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Consequences of Triplet Aromaticity in 4*n*π-Electron Annulenes: Calculation of Magnetic Shieldings for Open-Shell Species[**]

Valentin Gogonea, Paul von Ragué Schleyer[*], and Peter R. Schreiner

Dedicated to Professor Andrew Streitwieser on the occasion of his 70th birthday

This paper presents evidence that triplet states of 4*n*π-electron annulenes are aromatic[1] rather than antiaromatic. Not only the geometric and energetic, but also the magnetic properties of open-shell species, which are generally not accessible experimentally[2] but can be computed,[3] may be used to assess the aromaticity and antiaromaticity of a basic set of 4*n*π-electron annulene singlets and triplets: C_4H_4 (**1**), $C_5H_5^+$ (**2**), $C_6H_6^{2+}$ (**3**), $C_7H_7^-$ (**4**), C_8H_8 (**5**), and $C_9H_9^+$ (**6**).

According to simple Hückel MO theory, planar 4*n*π-electron annulenes in D_{nh} symmetry have degenerate ground states[4] and should be nonaromatic.[5] Breslow provided experimental evidence that the cyclopropenyl anion, **1**, **2**, and **4**[6] (or their derivatives) are destabilized and coined the "antiaromatic" designation.[6a] As early as 1959 Berthier and co-workers found that Pariser–Parr calculations favor the D_{7h} triplet as the ground state of **4**.[7] Borden[8] explained why **2**[9] and **4**[7] should have triplet ground states, whereas **1**[10] and **5**[11] favor singlet ground states and undergo Jahn–Teller distortion.

The idea that triplet 4*n*π-electron annulenes may be regarded as being aromatic rather than antiaromatic was suggested in 1972 by Baird, who concluded that the rules for aromaticity and antiaromaticity are exactly reversed in the lowest triplet state of annulenes.[1a] He pointed out that the proper way to evaluate the aromaticity or antiaromaticity of the lowest triplet state of a cyclic hydrocarbon is to define the aromatic stabilization energy (ASE) relative to the bonding energy for the lowest triplet state of the open-chain polyene which contains the same number of carbon atoms.[1a] The Dewar resonance energies of triplet D_{4h} cyclobutadiene (**1T**, 14.1 kcal mol^{-1}) and of triplet D_{8h} cyclooctatetraene (**5T**, 17.7 kcal mol^{-1}), calculated on this basis (NNDO semiempirical level), supported the aromaticity of these species.[1a] Other investigations support the aromaticity of triplet 4*n*π-electron annulenes.[1b–1h] We report here the first comprehensive high level ab initio calculations[12] of the adiabatic singlet/triplet separations (S → T), the ASEs, and the magnetic properties of the six neutral or charged 4*n*π-electron annulenes **1**–**6**.

The singlet/triplet separation energies (S → T, Table 1) for acyclic reference compounds butadiene and the pentadienyl cation $C_5H_7^+$ are much larger (57.0 and 47.1 kcal mol^{-1}, respectively) than for the cyclic species **1** (11.5 kcal mol^{-1}) and **2** (−7.6 kcal mol^{-1}). Consistent with triplet aromaticity, all triplet 4*n*π-electron annulenes are highly stabilized relative to the corresponding acyclic triplet reference species. The

Table 1. Singlet–triplet (S → T) adiabatic transitions for 4*n*π-electron annulenes calculated at B3LYP and CCSD(T) ab initio levels.[a]

Compound	Transition	B3LYP/ 6–311 + G(d,p)	CCSD(T)/cc-pVDZ// B3LYP/6–311 + G(d,p)
C_4H_4	**1S** → **1T**	5.9	11.5[b]
C_4H_6	S → T	54.2	57.0
$C_5H_5^+$	**2S** → **2T**	−10.5	−7.6
$C_5H_7^+$	S → T	44.1	47.1
$C_6H_6^{2+}$	**3S** → **3T**	−2.3	0.5
$C_7H_7^-$	**4S** → **4T**	−2.6	−1.0
C_8H_8	**5S** → **5T**[c]	15.5	24.3
$C_9H_9^+$	**6S** → **6T**[d]	−1.2	–

