

Homobenzene: Homoaromaticity and Homoantiaromaticity in Cycloheptatrienes

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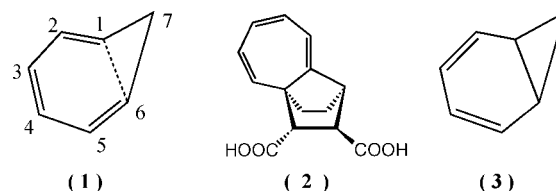
Cycloheptatriene (C_7) is firmly established to be a neutral homoaromatic molecule based on detailed analyses of geometric, energetic, and magnetic criteria. Substituents at the 7 (methylene) position, ranging from the electropositive BH_2 to the electronegative F, favor the equatorial conformation but influence the aromaticity only to a small extent. By the same criteria, the planar transition state (C_{2v}) for cycloheptatriene ring inversion is clearly antiaromatic. This is attributed to the involvement of the pseudo- 2π -electrons of the CH_2 group with the 6π -electrons of the ring to give an 8π -electron system. Similarly, the participation of the CH_2 groups into C_{2v} cyclopentadiene and cyclononatetraene lead to significant $4n + 2\pi$ electron aromaticity. The cyclization of cycloheptatriene to norcaradiene proceeds via a highly aromatic transition structure, but norcaradiene itself is less aromatic than cycloheptatriene. An annelated cyclopropane ring does not function as effectively as a double bond in promoting cyclic electron delocalization.

Introduction

The history of “homoaromaticity” began in 1901 with Thiele’s explanation of the weaker acidity of the methylene protons of cycloheptatriene (tropilidene, **1**) compared to those in cyclopentadiene.¹ The explanation, in terms of the aromaticity of the $C_5H_5^-$ anion, is apparent to us now, but not then. Instead, Thiele postulated that a partial 1,6-interaction in cycloheptatriene would confer benzene-like properties and that this “aromatic character” would be lost upon deprotonation. Thiele’s idea was revived in 1956 by Doering,² who described **1** as “mono-homobenzene”; he assumed incorrectly that cycloheptatriene had a planar structure, permitting aromatic 1,6- π -electron interaction. In the ensuing years, **1** was firmly established experimentally to have a boat conformation with C_s symmetry (Scheme 1) through vibrational spectroscopy,³ 1H NMR,⁴ electron diffraction,⁵ microwave spectroscopy,⁶ and X-ray crystallography.⁷ The boat form undergoes a facile conformational isomerization through a planar (C_{2v}) transition state. The invasion barrier estimated from dynamic NMR measurements, about 6 kcal/mol,⁴ has been supported by various theoretical computations.^{8–12}

The annelation in **2** results in an essentially planar seven-membered cycloheptatriene ring, but no special “homoaromatic features” were found in the X-ray structure or the UV spectrum.¹³ The rearrangements and cycloadditions of cycloheptatrienes have been scrutinized for over a century.¹⁴ The nature of the cycloheptatriene **1**–norcaradiene (**3**) equilibrium¹⁵ continues to elicit attention both experimentally¹⁶ and theoretically.^{10,17}

SCHEME 1



The possible aromaticity of **3**, due to the involvement of the cyclopropane ring as a double bond surrogate, also has been investigated.^{17b}

Estimates of the homoaromatic stabilization energy of **1** were based on the experimental energy difference (7.2 kcal/mol) between the heats of hydrogenation of **1** (−70.5 kcal/mol) and the sum of three cycloheptenes (−25.9 kcal/mol each),¹⁸ and on the computed resonance energy (3.9 kcal/mol) from force field computations.¹⁹ The homoaromaticity of **1** also was indicated by the 1.4 ppm shift difference of the methylene group hydrogens at −150 to −170 °C: the axial hydrogen, oriented toward the ring center, is shifted upfield relative to the equatorial hydrogen.⁴ Like the analogous behavior in related systems, this has been attributed to induced ring current effects, which result in a central “shielding cone.”²⁴ The magnetic susceptibility exaltation, $\Lambda = -8.1$ ppm cgs for **1** (59% of the −13.7 ppm cgs benzene value), provided additional evidence for its homoaromaticity over 3 decades ago.²⁰ Most recently the homoaromatic character of **1** was indicated by the anisotropy of the current-induced density (ACID) calculations²¹ and by computed NICS (nucleus-independent chemical shift)²² values.^{10c,23}

Although favored by the above criteria, the homoaromaticity of cycloheptatrienes remains controversial.^{9d} Childs and Pikulik (CP) questioned the reliability of the diamagnetic susceptibility exaltation criterion since their experimentally deduced −14.8

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TABLE 1: B3LYP/6-311+G-Optimized Bond Lengths (bn,^a Å), Bond Angles (an,^a deg), and Dihedral Angles (dn,^a deg) for 7-X-cycloheptatrienes as well as the b3 – b2 Difference^b**

X	b1	b2	b3	b3 – b2	b4	b5	a1	a2	a3	a4	d1	d2
H (1, C _s)	1.508	1.349	1.446	0.097	1.363	2.443	108.2	121.9	125.4	125.9	52.9	25.4
	<i>1.486</i>	<i>1.328</i>	<i>1.433</i>	<i>0.105</i>	<i>1.341</i>	<i>2.403</i>	<i>108.0</i>	<i>121.3</i>	<i>124.7</i>	<i>125.7</i>	<i>54.2</i>	<i>27.2</i>
H (1, C _{2v})	1.509	1.341	1.458	0.117	1.347	2.615	120.1	131.5	130.1	128.3	0.0	0.0
	<i>1.486</i>	<i>1.322</i>	<i>1.446</i>	<i>0.124</i>	<i>1.326</i>	<i>2.577</i>	<i>120.2</i>	<i>131.6</i>	<i>130.0</i>	<i>128.2</i>	<i>0.0</i>	<i>0.0</i>
1-TS	1.484	1.419	1.377	–0.042	1.420	1.853	77.2	121.8	123.4	122.2	65.8	18.9
3	1.506	1.470	1.350	–0.120	1.453	1.573	63.0	120.4	122.1	121.4	68.7	9.1
	<i>1.484</i>	<i>1.456</i>	<i>1.328</i>	<i>–0.128</i>	<i>1.441</i>	<i>1.530</i>	<i>62.1</i>	<i>119.7</i>	<i>122.0</i>	<i>121.2</i>	<i>69.6</i>	<i>8.1</i>
BH ₂	1.511	1.349	1.445	0.096	1.363	2.451	108.3	122.5	125.6	125.9	51.6	25.2
CH ₃	1.510	1.350	1.444	0.094	1.365	2.413	106.1	122.2	125.2	125.6	53.8	25.5
NH ₂	1.506	1.350	1.443	0.093	1.366	2.403	105.4	121.4	125.0	125.6	55.4	25.6
OH	1.509	1.348	1.445	0.097	1.363	2.437	107.7	122.6	125.5	125.9	51.9	25.0
F	1.499	1.347	1.446	0.099	1.363	2.437	108.8	121.3	125.3	125.9	54.1	25.2
CN	1.517	1.347	1.444	0.097	1.363	2.447	107.6	120.4	125.5	125.7	55.6	26.0
CMe ₃	1.510	1.351	1.443	0.092	1.365	2.400	105.2	121.7	125.3	125.3	54.9	25.8

