

Aromaticity and Antiaromaticity in Oligocyclic Annelated Five-Membered Ring Systems

Tosja K. Zywietz,^{†,‡} Haijun Jiao,[‡] Paul v. R. Schleyer,^{*,‡} and Armin de Meijere^{*,†}

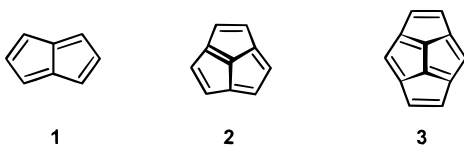
Institut für Organische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany, and Computer-Chemistry-Center, Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, 91054-Erlangen, Germany

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The aromaticity and antiaromaticity of oligocyclic annelated five-membered ring systems, pentalene (**1**), acepentalene (**2**), dicyclopenta[*cd,gh*]pentalene (**3**), and related compounds, have been evaluated computationally using density functional theory (B3LYP/6-31G*). The nucleus-independent chemical shifts (NICS) and magnetic susceptibility exaltations (Λ) of these unusual cross-conjugated π systems indicate **1** and **2** with 8 and 10 π electrons, respectively, to be antiaromatic. In contrast, **3**, with 12 π electrons, is aromatic. Although the rings are not identical, **3** has a more delocalized electronic structure than **1** and **2**. The dianions of **1–3** have delocalized structures and are aromatic. The magnetic criteria show the dications of **1** and **2** to be aromatic but the dication of **3** to be antiaromatic. The fused ring systems **2** and **3** are nonplanar. The calculated inversion barriers of acepentalene (**2**) and its free dianion **2**²⁻ are 7.1 and 5.4 kcal/mol, respectively.

Introduction

The annelated five-membered ring systems pentalene (**1**), acepentalene (**2**), dicyclopenta[*cd,gh*]pentalene (**3**), and their doubly charged systems have been studied experimentally¹ and theoretically^{2,3} for more than three decades. While experimentalists were attracted by the very unusual structures as challenging targets for synthesis, theoreticians focused on the correlation among the electronic structures, the stabilities, and the reactivities in relationship to the aromatic or antiaromatic character of these species.



Pentalene (**1**), a highly reactive species requiring substituents for stabilization, has only been observed

spectroscopically upon matrix isolation at $-196\text{ }^{\circ}\text{C}$.⁴ In contrast, the stable pentalene dianion (**1**²⁻) was synthesized in 1964 by Katz et al.⁵ The X-ray crystal structure of the dilithium salt (**2**[Li₂L₂, L = dimethoxyethane]), reported by Schleyer et al.⁶ in 1991, revealed that the nearly planar carbon skeleton has a delocalized C–C perimeter and lithium cations coordinated to five-membered ring faces at opposite sides. The localized electronic structure of pentalene was shown by the X-ray analysis of 1,3,5-tri-*tert*-butylpentalene and 1,3-di-*tert*-butyl-4,5-bis(methoxycarbonyl)pentalene.⁷ According to the Hückel ($4n + 2$) π -electron rule (extended to bicyclic systems), **1** with 8 π electrons is expected to be antiaromatic, whereas the dianion (**1**²⁻, 10 π electrons) and the dication (**1**²⁺, 6 π electrons) should be aromatic.

The existence of the highly strained acepentalene (**2**) with 10 π electrons has been demonstrated only recently by neutralization–reionization mass spectrometry (NRMS).⁸ HMO theory predicts the D_{3h} symmetric neutral **2** to have a triplet diradical ground state.^{2a} However, density functional theory (B3LYP/6-31G*) finds the symmetry of the singlet ground state of **2S** (C_s) to be lower than that (C_{3v}) of the triplet state (**2T**); the computed singlet and triplet splitting is only 2.5 kcal/mol.⁸ In contrast, acepentalene dianion (**2**²⁻) salts are quite stable and are prepared easily by treatment of triquinacene with a superbasic mixture.⁹ The upfield ⁷Li

* To whom correspondence should be addressed. (A.d.M.) E-mail: amejjer1@uni-goettingen.de.

[†] Georg-August-Universität Göttingen.

[‡] Universität Erlangen-Nürnberg.

