

# Magnetic Evidence for the Aromaticity and Antiaromaticity of Charged Fluorenyl, Indenyl, and Cyclopentadienyl Systems

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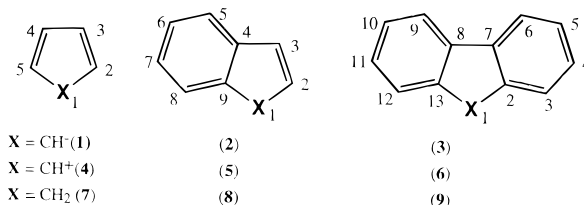
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**Abstract:** High level *ab initio* and density functional theory computations have been used to assess the aromaticity and antiaromaticity of the cations and anions derived from cyclopentadiene (C<sub>5</sub>H<sub>6</sub>), indene (C<sub>9</sub>H<sub>8</sub>), and fluorene (C<sub>13</sub>H<sub>10</sub>). On the basis of the IGLO calculated magnetic susceptibility exaltations ( $\Lambda_{\text{tot}}$ ) and the GIAO computed nucleus independent chemical shifts (NICS), the cyclopentadienyl (C<sub>5</sub>H<sub>5</sub><sup>-</sup>), indenyl (C<sub>9</sub>H<sub>7</sub><sup>-</sup>), and fluorenyl (C<sub>13</sub>H<sub>9</sub><sup>-</sup>) anions are, as expected, highly aromatic as compared with benzene, naphthalene, and anthracene. The aromaticity or antiaromaticity of the individual rings has been characterized by using the nucleus independent chemical shifts (NICS) based on the magnetic shieldings calculated at the ring centers. In addition to NICS, the computed Li<sup>+</sup> NMR chemical shifts, another useful aromaticity probe, provide data for the individual rings. The singlet cyclopentadienyl (C<sub>5</sub>H<sub>5</sub><sup>+</sup>) and indenyl (C<sub>9</sub>H<sub>7</sub><sup>+</sup>) cations are as antiaromatic as cyclobutadiene and benzocyclobutadiene. However, the fluorenyl cation (C<sub>13</sub>H<sub>9</sub><sup>+</sup>) is non-aromatic by the calculated magnetic susceptibility exaltation, due to the essentially complete compensation of the diamagnetic and the paramagnetic character. Such compensation effects are shown directly by the geometric, energetic, and magnetic differences between the delocalized and localized systems computed by means of the orbital deletion procedure (ODP), in which the critical carbocation p orbital is “deactivated”. This shows the delocalization energies of aromatic cations to be much larger than those of the antiaromatic cations, and the former are stabilized and the latter are destabilized relative to non-aromatic systems. In contrast to the cyclopentadienyl cation, which has a triplet ground state, the triplet indenyl and fluorenyl cations are higher in energy than their singlet states by 9.2. and 14.9 kcal/mol, respectively.

## Introduction

The (4*n* + 2)  $\pi$  electron cyclopentadienyl (**1**), indenyl (benzocyclopentadienyl, **2**), and fluorenyl (dibenzocyclopentadienyl, **3**) anions, as well as the corresponding 4*n*  $\pi$  electron cations **4–6**, are derived from cyclopentadiene (**7**), indene (**8**), and fluorene (**9**) (Scheme 1). The aromaticity of the (4*n* + 2)  $\pi$  electron anions (**1–3**) is widely accepted on the basis of their stability, and the measured acidities of the conjugated acids, **7–9**, are considerably larger than those of the corresponding conjugated, acyclic polyenes.<sup>1</sup> The *antiaromatic* character of the 4  $\pi$  electron cyclopentadienyl cation is well recognized.<sup>2–4</sup> The slow S<sub>N</sub>1 ionization rate of 5-iodo-1,3-cyclopentadiene,<sup>2a</sup> the recently measured deceleration<sup>2b</sup> by a factor of 10<sup>14</sup> in forming a cyclopentadienyl cation compared to formation of a cyclopentenyl cation model, the high oxidation potential of **1**,<sup>3</sup> and the low p*K*<sub>R</sub> of **4**<sup>4</sup> are examples. The triplet (CH)<sub>5</sub><sup>+</sup> ground state predicted from simple Hückel theory<sup>5</sup> also was confirmed