^a b1 = C₁–C₇; b2 = C₁–C₂; b3 = C₂–C₃; b4 = C₃–C₄; b5 = C₁–C₆; a1 = C₁–C₇–C₆; a2 = C₇–C₁–C₂; a3 = C₁–C₂–C₃; a4 = C₂–C₃–C₄; d1 = C₇–C₁–C₆–C₅; d2 = C₃–C₂–C₅–C₆ (for the numbering system see Scheme 1). ^b KMLYP/6-311+G** structural parameters are given in italic.

ppm cgs exaltation for 7-*tert*-butylcycloheptatriene²⁴ exceeded the Λ value (–13.7 ppm cgs) for benzene! Since it seems unlikely that 7-*tert*-butylcycloheptatriene is more aromatic than benzene, doubts were raised about the dependability of Λ as an aromaticity measure.²⁴ In contrast to Dauben et al.,²⁰ CP found that the exaltation varies as a function of the size of the 7-substituents; they speculated that the steric effect of the 7-*tert*-butyl group might shorten the C₁–C₆ separation and thus enhance the homoconjugation. However, CP's general conclusion that “the presence of an induced diamagnetic ring current is not a good criterion of aromaticity” has not been supported by more recent studies; instead, the opposite is true²⁵ (we reexamine this issue below).

On the basis of “two-center energy terms” computed at MNDO and AM1 semiempirical levels, Williams et al. even found a weak *destabilizing* nonbonded C₁–C₆ interaction in cycloheptatriene.^{9a} Williams's 2001 review states opposing views: “The most recent experimental and theoretical studies *do not* support the existence of any significant homoaromaticity in cycloheptatriene and its derivatives.”^{9d} Nevertheless, he concludes that cycloheptatriene “is marginally homoaromatic”.

In an elegant paper analyzing π -interaction topologies, Goldstein and Hoffmann²⁶ included homoaromaticity and homoantiaromaticity as special cases within the pericyclic category. They stressed that such stabilization interactions should be more important for charged species due to the smaller HOMO–LUMO energy gaps of the interacting fragments compared with their neutral analogues. Indeed, computations provide good support for homoaromaticity in positively charged systems.²⁵

Despite the extensive experimental and theoretical studies on cycloheptatriene systems, there are still many open questions; e.g., is cycloheptatriene definitely a neutral homoaromatic? How reliable is diamagnetic susceptibility exaltation (Λ) as an aromaticity criterion? Does a *tert*-butyl substituent really result in an extraordinarily large exaltation? This paper addresses these questions by comprehensive calculations on cycloheptatriene and related systems at adequately high levels of ab initio and density functional theory. Aromatic character is assessed using geometric, energetic, and magnetic criteria,²⁷ in particular the nucleus-independent chemical shifts (NICS).²² Cycloheptatriene and CP's set of 7-X substituted (X = H, BH₂, CH₃, NH₂, OH, F, CN, CMe₃) derivatives are shown to be neutral homoaromatic molecules; only small substituent effects were found. The computed magnetic susceptibility exaltation of the *tert*-butyl

derivative is the largest in the graded set, but it is not exceptional. Planar cycloheptatriene is significantly *antiaromatic* based on the same criteria. In addition, the cycloheptatriene (**1**) to norcaradiene (**3**) cyclization via an aromatic transition structure is analyzed. Norcaradiene (**3**) is shown to be less aromatic than cycloheptatriene; hence, the cyclopropane ring does not substitute for a double bond effectively.

Computational Details

The geometries of cycloheptatrienes (**1**, C_s and C_{2v}), norcaradiene (**3**, C_{2v}), and the 7-substituted (X = H, BH₂, CH₃, NH₂, OH, F, CN, CMe₃) cycloheptatrienes and reference molecules were fully optimized at the B3LYP/6-311+G** DFT level,²⁸ and the nature of the stationary points was characterized by vibrational frequency analysis. All computations used the Gaussian 03 program.²⁹

Magnetic properties and NICS²² were computed at GIAO-B3LYP/6-311+G** with the B3LYP/6-311+G** geometries. A more refined “dissected LMO NICS”^{22b,c} analysis, based on the individual gauge for localized orbitals (IGLO) method and Pipek–Mezey localization procedure³⁰ as implemented in the deMon NMR program,³¹ was performed with the IGLO-III basis set and B3LYP/6-311+G** geometries to reveal the individual contributions of bond and core electrons to the total shielding. All NICS values are in ppm. The geometries at the B3LYP/6-311+G** level will be discussed in the present work. The anisotropy of the current-induced density (ACID) was deduced using the method described by Herges et al.²¹ and are based on the B3LYP/6-311+G**-optimized geometries. Current densities were computed using Keith and Bader's³² CSGT method, as implemented Gaussian 03. Although B3LYP is known to overestimate the delocalization in systems such as [10]annulene³³ (based on KMLYP³⁴ results), comparison checks revealed no significant differences in cycloheptatriene systems (Tables 1 and 2).