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NMR chemical shift of -8.2 ppm in solution (-4.9 and -9.8 ppm in the solid state, where rapid exchange does not take place) indicate pronounced diamagnetic ring current effects for this 12 π -electron dianion, and the X-ray structure analysis reveals a curved molecular surface.⁹

Attempts to generate dicyclopenta[*cd,gh*]pentalene (**3**) have not been successful, although several substituted and unsubstituted derivatives with fewer double bonds have been synthesized.^{1g} Previous computational investigations, based on the HMO method (assuming planar geometries), on the MNDO approximation, and on low-level ab initio calculations, have clearly failed to describe the electronic and magnetic properties of the polyunsaturated annelated five-membered ring systems.³ According to ring current criteria, Jung^{3a} predicted **3** to be aromatic, but Binsch and Nakajima proposed **3** to be antiaromatic.^{3b,c} On the basis of his ring current index (RCI), Jug¹⁰ claimed that **3** should be even more antiaromatic than **1**.

In this paper, we present adequately high-level computations on the geometries, the energetics, and the magnetic properties of pentalene (**1**), acepentalene (**2**), and dicyclopenta[*cd,gh*]pentalene (**3**) as well as their doubly charged derivatives and some related compounds.

Computational Methods

Geometry optimizations and frequency calculations were carried out at the B3LYP/6-31G* density functional level using the Gaussian 94 program.¹¹ Single-point energies were computed at B3LYP/6-311+G* with the B3LYP/6-31G* geometries. All relative energies discussed are calculated at B3LYP/6-311+G*//B3LYP/6-31G* + ZPE (B3LYP/6-31G*, scaled by 0.96¹²). Magnetic susceptibilities were computed uniformly using Kutzelnigg's IGLO¹³ (individual gauge for localized orbitals) method with the DZ basis set. The nucleus-independent chemical shifts (NICS)^{14,15} at the points of interest were calculated at GIAO-SCF/6-31+G* with B3LYP/6-31G* geometries using the Gaussian 94 program. The computed total energies, zero-point energies, and numbers of imaginary frequencies (NIMAG) are summarized in Table 1.

Results and Discussion

Pentalene (1). The B3LYP/6-31G* geometries of the singlet (**1S**) and triplet (**1T**) pentalene are shown in Figure 1. Both **1S** and **1T** are energy minima at the B3LYP/6-31G* level, and **1T** is only 7.7 kcal/mol higher in energy than **1S**. The double-bond isomerization bar-

Table 1. Computed Total Energies (E_{tot} , au), Zero-Point Energies (ZPE, kcal/mol), and Numbers of Imaginary Frequencies (NIMAG)

	E_{tot}^a	ZPE (NIMAG) ^a	E_{tot}^b
1S (C_8H_6 , C_{2h})	-308.369 28	67.3 (0)	-308.436 45
1TS (C_8H_6 , D_{2h})	-308.357 83	65.7 (1)	-308.425 67
1T (C_8H_6 , D_{2h})	-308.356 24	66.3 (0)	-308.422 64
1²⁻ ($C_8H_6^{2-}$, D_{2h})	-308.209 86	61.5 (80)	-308.340 99
1²⁺ ($C_8H_6^{2+}$, D_{2h})	-307.634 12	67.3 (0)	-307.687 30
1Li₂ ($C_8H_6Li_2$, C_{2h})	-323.534 38	69.7 (0)	
2S ($C_{10}H_6$, C_s)	-384.490 71	74.1 (0)	-384.574 48
2TS ($C_{10}H_6$, C_{2v})	-384.480 99	73.9 (1)	-384.562 79
2T ($C_{10}H_6$, C_{3v})	-384.486 12	73.4 (0)	-384.569 43
2²⁻ ($C_{10}H_6^{2-}$, C_{3v})	-384.390 36	69.4 (0)	-384.533 53
2TS²⁻ ($C_{10}H_6^{2-}$, D_{3h})	-384.385 35	69.4 (1)	-384.524 97
2²⁺ ($C_{10}H_6^{2+}$, C_{3v})	-383.761 38	73.8 (0)	-383.829 66
2⁻ ($C_{10}H_6^{+}$, C_s)	-384.533 35	71.4 (0)	-384.638 73
2⁺ ($C_{10}H_6^{+}$, C_s)	-384.230 78	73.6 (0)	-384.303 54
4⁻ ($C_9H_6N^{+}$, C_{3v})	-401.264 46	73.4 (0)	-401.371 84
5⁺ ($C_9H_6B^{+}$, C_{3v})	-370.923 30	72.3 (0)	-370.994 44
2Li₂	-399.681 22	76.6 (0)	-399.768 94
2Li₂-TS1 ($C_{10}H_6Li_2$, C_s)	-399.663 92	76.0 (0)	-399.752 91
2Li₂-TS2 ($C_{10}H_6Li_2$, C_{2v})	-399.660 97	76.3 (0)	-399.752 81
2[Li(H₂O)]₂	-552.581 33	(0) ^c	
3S ($C_{12}H_6$, C_s)	-460.633 11	83.7 (0)	-460.732 27
3T ($C_{12}H_6$, C_s)	-460.622 92	82.8 (0)	-460.722 41
3²⁺ ($C_{12}H_6^{2+}$, C_1)	-459.923 52	80.6 (0)	
3²⁻ ($C_{12}H_6^{2-}$, C_{2v})	-460.536 33	77.5 (0)	