[a] In kcal mol^{-1}. [b] 11.2 (CCSDT) and 12.4 (MRCCSD(T))[10c]; 12.0 kcal mol^{-1} by flash photolysis of peralkylated cyclobutadiene (J. Wirz, A. Krebs, H. Schalstieg, H. Angliker, *Angew. Chem.* **1981**, *93*, 192; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 192). [c] Borden, Lineberger, and co-workers found experimentally a S → T separation of 12.1 kcal mol^{-1} for cyclooctatetraene ($D_{4h} \rightarrow D_{8h}$).[11a] The calculated [11b] and experimentally determined (J. F. M. Oth, *Pure Appl. Chem.* **1971**, *25*, 573) barrier for the ring inversion ($D_{2d} \rightarrow D_{4h} \rightarrow D_{2d}$) is around 13 kcal mol^{-1}. This gives a total S → T adiabatic transition ($D_{2d} \rightarrow D_{8h}$) of about 25 kcal mol^{-1}, which compares well with our result of 24.3 kcal mol^{-1} calculated at the coupled cluster level. [d] B3LYP/6–31G(d) geometries.

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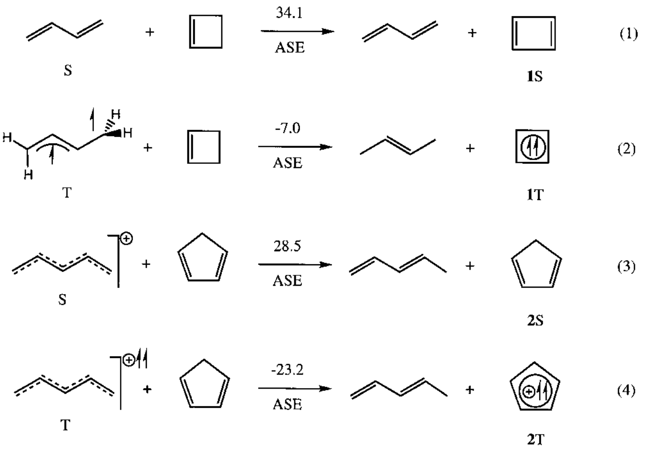
[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie (Liebig-Fellowship for P.R.S.), and the Alexander von Humboldt Stiftung (fellowship for V.G.). We also thank Prof. W. Kutzelnigg, Prof. P. Pulay, Prof. J. Michl, Dr. V. Malkin, and M. Mauksch for helpful comments. P.R.S. is grateful to Prof. A. de Meijere for his encouragement.

triplets **4T** and **6T** are even slightly more stable than the corresponding singlets **4S** and **6S** (Table 1). The ASEs computed at the CCSD(T)/cc-pVDZ level from isogyric equations of triplet cyclobutadiene ($-7.0\,\mathrm{kcal\,mol^{-1}}$) and $C_5H_5^+$ (-23.2 kcal/mol) confirm and extend Baird's proposal [Eqs. (2) and (4), Scheme 1].[1a] Species **1T** and **2T** are stabilized with respect to triplet acyclic reference molecules (triplet butadiene and the triplet pentadienyl cation). In contrast, Equations (1) and (3) show that the antiaromatic singlets **1S** and **2S** are destabilized with respect to singlet C_4H_6 and $C_5H_7^+$ (34.1 and $28.5\,\mathrm{kcal\,mol^{-1}}$, respectively). Thus, according to the energetic criteria of aromaticity, **1T** and **2T** are aromatic.[1f, 13]



Scheme 1. Aromatic stabilization energies [$\mathrm{kcal\,mol^{-1}}$] evaluated from isogyric equations at the CCSD(T)/cc-pVDZ level of theory.