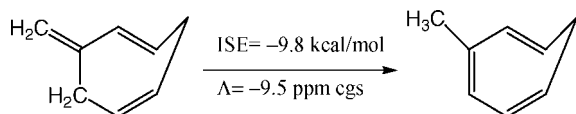
Results and Discussions

(a) **Cycloheptatriene (1)**. The molecular skeleton and numbering system of cycloheptatriene is shown in Scheme 1. The boat form of cycloheptatriene (**1**) is the energy minimum. The B3LYP geometry agrees excellently with the electron diffraction structure except for the C₁–C₆ distance and the related C₁–C₇–C₆ angle (Table 1).⁵

TABLE 2: GIAO-B3LYP/6-311+G//B3LYP/6-311+G**.-Computed NICS for Cycloheptatrienes Compared with the Benzene and Cyclobutadiene Values^{a,b}**

species	NICS(0)	NICS(0) _{zz}	NICS(1)	NICS(1) _{zz}
1 (<i>C_s</i>)	-4.2 ^c	-0.9	-5.4 (-6.2)	-9.3 (-13.6)
	-4.4		-5.4 (-6.4)	
1a (<i>C_{2v}</i>)	8.8 ^c	32.9	6.2	20.0 ^d
	10.3		6.0	
1-TS (<i>C_s</i>)	-12.9	-19.9	-9.2 (-12.4)	-16.7 (-32.5)
3 (<i>C_s</i>)	-3.5	11.2	-3.5 (-3.8)	-2.2 (-8.1)
	-2.8		-3.0 (-3.4)	
4 (<i>C₂</i>)	2.9	19.0	0.0	4.8
X = BH ₂	-4.2	-1.2	-5.5 (-6.2)	-9.5 (-13.9)
X = CH ₃	-5.1	-3.3	-6.0 (-6.9)	-10.5 (-15.8)
X = NH ₂	-5.9	-4.7	-6.8 (-7.4)	-11.7 (-16.8)
X = OH	-4.8	-1.0	-5.9 (-6.3)	-9.5 (-13.6)
X = F	-5.2	-1.6	-6.5 (-6.5)	-10.2 (-13.8)
X = CN	-5.5	-2.8	-6.6 (-6.9)	-10.6 (-15.1)
X = C(CH ₃) ₃	-5.5	-4.1	-6.3 (-7.3)	-10.8 (-16.7)
11 (<i>C_s</i>)	4.5	21.2	2.4	10.3
C ₆ H ₆ (<i>D_{6h}</i>)	-8.0	-14.5	-10.2	-29.3
	-8.6		-10.9	
C ₄ H ₄ (<i>D_{2h}</i>)	26.5	110.3	17.6	56.0
	29.7		19.4	

^a NICS values were computed 1 Å away from the geometric center of the homobenzene moiety on both the same side and on the opposite side as the methylene group. The opposite side values are given in parentheses. ^b GIAO-KMLYP/6-311+G**//KMLYP/6-311+G** NICS values are given in italics for comparison. ^c GIAO-HF/6-31G**//B3LYP/6-31G values of -4.2 and 8.2 ppm for **1-C_s** and **1-C_{2v}**, respectively, are reported in ref 10c. ^d The NICS(0)_{zzz} value^{22d,e} was +24.4 ppm.

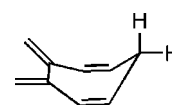
SCHEME 2

The C–C bond length alternation (defined as $b_3 - b_2$; see Table 1), 0.097 Å in **1**, is smaller than that (the largest in the molecule 0.115 Å) in the acyclic all-*trans*-1,3,6,8-nonatetraene reference molecule and also that (0.117 Å) in 1,3-cycloheptadiene. In particular, the C–C double bonds (1.349, 1.363 Å) are longer and the single (1.508, 1.446 Å) bonds are shorter than those in the acyclic octatetraene (1.339/1.340 vs 1.510/1.453 Å, respectively). These differences are consistent with those expected from the effect of homocyclic delocalization in **1**. The nonplanarity of **1**, which is attributed mainly to the reduction of angle strain, should result in larger rather than smaller bond length alternations if no homoaromatic conjugation were present.

Although the heat of hydrogenation of **1** is 7.2 kcal/mol lower than that of three cycloheptenes,¹⁸ this value is influenced by the strain energy differences, as has been discussed extensively.³⁵ This problem can largely be overcome by applying the “isomerization stabilization energy” (ISE) method.³⁶ This results in an ISE of -9.8 kcal/mol for **1** (Scheme 2), which may be compared with ISE = -33.2 kcal/mol for benzene.³⁶ Hence, cycloheptatriene is confirmed to be homoaromatic energetically.

In addition to the geometric and energetic criteria, magnetic susceptibility exaltations (Λ), attributable to the ring current effects resulting from cyclic electron delocalization, provide decisive evidence for aromaticity.²⁷ Derived from the equation in Scheme 2, the Λ of **1** is -9.5 ppm cgs. This is close to the -8.1 ppm cgs value deduced from experimental data by Dauben et al.²⁰ and is 56% of the benzene exaltation (-13.7 ppm cgs).²⁷ Thus, **1** also is homoaromatic magnetically.

Consistent with the expected paramagnetic ring current deshielding effect outside the ring, the GIAO-B3LYP/6-311+G** ¹H NMR chemical shifts, particularly at C_{2,5} (6.3 ppm) and at C_{3,4} (7.0 ppm), are shifted downfield with respect to typical vinylic hydrogen values. The computed ¹H chemical shift difference between the two methylene hydrogens (1.3 ppm), nearly the same as the 1.4 experimental difference,⁴ also can be attributed to the presence of a diamagnetic ring current in homoaromatic cycloheptatriene. The chemical shift of the axial hydrogen (at 1.7 ppm) is at higher field than that of the equatorial hydrogen (at 3.0 ppm). The computed ¹H chemical shift difference between the two ring CH₂ hydrogens is only 0.8 ppm in an analogous nonaromatic model compound with six sp² carbons in the seven-membered ring 3,4-dimethylene-1,5-cycloheptatriene (**4**). Since the distal double bond in **1** is replaced by two exocyclic methylene groups, **4** is merely conjugated, rather than aromatic.