^a At B3LYP/6-31G*. ^b At B3LYP/6-311+G*//B3LYP/6-31G*. ^c At HF/6-31G*.

rier of **1S** through a D_{2h} transition state (**1TS**), 5.2 kcal/mol, is close to the experimental value of 3.8 kcal/mol for 1,3,5-tri-*tert*-butylpentalene.¹⁶

At B3LYP/6-31G*, the pentalene dianion (**1²⁻**) has a completely delocalized D_{2h} geometry; the computed bond lengths both for the free dianion and for the dilithium salt (**1Li₂**) agree well with the X-ray values for the dilithium complex.⁶ Note that the dianion carbon skeleton is hardly affected by the counterions. Like the dianion, the pentalene dication (**1²⁺**) also has a delocalized D_{2h} structure, although its bond length alternation (0.049 Å) is larger than that (0.014 Å) of the dianion (Figure 1).

Acepentalene (2). As discussed in the Introduction, the singlet acepentalene (**2S**) has a C_s ground state, but the C_{3v} triplet structure **2T** is only 2.5 kcal/mol higher in energy.⁸ As shown in Figure 2, the geometry of **2S** is localized whereas **2T** is delocalized. The central carbon environment is less pyramidal in **2S** ($\Sigma\text{CCC}'s = 340.5^\circ$) than in **2T** ($\Sigma\text{CCC}'s = 332.4^\circ$). The C_{2v} transition state **2TS** for the ring inversion of **2S** corresponds to a computed barrier of 7.1 kcal/mol. As expected, the radical anion (**2⁻**) and radical cation (**2⁺**) have C_s symmetry. The calculated adiabatic electron affinity (EA) of 1.87 eV for **2S** is close to the experimental value of 1.5 eV estimated from a neutralization-reionization mass spectrometric measurement. At the same level, the adiabatic ionization energy (IE) of **2S**, not yet determined experimentally, is computed to be 7.35 eV.

At B3LYP/6-31G*, the dianion (**2²⁻**) is an energy minimum with a C_{3v} delocalized structure. The central carbon in **2²⁻** is slightly pyramidal as shown by the sum (350°) of the three CCC angles. The inversion barrier through a D_{3h} transition state **2TS²⁻** is only 5.4 kcal/mol.

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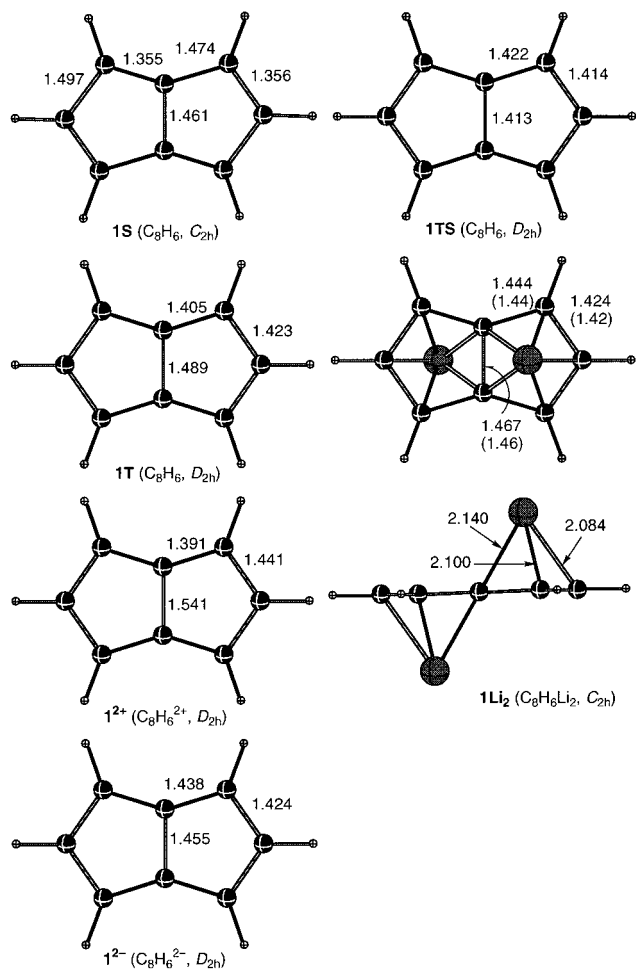


