies appear reasonable but bear some misleading features. For instance, all naphthylcarbene rearrangements should eventually lead to **8** (the AM1 global minimum), but this has not been observed experimentally. The true global minimum (**3**) ranks only second in relative energy at AM1. Singlet **5** incorrectly is a minimum at AM1. As a consequence, the experimental observations cannot be explained with the AM1 data. We therefore conclude that semiempirical

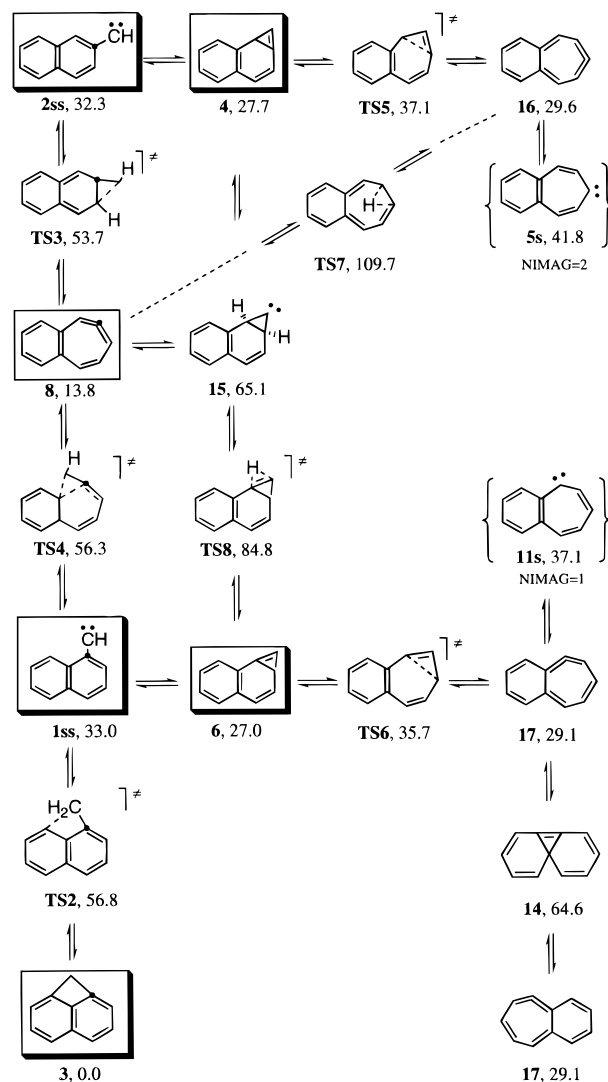
(40) (a) Wittig, G.; Meske-Schüller, I. *Liebigs Ann. Chem.* **1968**, 711, 65. (b) Wittig, G.; Krebs, A.; Pohlke, A. *Angew. Chem.* **1960**, 72, 324. (c) Meier, H.; Molz, T.; Merkle, U.; Echter, T.; Lorch, M. *Liebigs Ann. Chem.* **1982**, 914.

(41) (a) Maier, J.; Layer, M.; Combrink, W.; Schniepp, S. *Chem. Ber.* **1976**, 109, 1650. (b) Wittig, G.; Heyn, H. *Chem. Ber.* **1964**, 97, 1609.

(42) Of course, they may well be other, lower lying minima of the general formula C₁₁H₈ which do not resemble a naphthyl moiety.

(43) Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. *J. Tetrahedron* **1985**, 41, 1601.

Scheme 3



methods are not generally suitable for the study of this and other problems associated with aromatic stabilizations or small ΔE_{ST} 's.

To facilitate comparisons, all *ab initio* optimized structures are summarized in Scheme 2, and the resulting singlet naphthylcarbene rearrangement PES is depicted in Scheme 3. Only the “framed” structures have been characterized experimentally to some extent (**1–4** and **6**) or were suggested (**8**).

Both the similar relative energies of **2**, **4**, as well as **16** (usually depicted as **5**) and the ΔE_{ST} for **2** (all energies within 5 kcal mol⁻¹) are consistent with the experimentally observed facile interconversion of these structures at ambient temperatures. The barrier (via **TS5**) for ring-opening of **4** to **16** is also relatively small (9.4 kcal mol⁻¹), allowing all species to equilibrate. Most notably, **5s**, although only 9.5 kcal mol⁻¹ above **2ss**, is not a minimum (NIMAG = 2) and can thus not participate. It should rather be ascribed to the allenic structure **16**, which is remarkably stable (2.7 kcal mol⁻¹ lower in energy than **2ss**!).

By analogy, isomers **1**, **6**, and **17** also should rearrange. However, only **1** and **6** have been observed experimentally. Not surprisingly, structure **11** was postulated but has never been characterized, due to its non-stationary nature.^{2,5,7,10} Instead, allene **17** should be the species involved in the rearrangement of 1-naphthylcarbene. Since the barriers for rearrangement of **1ss** to **8** (via **TS4**, 23.3 kcal mol⁻¹) and to **3** (via **TS2**, 23.8

Table 10. Nucleus Independent Shift Values (NICS, for Singlets Only, See Text)³⁴ for Some C₁₁H₈ Isomers at GIAO RHF/6-31G*

NICS	1as	3	4	5s	8	11s	13	14	15	16	17	18	19
ring A ^a	-10.3	-11.4	-11.4	-12.5	-11.8	-10.2	-11.4	-2.5	-10.5	-9.7	-8.8	-10.9	-11.4
ring B	-8.5	-11.4	-3.3	-6.1	-4.7	-6.4	-11.0	-2.5	-2.4	-6.5	-3.8	-1.0	-11.4

^a Ring A refers to the fused phenyl ring.

kcal mol⁻¹) are higher than the barrier (*via* **6** and **TS6**, 8.7 kcal mol) for rearrangement of **1ss** to **17**, the latter is very likely to be an observable species at low temperatures (note, however, that the activation energy for the **17** → **6** reaction only is 6.6 kcal mol⁻¹). Further degenerate rearrangement of **17** via high-lying **14** (35.4 kcal mol⁻¹ above **17**) is, however, impossible.