**4**

NICS also characterizes the homoaromaticity of **1** (Table 2) magnetically. NICS, a simple and efficient aromaticity probe, is the negative of the absolute magnetic shielding and can be computed directly and easily, e.g., at or away from ring centers.²² Compared with Λ , NICS has the advantage of not requiring an increment scheme or reference compounds for its evaluation. Of course, interpretations of NICS can benefit from comparisons with data of related molecules. Unlike stabilization energies, neither NICS nor Λ are perturbed directly by strain. However, not only the π -systems but also the σ -systems influence NICS values. The local σ -contributions, which are net paratropic and reduce isotropic NICS(0) in the centers of rings, are diminished at 1 Å above the ring center.^{22b} In addition, NICS(1)_{zz}, the perpendicular tensor of NICS(1), which correlates better with the aromatic stabilization energies for planar π -rings,^{22d} also may be employed for nonplanar systems. The most refined NICS index, NICS(0)_{zzz}, includes only the zz tensor contributions of the π -MOs, but is best applied to planar systems because of their strict σ - π -separation.

Due to the nonplanarity of **1**, we calculated NICS(1) values 1 Å away from the geometric center of the six-carbon homobenzene moiety, both on the same and on the opposite side as the methylene group (Table 2). At GIAO-B3LYP/6-311+G**//B3LYP/6-311+G**, NICS(0) at the center of **1**, -4.2 (the same value reported by Komatsu and co-workers^{10c}), is about half the benzene value (-8.0). Isotropic NICS(1) above and below the ring are -5.4 and -6.2 compared to the -10.2 NICS(1) of benzene. The cycloheptatriene NICS(1)_{zz} values (-9.3 and -13.6) also are a substantial fraction of benzene's -29.3.²²

These indications of the significant aromaticity of cycloheptatriene are further supported by dissected IGLO/III//B3LYP/6-31+G** LMO-NICS comparisons with the reference molecules **5–10** (Table 3; data at this level differ insignificantly from the GIAO values discussed above). For uniformity and interpretative simplicity, e.g., to enforce strict σ - π -separation, planar ring symmetries for **5–10** were imposed. As indicated by their slightly positive 1.0–1.2 NICS(0) values, **5–8** are “nonaromatic”. While the paratropic C–C(σ) contributions are nearly the same for **5–8**, both for NICS(0) and NICS(1), the

TABLE 3: Dissected NICS (in ppm) at Ring Center and 1 Å above at the IGLO/III/B3LYP/6-311+G** Level

		C ₆ H ₆ (D _{6h})	1 (C _s)	1 (C _{2v})	1-TS (C _s)	3 (C _s)	5 (D _{7h})
NICS	0	-8.8	-4.9	9.6	-13.4	-4.2	1.0
NICS	1	-10.6	-6.7	5.8	-9.5	-4.4	0.8
C-C(σ)	0	13.8	10.5	11.1	7.4	8.4 ^a	7.7
	1	2.3	1.1	3.8	3.7	0.3	3.5
C-C(π)	0	-20.7	-12.9	-2.3	-17.4	-8.0	
	1	-9.6	-4.7	2.1	-10.4	-2.0	
C ¹ -H	0	-1.3	-1.8	-0.7	-2.4	-0.8	
	1	-3.0	-2.6	-1.8	-2.1	-1.7	
C ² -H	0		-0.3	1.8	-0.3	-0.4	
	1		-0.2	1.9	-0.3	-0.5	
C ³ -H	0					-0.8	-7.0
	1					-0.4	-3.5
		6 (C _{2v})	7 (C _{2v})	8 (C _{2v})	9 (C _{2v})	10 (C _{2v})	
NICS	0	1.2	0.5	1.1	9.8	-6.9	
NICS	1	0.7	-0.4	-0.3	5.2	-9.7	
C-C(σ)	0	8.0	8.9	10.0	16.4	12.6	
	1	3.6	3.6	3.8	3.6	3.4	
C-C(π)	0	-1.9	-3.6	-5.2	-5.7 ^b	-17.7	
	1	-0.7	-1.2	-1.8	-0.6 ^b	-10.5	
C ¹ -H	0	0.0	-0.4	-0.4	-0.6	-1.4	
	1	-0.4	-0.8	-1.0	-1.8	-2.1	
C ² -H	0	-2.4	-2.8	-3.2	-0.2		
	1	-0.6	-1.2	-1.2	0.0		
C ³ -H	0	-2.4	-1.8				
	1	-1.5	-0.7				

^a The total contribution of the three membered ring C-C bonds is -3.0 ppm. ^b The exo C-C(π) contribution is 4.9 (4.5), and C-C(π)_{tot} is -0.8 (3.9).

diatropic NICS_π contributions increase with the increasing number of π-electrons in going from **5** to **8**; the effect is roughly additive (ca. -1.9 ppm per π-bond). However, the behavior of both cycloheptatriene (**1**, C_s) and the (4*n* + 2)π-electron aromatic tropylium cation (**10**) deviates considerably from expectations based on **5**-**8**. Instead of the expected NICS(0)_π values of ca. -5.7, based on additivity (see above), or the -5.9 contributed by the three endocyclic double bonds of methylenecycloheptatriene (**9**), the diamagnetic C-C(π) contributions (-12.9 for **1**, -17.7 for **10**) are exceptionally large. These dominate the local C-C(σ) and the C-H contributions (10.5 and -2.1 for **1**, 12.6 and -1.4 for **10**, respectively). Thus, the resulting diatropic total NICS(0) values, -4.9 for **1** and -6.9 for **10**, signify their aromaticity. The same general conclusions as above are reached by analysis of the dissected NICS(1) data (also given in Table 3). Note that the methylene C-H bond contributions to NICS of **1** are slightly negative (-0.3 ppm); this also was found for all other methylene groups in the reference molecules.

ACID is a powerful method to investigate and to quantify conjugative effects in ground,³⁷ excited, and transition states.³⁸ The ACID scalar field can be interpreted as the density of

delocalized electrons.²¹ Through-bond (σ-conjugation, hyperconjugation, etc.) and through-space interactions (secondary orbital effects, homoaromaticity, etc.) between two atoms or groups are quantified by the critical isosurface value (CIV). Applied to the cycloheptatriene molecule, ACID clearly indicates a considerable density of delocalized electrons bridging carbons C₁ and C₆ through space (Figure 1). The CIV value of the through-space conjugation in cycloheptatriene, 0.030 [38% of the π-conjugation in benzene (0.074)], indicates pronounced homoconjugation. The additional through-bond conjugation involving the CH₂ group (C₇) is slightly stronger (CIV = 0.032, 43% of benzene) than the through-space interaction. Cyclic conjugation implies a ring current, which can be visualized by plotting the current density vectors onto the ACID isosurface (Figure 1). Following the arrows, the ring current branches at C₁ and C₆; one part flows through space and a stream of similar size flows through bond (and includes the CH₂ group).