Figure 1. B3LYP/6-31G* bond lengths (Å) for pentalene 1 and related systems.

The experimental ^7Li (one signal), ^1H (one signal), and ^{13}C (three signals) NMR spectra (down to $-110\text{ }^\circ\text{C}$) indicate that the acepentalene dianion (2Li_2) should have at least 3-fold symmetry. In addition, some process, such as fluctuational ring inversion, leads to the equivalence of the ^7Li chemical shifts. Neither the stable monomer of 2Li_2 nor a dimer–monomer equilibrium explain this behavior.⁹ We also optimized dilithium acepentalenediide (2Li_2) in which one of the lithium coordinates to one of the five-membered rings on the outside of the bowl; the second lithium on the concave face of the molecule coordinates formally to two of the five-membered rings. In the X-ray structure, both lithium cations coordinate to individual five-membered rings due to the further coordination with the solvent (dimethoxyethane). Indeed, this is shown by our model systems $2[\text{Li}(\text{H}_2\text{O})]_2$ in which H_2O was used as solvent. Due also to the solvents, the Li–C distances in 2Li_2 are shorter than those in $2[\text{Li}(\text{H}_2\text{O})]_2$. The X-ray structure analysis and optimized structures show that the parameters of the carbon skeleton of the dianion are affected but little by the gegenion complexation; the optimized bond lengths agree well with the experimental values.

Why is only one single lithium chemical shift observed experimentally in solution? At B3LYP/6-31G*, the D_{3h} 2Li_2 with two imaginary frequencies is not an authentic transition state. At the same level, there is a C_s transition state 2LiTS1 with a nonplanar carbon skeleton. The lithium cation on the outer side of the convex side moves

from one five-membered ring face to another, and the second lithium cation in the concave region moves in another direction in a concerted and synchronous mode (Figure 3). The computed barrier for this lithium migration is 9.5 kcal/mol. However, this mechanism does not exchange the Li's and explain the single lithium chemical shift of 2Li_2 in solution.

A C_{2v} transition state (2LiTS2) has a planar carbon skeleton and only one imaginary frequency. This accounts not only for the ring inversion but also for the interchange of the two lithium cations (Figure 3). This mechanism can explain the observed single lithium chemical shift in solution. Moreover, the calculated barrier of 9.8 kcal/mol is almost the same as for the lithium migration (via 2LiTS1) but is larger than that of the free dianion ring inversion of 5.4 kcal/mol. On the basis of these calculated results and on the experimental observation, the ring inversion barrier for 2Li_2 in solution should be larger than for the free dianion but smaller than the 2Li_2 result due to the coordination of lithium cation with solvents.

In contrast to the stable dianion, no experimental observation of the dication (2^{2+}) has been reported. The dication also has C_{3v} symmetry and a delocalized structure. However, the central carbon environment is highly pyramidal ($\Sigma\text{CCC} = 315.2^\circ$). In addition, we also have computed the species isoelectronic with 2^{2-} and 2^{2+} , e.g., the azaacepentalene anion (4^- , 12 π electrons) and boraacepentalene cation (5^+ , 8 π electrons). Note that an azatriquinane, which has the azaacepentalene skeleton and might be an excellent precursor for both azaacepentalene and the corresponding monoanion 4^- , has been synthesized by Mascal et al.¹⁷ Both 4^- and 5^+ have C_{3v} symmetry and delocalized structures, while 4^- is nearly planar (central ΣCNC angle of 357.3°) and 5^+ is pyramidal (central ΣCBC angle of 284.4°).