The planar singlet $4n\pi$-electron annulenes **1S**[10] and **2S**[9b] are highly antiaromatic and show the largest alternations in bond length (0.244 and 0.228 Å, respectively; Figure 1). The differences in bond lengths of the nonplanar singlets are 0.070 (**3S**), 0.139 (**4S**), 0.132 (**5S**), and 0.125 Å (**6S**). In contrast, the triplet $4n\pi$-electron annulenes **1T**, **2T**, **4T**, and **5T** prefer D_{nh} symmetry and C–C bond lengths close to the 1.395 Å of benzene: 1.440 (**1T**), 1.424 (**2T**), 1.414 (**4T**), and 1.403 Å (**5T**). The planar D_{6h} and the nearly planar D_{3d} structures of the triplet benzene dication (**3T**) have almost the same energy. The C–C bond lengths in **3T** are all 1.427 Å. Like the Hückel-aromatic $C_9H_9^-$ anion,[14] triplet $C_9H_9^+$ (C_s, **6T**) has two minima. The less stable C_s form has one hydrogen atom pointing inwards. The more stable **6T** also is highly planarized (Figure 1, the C-C-C-C torsion angles range from 0 to 32°), and the bond lengths are all nearly equal (1.404–1.409 Å). (The planar Hückel D_{9h} $C_9H_9^-$ anion has a C–C distance of 1.404 Å at the same level.) The planar preference of triplet $C_7H_7^-$ (**4T**), C_8H_8 (**5T**), and the planarized geometry of triplet $C_9H_9^+$ (**6T**) are particularly noteworthy because of the considerable angle strain which must be overcome to adopt such structures. The average C-C-C bond angle in **6T** is 137° (close to the 140° bond angle in the D_{9h} $C_9H_9^-$ anion), whereas **6S** has an average C-C-C bond angle of 127°.

The singlets **4S**–**6S** and the parent hydrocarbons cycloheptatriene, cyclooctatetraene, and 1,3,5,7-nonatetraene are all strongly nonplanar with strongly alternating bond lengths.