(b) Influence of Substituents (X = H, BH₂, CH₃, CN, NH₂, OH, F, CMe₃). As discussed in the introduction, CP reported very large effects on the diamagnetic susceptibility exaltations in cycloheptatrienes substituted by -CH₃, -CN, and especially by -CMe₃ groups and questioned the reliability of magnetic

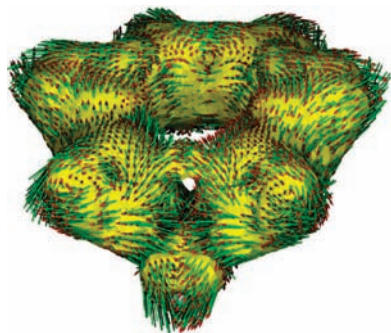


Figure 1. ACID isosurface of cycloheptatriene at an isosurface value of 0.027. Current density vectors are plotted onto the ACID surface. The vector of the magnetic field is orthogonal with respect to the plane, which is defined by the carbon atoms 2, 3, 4, 5 and is pointing upward.

TABLE 4: B3LYP/6-311+G + ZPE (B3LYP/6-31*)-Computed Isomerization Stabilization Energy (ISE, kcal/mol) and CSGT-B3LYP/6-311+G**//B3LYP/6-311+G**-Calculated Magnetic Susceptibilities Exaltations (Λ , ppm cgs) for 7-X-cycloheptatrienes**

X	ISE	Λ
H	-9.8	-9.5
BH ₂	-9.9	-10.1
CH ₃	-10.8	-10.8
NH ₂	-11.1	-11.1
OH	-11.0	-10.6
F	-10.3	-9.7
CN	-11.3	-10.9
CMe ₃	-11.7	-11.6

susceptibility exaltation as a criterion of aromaticity.²⁴ However, our computations on systems with various substituents ranging from electropositive BH₂ to electronegative F substituent as well as the bulky CMe₃ group ameliorate their findings and challenge their conclusions. Appreciable variations in Λ are not found. The value for the *t*-Bu compound, -11.7, hardly exceeds that for the CN, NH₂, and OH derivatives (-11.3, -11.1, and -11.0, respectively; Table 4). Indeed, this invariance also is true for our aromatic stabilization energy (ISE) evaluations (also given in Table 4 for comparison).

The optimized B3LYP/6-311+G** geometries of the more stable 7-equatorial monosubstituted cycloheptatriene minima differ very little from the geometry of **1**. The bond lengths (*bn*), bond angles (*an*), and dihedral angles (*dn*) are insensitive to substitution. However, the CMe₃ substituent does result in the largest change in the important C₁-C₆ separation; *b*₅ is 0.043 Å shorter for this derivative than for the parent. In addition, the *b*₂ - *b*₃ bond length difference (a measure of the bond length alternation) for the CMe₃ derivative (0.092 Å) is smallest for this set of molecules (albeit by only 0.007 Å). But these modest geometrical changes can hardly produce the highly abnormal effect reported by CP.²⁴

Our computed magnetic susceptibility exaltation (-11.7 ppm cgs) of 7-*tert*-butylcycloheptatriene is smaller than that deduced by CP (-14.8 ppm cgs) and also is smaller than that of benzene (-13.7 ppm cgs). We find (Table 4) the behavior of the *tert*-butyl derivative not really to be exceptional. Our results suggest that CP's experimental MS exaltation of 1-C(CH₃)₃ may be overestimated. We question their resulting conclusion regarding

its exceptional homoaromaticity and their negative judgment concerning of the merits of MS exaltation as an aromaticity criterion. Other than an experimental redetermination of the magnetic susceptibility exaltation of 7-*tert*-butylcycloheptatriene, we see no way to resolve or rationalize the discrepancy with theory.

(c) Planar 1,3,5-Cycloheptatriene. Doering rejuvenated Thiele's much earlier suggestion¹ by describing planar cycloheptatriene (**planar-1**, *C*_{2v}) as mono-homobenzene in 1956² by presuming a 1,6- π -interaction. Actually, **planar-1** is a transition structure for ring inversion of the boat minimum, **1**. The inversion barrier, determined experimentally to be ca. 6 kcal/mol by NMR,⁴ usually is ascribed to the "angle strain" arising from the greater deviation of the C-C-C angles from normal values in the planar conformation. The increase in the C-C-C angles in going from the *C*_s to the *C*_{2v} geometries (see data in Table 1) are 11.9° for a₁, 9.6° for a₂, and 4.7° for a₃, and 2.4° for a₄ at B3LYP/6-311+G**.

Like many other theoretical estimates of ring inversion barriers, the semiempirical (MNDO, AM1, PM3, SAM1),¹⁰ force field (MM3, MM4),¹¹ and ab initio HF values are too low, while MP2 is too high¹² (8.6 kcal/mol at the MP2/6-31G**/HF/6-31G* level¹⁰ or 11.4 kcal/mol at the optimized MP2/6-311+G** level in the present work). Much better agreement is achieved with density functional theory at the B3LYP/6-31G* level (5.2 kcal/mol, the imaginary frequency is 104i cm⁻¹),¹⁰ and at B3LYP/6-311+G**+ZPE (5.8 kcal/mol, the imaginary frequency is 112i cm⁻¹).

Although our evidence establishes the boat form of cycloheptatriene (**1**) to be homoaromatic, the planar geometry (**1a**) does not have the homoconjugative 1,6- π -interaction Doering assumed.² Comparisons of the computed magnetic properties of the *C*_s (**1**) and *C*_{2v} (**planar-1**) forms are remarkable. While, as expected, the *C*_s form has a highly negative total magnetic susceptibility (-58.6 ppm cgs), the value of the *C*_{2v} form (only -34.6 ppm cgs) is 20.6 ppm cgs less negative. **Planar-1** is computed to have a *paramagnetic* magnetic susceptibility exaltation of 9.8 ppm cgs, based on the modified isomerization equation in Scheme 2 (using planar geometries). Hence, planar cycloheptatriene (**planar-1**) is *antiaromatic*!