Dicyclopenta[cd,gh]pentalene (3). In contrast to 1 and 2, 3 is still unknown experimentally despite the theoretical investigations by Jung,^{3a} Binsch, and Nakajima.^{3b,c} At B3LYP/6-31G*, the singlet ground state of dicyclopenta[cd,gh]pentalene (3S) has C_s symmetry. The perimeter lengths are 1.393–1.494 Å; only the central C=C double bond has a typical (1.337 Å) value. The triplet state 3T has also C_s symmetry and a delocalized structure. The computed singlet–triplet splitting for 3 of 5.3 kcal/mol is smaller than that for 1 (7.7 kcal/mol) but larger than that for 2 (2.5 kcal/mol).

As for 1 and 2, we have computed the dianion (3^{2-}) and dication (3^{2+}) of dicyclopenta[cd,gh]pentalene to aid experimental investigations. As expected, 3^{2-} has C_{2v} symmetry and only small bond alternations. In contrast, the 3^{2+} is unsymmetrical (C_i) and has a less delocalized structure (Figure 4).

Aromaticity and Antiaromaticity

The defining characteristic of an aromatic species is the ability to sustain a diatropic ring current. Cyclic

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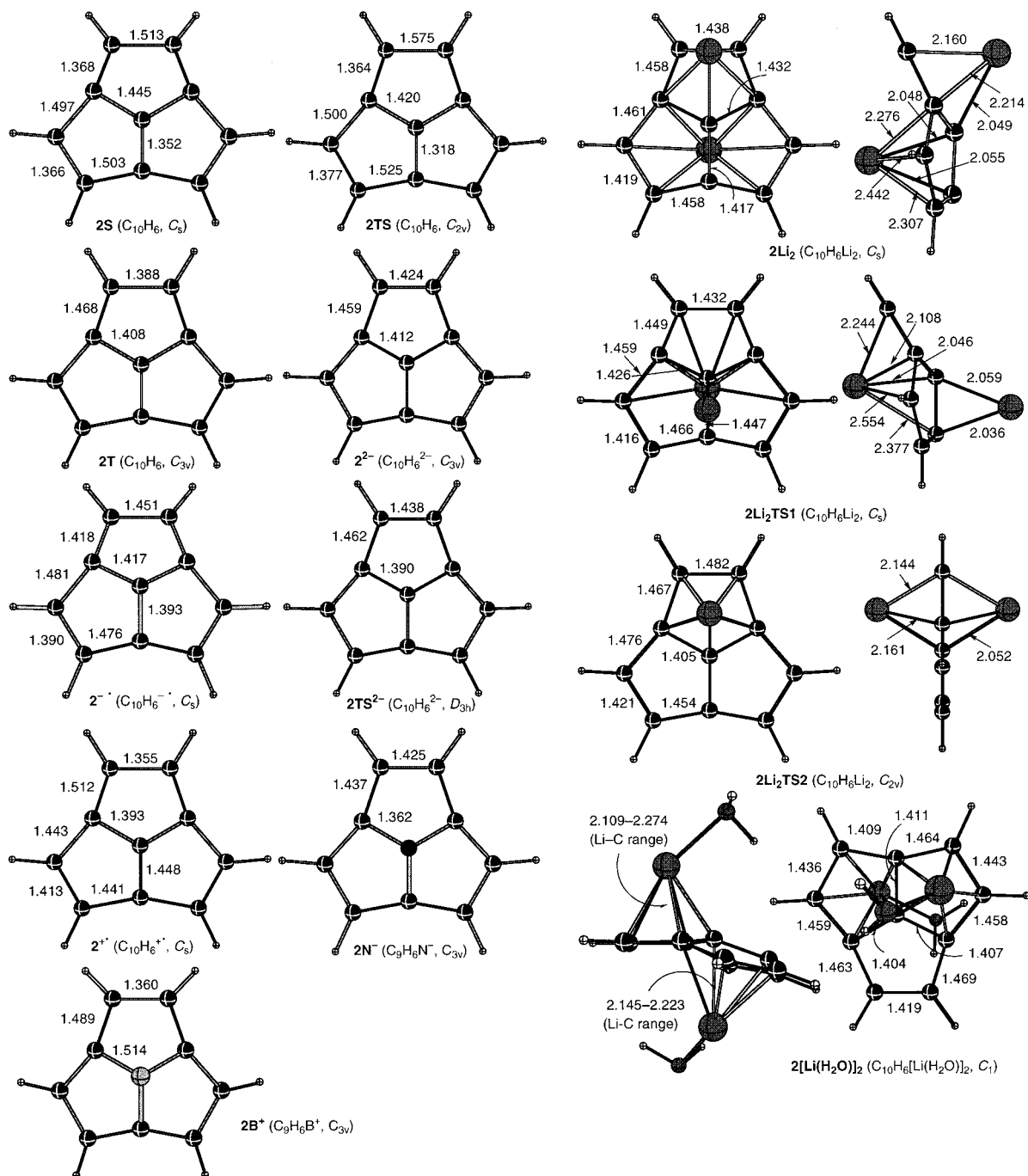