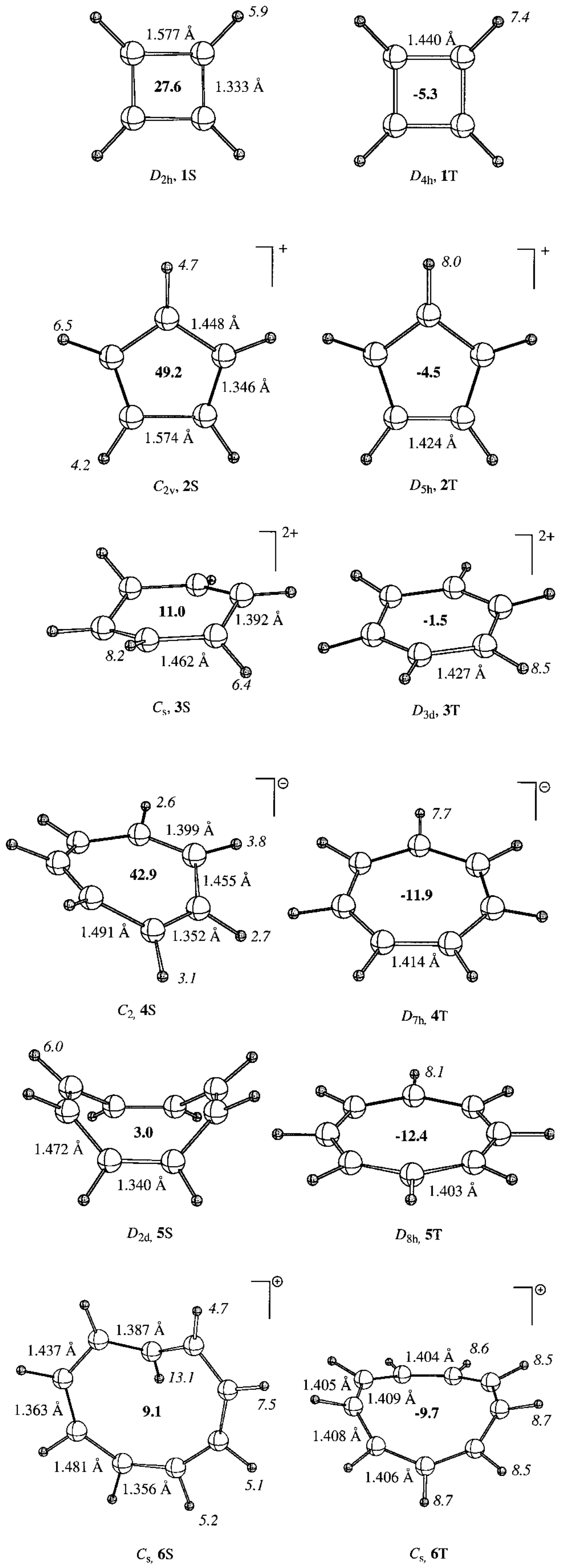


Figure 1. B3LYP/6–311 + G(d,p) geometries and ^1H NMR chemical shifts of singlet and triplet species. NICS values are given in the middle of the rings, and ^1H NMR chemical shifts in italics.

Hence, the corresponding triplet $4n\pi$-electron annulenes **4**T–**6**T clearly are aromatic according to the geometric criteria of aromaticity.[1f, 13]

The magnetic shieldings for open-shell species are generally not accessible by NMR measurements owing to line broadening,[2, 15] but they can be computed.[3] These open-shell calculations of magnetic properties[16] may be "unphysical",[16b] but they are instructive and useful for many purposes. We use them here as an "index" to compare the behavior of the triplet with the singlet states. Nuclear-independent chemical shifts (NICS)[17] and magnetic susceptibility exaltations (Λ;[18] Table 2, Figure 1) are positive for the singlets and negative for the triplets. Singlet $C_9H_9^+$ (**6**S) has a strongly nonplanar conformation and pronounced alternations in bond lengths, while triplet **6**T is clearly aromatic (NICS = – 9.7 ppm). Table 2 and Figure 1 show charge-corrected[19] ^{1}H NMR chemical shifts for the $4n\pi$-electron annulenes. The average ^{1}H NMR chemical shifts for the singlet species are in the olefinic range, but those for the triplets are downfield (Table 2).

The consequences of triplet aromaticity in $4n\pi$-electron annulenes **1**T–**6**T are the following: planarity or near planarity, equalization of bond lengths, low-energy triplet states (Table 1), appreciable aromatic stabilization energies (based on triplet reference states), negative nuclear-independent chemical shifts, downfield ^{1}H NMR chemical shifts, and, in the absence of the paramagnetic effects of unpaired electrons, significant diamagnetic susceptibility exaltations (Table 2). The stability of the triplet cyclononatetraenyl cation (**6**T), which is remarkable in view of the high degree of angle strain, extends Borden's generalization[5, 8] to nonplanar annulenes that do not have degenerate SOMOs.[20]

Table 2. Nucleus-independent chemical shifts (NICS), magnetic susceptibilities, and magnetic susceptibility exaltations (Λ) for singlet and triplet species calculated at the GIAO-SCF level.[a]

Compound		Point group	Electronic state	$\delta(^1H)$[b, c]	NICS[c]	Magnetic suscept.[c]	Λ[c]
C_4H_4	**1**S	D_{2h}	$^1A_{1g}$	5.9	27.6	– 7.7	12.5[d]
	1T	D_{4h}	$^3A_{2g}$	7.4	– 5.3	– 22.8	– 3.5[e]
$C_5H_5^+$	**2**S	C_{2v}	$^1A_1$	5.2	49.2	4.8	30.5[f]
	2T	D_{5h}	$^3A_1'$	8.0	– 4.5	– 28.4	– 3.3[g]
$C_6H_6^{2+}$	**3**S	C_s	$^1A'$	7.0	11.0	– 13.7	
	3T	D_{3d}	^3B_g	8.5	– 1.5	– 28.2	
$C_7H_7^-$	**4**S	C_2	^1A	3.1	42.9	24.7	
	4T	D_{7h}	$^3A_1'$	7.7	– 11.9	– 64.5	
C_8H_8	**5**S	D_{2d}	$^1A_1$	6.0	3.0	– 46.2	
	5T	D_{8h}	$^3A_{2u}$	8.1	– 12.4	– 81.6	
TS[h]		D_{4h}	$^1A_{1g}$	3.1	30.1	4.1	60.4[i, j]
$C_9H_9^+$	**6**S	C_s	$^1A'$	1.0	9.1		
	6T[k]	C_s	$^3A'$	8.6	– 9.7		
C_5H_5 radical		C_{2v}	$^2A_1$	6.5	2.6	– 30.6	
benzene		D_{6h}	$^1A_{1g}$	7.8	– 9.7[i]	– 51.3	– 13.4[i, j]