This conclusion is supported by the computed *positive* NICS values (Table 2) and by dissected NICS analysis (Table 3). Instead of a NICS _{π} of ca. -5.7 ppm expected on the basis of additivity of C-C(π) contribution to nonaromatic seven-membered ring systems, its diamagnetic C-C(π) contributions is abnormally small, -2.3 ppm, at the ring center. This "hidden" paratropic influence of ca. 3.4 ppm signifies the antiaromatic character of the planar form of **1**, which is confirmed by the paratropic 24.4 ppm NICS(0) _{π zz}^{22d,e} value (Table 2). The methylene C-H contributions are constant (Table 3): all CH₂ groups have negative NICS contributions with the exception of the CH₂ group of **planar-1**. For example, the NICS contribution of the CH₂ in **planar-1** is 1.8 ppm, while that in the planar 1,4-cycloheptadiene is -3.2 ppm. We ascribe this to the pseudo-2 π -electron effect of the CH₂ group in **planar-1**. The resulting pseudo-8 π -electron system of **planar-1** resembles planar cyclooctatetraene (COT).³⁹ Like the latter, planar *C*_{2v} cycloheptatriene is an antiaromatic transition structure for ring inversion.

The ACID method (Figure 2) corroborates the NICS analysis. Compared to the boat conformation (CIV between C₁ and C₆ = 0.030) the through-space interaction increased (CIV = 0.033). However, there is a strong paramagnetic ring current involving

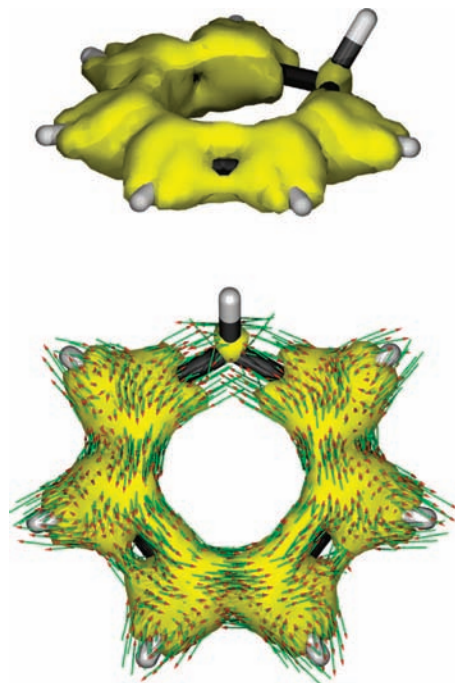
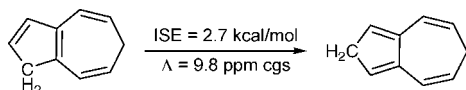


Figure 2. ACID plot of planar cycloheptatriene at an isosurface value of 0.050. Current density vectors plotted onto the ACID surface (bottom) indicate a paramagnetic ring current (counter clockwise). The vector of the magnetic field is orthogonal to the ring plane and points toward the viewer.

SCHEME 3



the CH₂ group, indicating considerable “negative conjugation” and antiaromaticity.

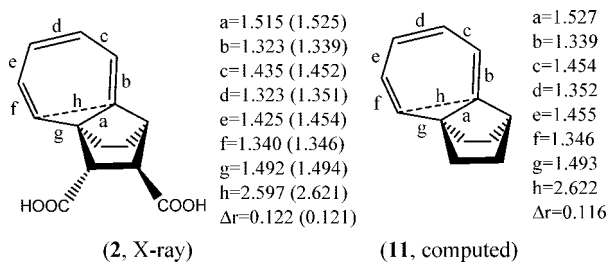
Relative to the delocalized structures of aromatic compounds (with equalized bond lengths), antiaromatic species have more highly localized geometries (highly alternating CC bond lengths). The B3LYP/6-311+G** (Table 1) bond length alternation in planar cycloheptatriene, 0.117 Å, is larger than that in the C_s form (0.097 Å). The C₁–C₇ single bond length, 1.509 Å, is longer than the corresponding C–C distance of 1.497 Å in 1,3,5-heptatriene.⁴⁰

The GIAO-B3LYP/6-311+G** ¹H NMR chemical shifts have been computed for both the C_s (**1-C_s**) and C_{2v} (**1-C_{2v}**) cycloheptatriene geometries. Compared with the ¹H NMR chemical shifts (5.4 ppm at C_{1,6} and especially 6.3 ppm at C_{2,5} as well as 7.0 ppm at C_{3,4}) of **1-C_s**, the 5.2–5.5 ppm ¹H resonances of **1-C_{2v}** are upfield shifted. The ¹H chemical shifts for the methylene group (4.0 ppm) in the planar **1-C_{2v}** are distinctly downfield from those of the **1-C_s** boat form (1.7 axial and 3.0 ppm equatorial). These differences are consistent with the presence of ring currents, more diatropic in **1-C_s** and more paratropic in **1-C_{2v}**.

Antiaromatic systems are destabilized relative to their aromatic analogs.⁴¹ The small, but positive ISE (2.7 kcal/mol, Scheme 3) computed for planar derivatives of **1-C_{2v}** supports its antiaromatic character. This conclusion is also supported by the 6.5 antiaromatic destabilization energy of planar cycloheptatriene obtained by Frenking et al.⁴² based on energy decomposition analysis (EDA).⁴³

The pseudo-2π-electron effect of the CH₂ group, which is responsible for the antiaromatic 8π-electron behavior of planar-

SCHEME 4



1, also results in the (4*n* + 2)π-electron aromatic behavior of its analogues C₅H₆ (C_{2v}) and C₉H₁₀ (C_{2v}).⁴² The NICS(0), NICS(1), and especially the NICS(1)_{zz} and NICS(0)_{πzz}^{22d,e} values (−3.1, −4.9, −12.7 and −11.4 for C₅H₆, −3.8, −4.2, −12.3, and −19.9 for C₉H₁₀, respectively) clearly show the effects of CH₂ hyperconjugation of these planar ring systems. Frenking’s EDA data agree. On the basis of the rather small NICS(0) and NICS(1) values, we considered cyclopentadiene to be nonaromatic or only borderline aromatic earlier.²² We now revise this conclusion, as the larger, more refined NICS(1)_{zz} and NICS(0)_{πzz} C₅H₆ values (as well as those for C_{2v} C₉H₁₀) indicate appreciable aromaticity.