Figure 2. B3LYP/6-31G* bond lengths (Å) for acepentalene **2** and related systems.

electron delocalization results in enhanced special chemical geometrical and magnetic properties.¹⁸ Recently, Schleyer et al.¹⁴ proposed the use of the negative of the computed magnetic shieldings at the ring center, referred to “nucleus-independent chemical shifts” (NICS), as a simple and effective criterion for aromaticity. NICS, as an indicator of aromaticity, agrees well with the energetic, geometric, and magnetic criteria and does not require increment systems for other references. NICS also is an effective probe of the individual rings in polycyclic systems.¹⁵ However, NICS values computed

in the ring centers of first-row compounds are reduced due to the local paramagnetic contributions of the σ bonds.¹⁹ Hence, the NICS values at points 0.5 Å over the ring centers are discussed here, but the NICS values at the ring center are given in parentheses for comparison. The sums of various individual NICS values are given in Table 2.

While NICS is useful for individual rings, we have calculated the magnetic susceptibility exaltation (Λ , a property directly associated with aromaticity) to assess

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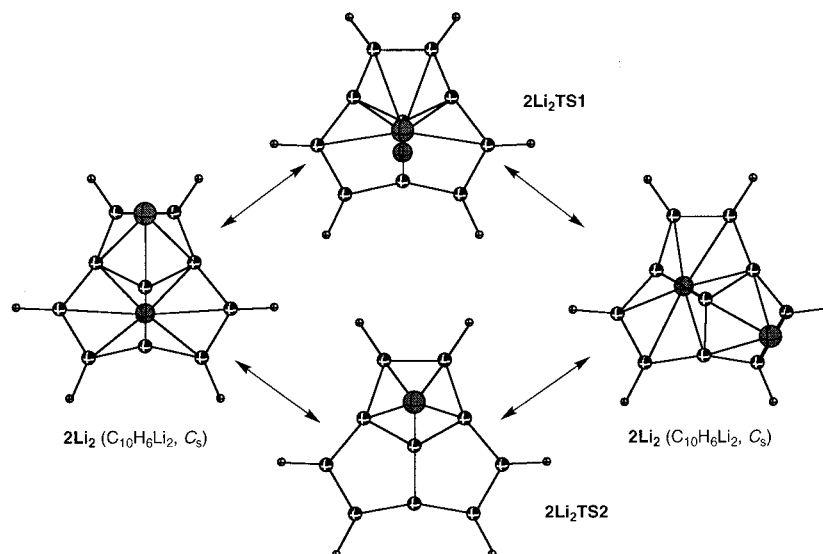


Figure 3. Schematic presentation of the mechanisms of the lithium cation immigration and ring inversion in dilithium acpentalenediide ($2Li_2$).