Since the barriers for **2ss** → **8** (*via* **TS3**, 21.4 kcal mol⁻¹), **1ss** → **8** (*via* **TS4**, 23.3 kcal mol⁻¹), and **1ss** → **3** (*via* **TS2**, 23.8 kcal mol⁻¹) are very similar, the experimental difficulties in interpreting and identifying the pathways for interconversion of **2ss** to **1ss** and further to **3** are easily understood. At low temperatures, **2ss** only equilibrates with **4** and **16** (and **1ss** with **6**, possibly also with **17**), while much higher temperatures only give **3** via transient **1ss**. Although **8** is a stable species, it is difficult to observe under high-energy conditions. Thus, **8** should be synthesized and characterized directly from precursors which do not require elevated temperatures or the intermediate formation of naphthylcarbenes.

We also located a very high lying hydrogen shift transition structure (**TS7**) connecting **8** and **16** directly, but **TS7** is too high in energy (109.7 kcal mol⁻¹ vs. **3**) to be important. It would also lead to unexpected C-scrambling. The involvement of **15** in the naphthylcarbene rearrangements is precluded by its high relative energy (51.3 kcal mol⁻¹) versus **8**.

Most of the qualitative features of the naphthylcarbene PES compare very well to phenylcarbene (*cf.* Table 6).³ Both the triplet rotational barriers of the *exo*-methylene group (3.5 and 4.4 kcal mol⁻¹ for 2-naphthylcarbene and phenylcarbene, respectively) and the ΔE_{ST} 's (both around 5 kcal mol⁻¹) are quite comparable. More strikingly, the allenic species (**8**, **16**, and **17** on the C₁₁H₈ PES) are generally low-lying minima (note that cycloheptatetraene is the cyclic C₇H₆ minimum). Although this is a well-known feature of the C₇H₆ PES, the importance of allenic species in naphthylcarbene rearrangements was underestimated.

Aromaticity. The nucleus independent chemical shifts (NICS, see Methods above) were computed to estimate the aromatic character of the relevant singlet species. Based on the NICS of -11.4 for naphthalene (**12**) at the same level, we find that the naphthylcarbenes (**1** and **2**) are not much perturbed by the adjacent carbene carbon (Table 10): the NICS value for, e.g., **1as**, is -10.3 for the fused benzene ring (A) and -8.5 for the ring bearing the CH group. Note that methyl substitution also decreases the NICS somewhat in methylnaphthalene (**13**, NICS: -11.0). In general, the aromatic character in the fused benzene ring (A) is affected little by perturbation of the second ring. The A-ring NICS of **3** (NICS = -11.4), **5s** (NICS = -12.5), and **8** (NICS = -11.8) serve as examples. But even **16** and **17** have large negative NICS's (-9.7 and -8.8) in ring A, although strong bond-length alternation is indicated. Since the allenic species are relatively low in energy, despite their localized geometry, we conclude that bond-length equalization (not found) cannot be a single conclusive measure for aromaticity in this case.⁴⁴

Conclusions

Cyclobuta[*de*]naphthalene (**3**) is the global minimum on the C₁₁H₈ PES. Generally, seven-membered carbenes fused to a benzene ring are not minima and optimize to the corresponding allenes.

Both 1- and 2-naphthylcarbene (**1** and **2**) have triplet ground states, but the ΔE_{ST} 's are small (around 5 kcal mol⁻¹), similar to phenylcarbene. The triplet rotational barrier for the *exo*-methylene in **2** is relatively small (3.5 kcal mol⁻¹) due to comparable electronic interactions in the ground and transition structures. An in-plane triplet transition structure ("linear" inversion) is a stationary point of Hessian index two, but is also low-lying.

At low temperatures, singlet 2-naphthylcarbene (**2s**) equilibrates with 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**4**) and with bicycloheptatetra-1,3,5,7-ene (**16**, a benzocycloheptatetraene), but not with singlet 4,5-benzocycloheptatrienyliene (**5s**). The latter is not a minimum (NIMAG = 2) and can thus not be involved in the naphthylcarbene rearrangements. 2-Naphthylcarbene (**2s**) can rearrange further to bicycloheptatetra-1,2,4,6-ene (**8**, the second lowest minimum), which may not have been observed due to similar barriers for further rearrangement of 1-naphthylcarbene (**1s**) to cyclobuta[*de*]naphthalene (**3**).

1-Naphthylcarbene (**1s**), 2,3-benzobicyclo[4.1.0]hepta-1,4,6-triene (**6**), and bicycloheptatetra-2,3,5,7-ene (**17**) equilibrate similarly. The postulated singlet 4,5-benzocycloheptatrienyliene-3-ene (**11s**) is not a minimum.

The allenes bicycloheptatetra-1,2,4,6-ene (**8**), bicycloheptatetra-1,3,5,7-ene (**16**), and bicycloheptatetra-2,3,5,7-ene (**17**) are thermodynamically remarkably stable and should be observable at low temperatures.

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Supporting Information Available: Tables of Cartesian coordinates for all theoretical structures (7 pages). See any current masthead page for ordering and Internet access instructions.

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