However, substituting the two CH₂ hydrogens by F atoms reverses the hyperconjugative effect; the electrons are drawn to the more electronegative F atoms inductively, and the CF₂ group acts as a π-electron acceptor. As a consequence, planar 7,7-difluorocycloheptatriene (C_{2v}) exhibits some aromatic character, as indicated by its NICS(1)_{zz} and NICS(0)_{πzz} values (−5.1 and −7.9, respectively) and the much lower boat (C_s) to planar (C_{2v}) inversion barrier (only 0.7 kcal/mol).

A planar cycloheptatriene derivative (**2**) has been characterized experimentally, e.g., by X-ray structure analysis, UV spectra, and ¹H NMR chemical shifts.¹³ In comparison with nonplanar cycloheptatrienes, the C–C bond lengths of the *cis*-hexatriene moiety of the planar ring alternate more (Δ*r* = 0.112 Å) and the UV spectrum is shifted substantially by ca. 60 nm to longer wavelengths.¹³ These data do not support the special homoaromatic effects in the planar cycloheptatriene ring system suggested by Doering.²

For comparison with the experimental findings, we optimized the parent system (**11**) of the *endo,exo*-dicarboxylic acid **2** (Scheme 4) in C_s symmetry (which imposes planarity on the cycloheptatriene moiety). Following a referee’s suggestion, we also computed **2** for direct comparison with the X-ray structure (Scheme 4, the optimized bond lengths are given in parentheses in comparison with the experimental data), but again there were no significant differences. Vibrational frequency analysis showed **11** to be a minimum at the B3LYP/6-311+G** level. The refined B3LYP/6-311+G** seven-membered ring geometry agrees only within about 0.03 Å with the X-ray data for **2** (the average estimated standard deviations of the bond lengths are reported, perhaps optimistically, to be only 0.003 Å). The C–C bond lengths in **11** alternate more than in **1**, but some are close to the Δ*r* = 0.117 Å of the parent C_{2v} form (**1a**). Indeed, **11** is nonaromatic or even antiaromatic, as indicated by the positive NICS(0) (4.5 ppm), NICS(1) (2.4 ppm), and NICS(1)_{zz} (10.3 ppm) values of the seven-membered ring. The same conclusion is drawn for **2** based on the B3LYP/6-311+G**-optimized structure, as indicated by NICS(0) (5.4 ppm), NICS(1) (2.0 and 2.2 ppm, respectively, at 1 Å above and below the ring center), and NICS(1)_{zz} (9.0 and 9.7 ppm) of the seven-membered ring.

(d) Cyclization from 1 to 3. The cyclization of cycloheptatriene to norcaradiene is one of the concerted disrotatory ring

closure reactions considered by Woodward and Hoffmann.⁴⁴ The parent 1,3,5-hexatriene to 1,3-cyclohexadiene cyclization has been investigated extensively.⁴⁵ The disrotatory transition structure is aromatic based on geometric (equalized bond lengths), energetic (large energy of concert), and magnetic (exalted magnetic susceptibility and magnetic susceptibility anisotropy as well as ¹H and Li⁺ chemical shifts) criteria. Hence, the cycloheptatriene to norcaradiene cyclization is expected to have an aromatic transition structure as well.

The C₁–C₆ separation (1.853 Å) in the disrotatory transition structure (**1-TS**) is shorter than that in the educt, **1** (2.443 Å). The other C–C bond lengths in **1-TS** are equalized substantially (b₃ – b₂ = –0.042 Å) at the B3LYP/6-311+G** level, where the **1-TS** imaginary frequency is 426i cm^{–1}, and the computed (**1** to **1-TS**) activation enthalpy, 10.3 kcal/mol (with the ZPE correction), agrees with the experimental value of ca. 11 kcal/mol.^{16c} Both are considerably lower than the 1,3,5-hexatriene to cyclohexadiene barrier (30.6 kcal/mol at B3LYP/6-311+G**//MP2(fc)/6-31G* + ZPE MP2(fc)/6-31G*).⁴⁵

The computed magnetic susceptibility of **1-TS** is 10.7 ppm cgs more negative than that of **1**. The NICS(0) (–12.9), NICS(1) (same side as CH₂, –9.2; opposite side, –12.4) and NICS(1)_{zz} (same side, –16.7; opposite side, –32.5) at the geometric center of the TS homobenzene moiety are much more negative than that of **1** (–4.2, –5.4, and –6.2, –9.3, and –13.6, respectively). The dissected NICS results (Table 3) also strengthen the conclusion that **1-TS** is aromatic. In addition, the diamagnetic C–C(π) contribution (–17.4 ppm) is much larger than that of homoaromatic **1** (–12.9 ppm) and is similar to the –17.7 ppm tropylium ion (**9**) value. Furthermore, the calculated ¹H chemical shift difference (4.3 ppm at GIAO-B3LYP/6-311+G**//B3LYP/6-311+G**) between the two methylene hydrogens in **1-TS** is larger than the corresponding values in **1**. Moreover, the π-contribution is chiefly responsible for the Δ^δ ¹H effect in **1-TS**. Thus, the cyclization of **1** to **3** indeed proceeds via an aromatic transition structure.^{16c}

According to the ACID analysis, the aromaticity of the transition state is like that of other typical pericyclic reactions (Figure 3). The 0.085 CIV indicates that the conjugation between C₁ and C₆ is even stronger than the π-conjugation in benzene. The lowest CIV in the cyclically electron delocalized transition state (0.068 between C1 and C2) compares well with the corresponding CIV (0.069) in the parent Diels–Alder reaction.

(e) Is Norcaradiene Aromatic? The effects of strained three-membered cyclopropane and related rings are unusual.^{46,47} Can an annulated cyclopropane ring function like a double bond in promoting cyclic electron delocalization? Available evidence supports this possibility. Norcaradiene has been suggested to be somewhat aromatic; a modest resonance energy of 5–8 kcal/mol has been deduced from experimental heats of hydrogenation.³⁵ Consistent with earlier theoretical results,^{10d} the ZPE-corrected B3LYP/6-311+G** energy favors **1** over **3** by 8.1 kcal/mol (the roughly approximated experimental value is 4 kcal/mol).^{16c} However, these differences are much less than the conventional ring strain energy of cyclopropane, 27 kcal/mol, which should destabilize **3** relative to **1**. The C₁–C₆ distance in norcaradiene (**3**), 1.572 Å at B3LYP/6-311+G**, is longer than normal C–C single bond lengths and substantially longer than the 1.51 Å length in cyclopropane.