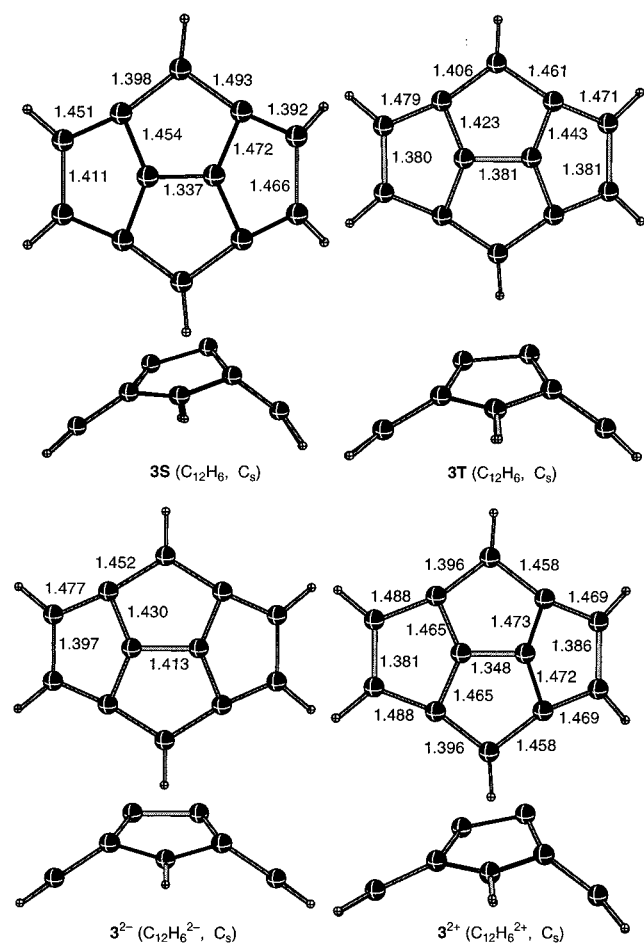


Figure 4. B3LYP/6-31G* bond lengths (Å) for dicyclopenta-[*cd,gh*]pentalene **3** and related systems.

the aromaticity of these polycyclic systems as a whole. Normally, Λ is the difference between the bulk magnetic susceptibility (χ_M) of a compound and the susceptibility (χ_M) estimated from an additivity scheme of group increments for the same structure without cyclic delocalization ($\Lambda = \chi_M - \chi_M$).^{20,21} Due to ring current effects, aromatic systems show diamagnetic susceptibility

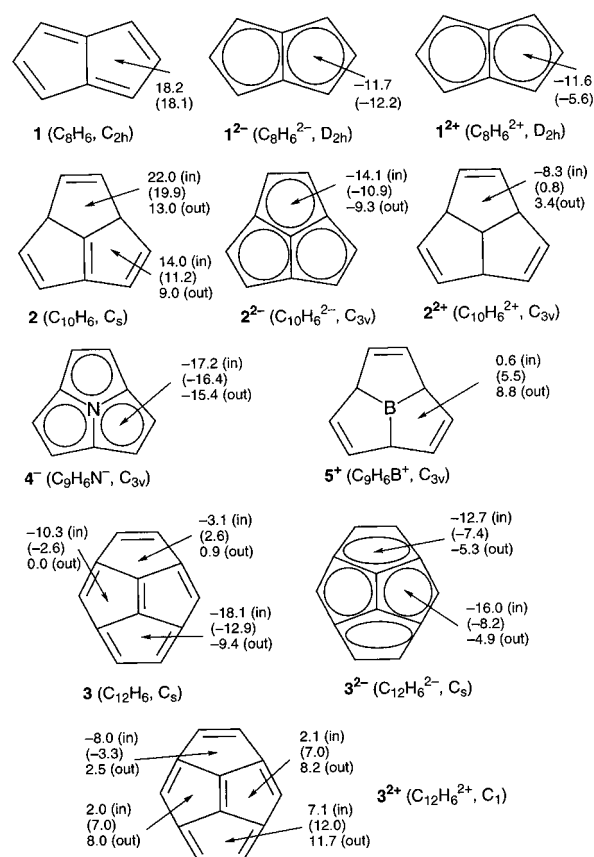


Figure 5. GIAO-SCF/6-31+G**/B3LYP/6-31G* computed NICS values for **1–3** and related systems. NICS(in) and NICS(out) are NICS values calculated at points 0.5 Å in and out of the bowl, and NICS values at the individual ring center are given in parentheses for comparison.

exaltations (more negative values of χ_M than those from the group increment additivity), and antiaromatic compounds have positive Λ values.

In agreement with the Hückel rule, pentalene (**1**) with eight π electrons is antiaromatic as indicated by NICS (+18.1 ppm) and the paramagnetic exalted susceptibility ($\Lambda = 17.1$ ppm cgs). On the other hand, the correspond-

Table 2. IGLO/DZ Calculated Magnetic Susceptibilities (χ_{tot} , ppm cgs) and Magnetic Susceptibility Exaltations (Λ , ppm cgs)^{a,b} as Well as Sum of Various NICS Values

	χ_{tot}	Λ	$\Sigma\text{NICS(in)}$	$\Sigma\text{NICS(out)}$	ΣNICS
1S	-54.0	17.7	36.4	36.4	36.2
1²⁻	-117.6	-33.5	-23.4	-23.4	-24.4
1²⁺	-80.6	-40.3	-23.2	-23.2	-11.2
2S	-62.4	23.1	50.0	31.0	42.3
2²⁻	-141.0	-43.1	-42.3	-27.9	-32.7
2²⁺	-72.9	-18.8	-24.9	2.4	10.2
4⁻	-144.9	-53.8	-51.6	-49.2	-46.2
5⁺	-50.7	15.0	1.8	16.5	26.8
3S	-119.1	-19.8	-41.8	-8.5	-15.5
3²⁻	-147.5	-34.0	-57.4	-31.2	-20.4
3²⁺	-54.0	13.9	3.1	22.7	30.4