[a] B3LYP/6–311 + G(d,p) geometries. [b] Average value for species with nonequivalent protons. The ^{1}H NMR chemical shifts for charged species were corrected based on Haddon's suggestion that one unit of electrostatic charge on the carbon atom which binds the proton produces a change of 10 ppm in the ^{1}H NMR chemical shift (R. C. Haddon, V. R. Haddon, L. M. Jackman, *Top. Curr. Chem.* **1971**, *16*, 103). The charge on the carbon atom was calculated as the sum of the natural charges on the connected carbon and hydrogen atoms. [c] HF/6–31 + G*. [d] Equation (1). [e] Equation (2). [f] Equation (3). [g] Equation (4). [h] Planar transition state with alternations in bond lengths. [i] GIAO-SCF/6–31 + G(d).[17] [j] Calculated from increments.[17] [k] The B3LYP/6–31G(d) potential energy surface of **6**T is quite flat.

Received: June 20, 1997
Revised version: December 15, 1997 [Z10567IE]
German version: *Angew. Chem.* **1998**, *110*, 2045–2049

Keywords: ab initio calculations · aromaticity · excited states · magnetic properties

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Metal–Ligand versus Metal–Metal Redox Chemistry: Thallium(I)-Induced Synthesis of 4,9-Diaminoperylenequinone-3,10-diimine Derivatives**

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Ina Rüdenauer, Lutz H. Gade,* Ian J. Scowen, and
Mary McPartlin

While the structural chemistry of thallium(I) amides and related molecular compounds in the solid state is characterized by supramolecular forms of aggregation defined by weakly attractive metal–metal contacts,[1–3] redox disproportionations of the monovalent metal complexes of thallium and indium dominate their reactivity in solution.[4] These may either lead to the mixed-valent $M^{I}M^{II}$ and $M^{I}M^{III}$ compounds ($M = In, Tl$) or, alternatively, generate the products of partial or complete thermal demetalation. In the latter case the corresponding amines are formed probably via nitrogen radical intermediates.

It was our aim to study the demetalation more closely and use it preparatively for the specific coupling of the transient intermediates generated by the demetalation. We thus set out to investigate the thallium(I) and indium(I) amide chemistry of such ligands which upon thermal demetalation would give intermediates of greater stability and lifetime. Instead of immediately abstracting hydrogen atoms from the solvent, they could undergo C–C coupling and related reactions. To this end we chose a bidentate amido ligand derived from 1,8-diaminonaphthalene which, given the known redoxchemistry of arylamines,[5] offered the opportunity of directing the chemically induced redox conversions into pathways other than simple demetalations.

As starting material we selected 1,8-bis(trimethylsilylamino)naphthalene (**1**), which was readily converted into the lithium amide $[Li_2\{C_{10}H_6(NSiMe_3)_2\}(thf)_4]$ (**2**).[6] The attempted metal exchange of **2** with InCl in THF led to an immediate redox disproportionation of the monovalent In^{I} compound and the generation of the dinuclear In^{II}–In^{II} complex $[In\{C_{10}H_6(NSiMe_3)_2\}(thf)]_2$ (**3**; Scheme 1, Table 1). Its formulation was established by elemental analysis and the NMR spectra, while a single-crystal X-ray structure analysis[7] of the bright yellow compound confirmed the presence of a metal–metal bond (Figure 1). The In–In distance of 2.7237(6) Å is the shortest established for a diindane to date.[4c, 8] The midpoint of the In–In vector lies on a crystallographic center

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[**] This work was funded by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Engineering and Physical Science Research Council, the Deutscher Akademischer Austauschdienst, and the British Council (ARC grant to L.H.G. and M.McP.). We thank Professor Werner for his support.