Moreover, the ¹H chemical shift difference (2.4 ppm) between the two hydrogens of the norcaradiene methylene group is larger than the 1.3 ppm difference in **1**. Furthermore, the isotropic NICS(0) at the center of the six-membered ring of **3** (–3.5 at GIAO-B3LYP/6-311+G**//B3LYP/6-311+G**, –4.2 at IGLO/

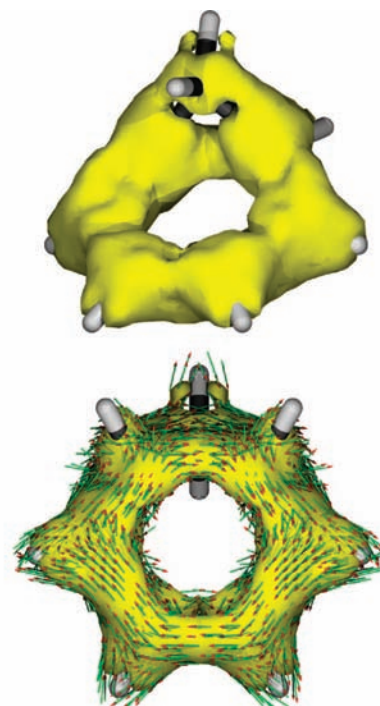
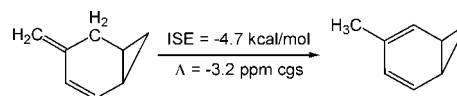


Figure 3. ACID plot of the transition state of the electrocyclic ring closure of cycloheptatriene to norcaradiene at an isosurface value of 0.050. Current density vectors plotted onto the ACID surface (bottom) indicate a diamagnetic ring current (clockwise). The vector of the magnetic field is orthogonal to the ring plane and points toward the viewer.

SCHEME 5



III//B3LYP/6-311+G**) indicates weak electron delocalization. However, dissected NICS analysis indicates that the –8.0 ppm diamagnetic contribution of the C–C(π) bonds to the total NICS of the six-membered ring of **3** is –2.3 ppm more negative than the value expected from C–C(π) additivity. The total NICS(0) value is reduced by the paratropic CC(σ) contributions in the six-membered ring.

The isomerization reaction (ISE, Scheme 5) was employed to evaluate the aromatic stabilization (ISE) and the diamagnetic susceptibility exaltation (Λ) of norcaradiene. The computed –4.7 kcal/mol ISE and –3.2 ppm cgs Λ of norcaradiene indicate less pronounced aromaticity than cycloheptatriene **1** (ISE = –9.8 kcal/mol and Λ = –9.5 ppm cgs).

According to ACID analysis, norcaradiene (**3**) is best described as a nonaromatic conjugated system comprised of largely localized components. The double bonds in the six-membered ring of **3** interact weakly with the Walsh orbitals of the cyclopropane ring (Figure 4). However, the double bond–cyclopropane conjugation in **3** (CIV = 0.066) is stronger than that in the parent vinylcyclopropane (CIV = 0.052) and is close to the conjugation of the two double bonds in butadiene (CIV = 0.068). The ACID plot shown in Figure 4 indicates that there is no pronounced ring current in the six-membered ring of norcaradiene (**3**), which resembles a “nonaromatic cyclohexatriene”. As expected,⁴⁸ the cyclopropane ring of **3** is σ-aromatic.

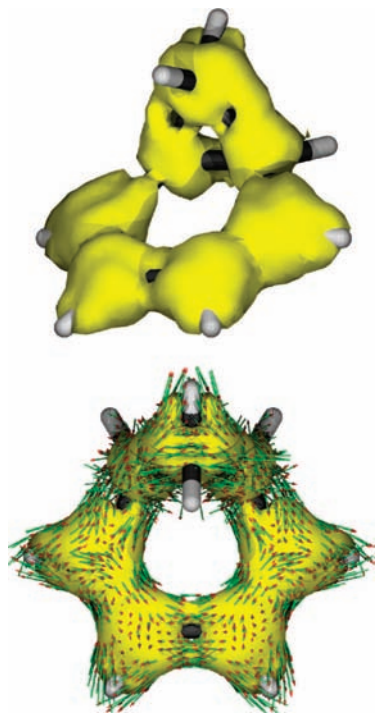


Figure 4. ACID plot of norcaradiene at an isosurface value of 0.050. Current density vectors plotted onto the ACID surface (bottom) indicate that there is no pronounced ring current. The vector of the magnetic field is orthogonal to the plane of the six-membered ring and points toward the viewer.

Conclusions

The geometric (small bond length alternation), energetic (stabilization), and magnetic (magnetic susceptibility exaltation, NICS, and ACID) criteria firmly establish the parent cycloheptatriene (**1**, C_7) to be the prototype neutral homoaromatic system. The homoaromaticity of equatorial monosubstituted cycloheptatrienes, 7-*X*-**1** ($X = \text{H}, \text{BH}_2, \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}, \text{CN}, \text{and CMe}_3$), evaluated by the same criteria, show only small ($\pm 10\%$) variations. The exceptional behavior reported by Childs et al., for the *tert*-butyl derivative is not substantiated, although its data lie at the bounds of the substituent ranges. Planar cycloheptatriene (**1**, C_{2v}), known experimentally in a strained system (**2**), actually is antiaromatic based on the same criteria of aromaticity. Akin to analogous acyclic pericyclic reactions, the transition structure for the cycloheptatriene to norcaradiene cyclization is highly aromatic. Norcaradiene is less aromatic than cycloheptatriene and cannot be considered to be a benzene analog. A cyclopropane ring does not function effectively as a double bond surrogate in a cyclically delocalized system. We support the view that cyclopropanes can extend, but not transmit, conjugation.⁴⁹

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Supporting Information Available: Full citation of ref 29 and the B3LYP/6-311+G**-optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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