^a Deduced from the increment values, e.g., *cis*-CH=CH⁻ (-19.3) from *cis*-2-butene (-54.9)-ethane (-35.6); >C=C< (-13.8) from 2,3-dimethyl-2-butene (-85.4)-2 × ethane; >CH⁺ (4.0) from 2-propyl cation (-31.6)-ethane; >CH⁻ (-13.1) from 2-propyl anion (-66.5)-ethane; >N⁻ from trimethylamine (-59.7)-3 × methyl; >B⁻ from trimethylborane (-56.2)-3 × methyl. ^b For uniformity, the charges of the dianion and dication are formally localized at the >C= centers.

ing dianion (**1²⁻**, NICS = -12.2 and Λ = -33.5 ppm cgs) and dication (**1²⁺**, NICS = -11.6 and Λ = -40.3 ppm cgs) are aromatic (Table 2).

Due to the nonplanarity of the acepentalene systems, we have computed additional sets of NICS points for the individual rings 0.5 Å away from the ring centers. These points on the convex side are designated NICS(in) and those on the concave face NICS(out). The two types of five-membered rings of acepentalene (**2**) are both antiaromatic, and NICS(in) is larger than NICS(out). The antiaromaticity of acepentalene is also indicated by the paramagnetic exaltation of 23.1 ppm cgs.

Consistent with the experimental behavior, the acepentalene dianion (**2²⁻**) is highly aromatic. This is not only indicated by the Λ (-43.1 ppm cgs) but also by the NICS values, e.g., NICS(in) = -14.1 and NICS(out) = -9.3. This 4.8 ppm difference between NICS(in) and NICS(out) also is reflected by the solid-state NMR chemical shifts of the two Li⁺ cations (-4.9 vs -9.8) on

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(21) (a) Sulzbach, H. M.; Schleyer, P. v. R.; Jiao, H.; Xie, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 1367. (b) Schleyer, P. v. R.; Jiao, H.; Sulzbach, M. H.; Schaefer, H. F., III. *Ibid.* **1996**, *118*, 2093. (c) Jiao, H.; v. E. Hommes, N. J. R.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1996**, *61*, 2826.

the two faces. In contrast, the aromaticity of the acepentalene dication (**2²⁺**) is strongly reduced as shown by the Λ (-18.8 ppm cgs), the NICS(in) of -8.3 ppm, and NICS(out) of 3.4. These NICS data show that both aromatic (or antiaromatic) ring current effects are higher inside the bowl than outside.

The azaacepentalene anion (**4⁻**), isoelectronic to **2²⁻**, has more negative NICS values (-17.2 and -15.4) than **2²⁻**, and the former is more aromatic than the latter. However, the positive NICS values of the boraacepentalene (**5⁺**), isoelectronic to **2²⁺**, indicate some antiaromatic character.

We agree with Jung^{3a} but not with Binsch and Nakajima^{3b,c} or with Jug¹⁰ our NICS and Λ (-19.8) values show that dicyclopenta[*cd,gh*]pentalene (**3**) is aromatic. The *C*_{3v} dianion (**3²⁻**) with negative NICS values and Λ (-34.0) is highly aromatic. In contrast, the dication (**3²⁺**) has positive NICS values and according to its Λ (13.9) is antiaromatic.

Conclusions

High-level DFT computations (B3LYP/6-311+G*) show that neutral pentalene, acepentalene, and dicyclopenta[*cd,gh*]pentalene, as compared with their triplet states, have singlet ground states. In contrast to the antiaromatic pentalene and acepentalene, which have localized electronic structures and positive NICS and Λ values, dicyclopenta[*cd,gh*]pentalene is aromatic with a delocalized structure and negative NICS and Λ values. The dianions of these three molecules and azaacepentalene anion are highly aromatic species as indicated not only by their delocalized structures but also by the negative NICS and Λ values. On the other hand, pentalene and acepentalene dications are aromatic and dicyclopenta[*cd,gh*]pentalene dication is antiaromatic. The triplet states have delocalized structures.

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Supporting Information Available: 6-31G* data for compounds **1–3** (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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