## Scheme 1



by ESR spectra<sup>6</sup> and by the latest *ab initio* computations,<sup>7</sup> which show a *C*<sub>2*v*</sub> singlet minimum (one of the Jahn–Teller distorted forms with a *cis*-butadiene moiety) to be 8.7 kcal/mol higher in energy than the *D*<sub>5*h*</sub> triplet ground state.

The indenyl (**5**) and fluorenyl (**6**) cations have been considered to be *antiaromatic*, like the singlet cyclopentadienyl cation (**4**). Both **5** and **6** have lower p*K*<sub>R</sub> values and related solvolysis rates, and are less stable compared to their benzhydryl analogs.<sup>8–10</sup> The antiaromatic destabilization of **6** was estimated to be 10.1 kcal/mol from MINDO/3 calculations<sup>9</sup> and 10.0 kcal/mol by HF/6-31G<sup>\*/</sup>3-21G<sup>10</sup> for the isodesmic hydride ion transfer between **9** and Ph<sub>2</sub>CH<sup>+</sup> to give Ph<sub>2</sub>CH<sub>2</sub> and **6**. However, the experimental <sup>1</sup>H NMR chemical shifts of the 9-methylfluorenyl cation (9-Me-**6**,  $\delta H = 7.04–7.62$ ) show diatropic ring current effects of the six-membered rings only somewhat reduced

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compared to  $\text{Ph}_2\text{CH}^+$  ( $\delta H = 7.53-8.12$ ) observed in super acid, and argue against major antiaromaticity effects in fluorenyl cations.<sup>9</sup> Amyes, Richard, and Novak<sup>10</sup> also measured  $pK_R$  values for **6** ( $-15.9$ ) and  $\text{Ph}_2\text{CH}^+$  ( $-11.7$ ), calculated from these a destabilization of 5.7 kcal/mol for **6**, and concluded that the difference in  $\pi$ -stabilization energies of **6** and  $\text{Ph}_2\text{CH}^+$  is relatively small and that **6** is not antiaromatic.

Both aromaticity and antiaromaticity are fundamental concepts in chemistry. The criteria upon which definitions and quantification of these concepts are the following: energies (aromatic stabilization and antiaromatic destabilization), geometries (aromatic bond length equalization and antiaromatic bond length alternation),<sup>11</sup> and magnetic effects resulting from diatropic "aromatic" or paratropic "antiaromatic" ring current effects, <sup>1</sup>H-NMR chemical shifts,<sup>12</sup> magnetic susceptibility exaltation ( $\Lambda$ ),<sup>13</sup> and anisotropy as well as NICS (see below).<sup>14</sup> The quantitative relationships among the geometric, energetic, and magnetic criteria of aromaticity were demonstrated for a wide ranging set of five-membered heterocycles in which the cyclopentadienyl anion (**1**) is the most aromatic, the singlet cyclopentadienyl cation (**4**) is the most antiaromatic, and cyclopentadiene (**7**) is non-aromatic.<sup>15</sup> However, in more complex polycyclic systems, other interactions may dominate, and the various aromaticity criteria are not necessarily parallel.<sup>13b</sup> The magnetic criterion may be the most specific and unambiguous manifestation of aromaticity<sup>14-17</sup> (negative  $\Lambda$ , diamagnetic susceptibility exaltation) and antiaromaticity (positive  $\Lambda$ , paramagnetic susceptibility exaltation). These criteria have been applied to many other systems, e.g., homoaromatic carbocations<sup>18</sup> and aromatic pericyclic transition states.<sup>19</sup>

The magnitude of the magnetic susceptibility exaltation ( $\Lambda$ ) due to ring current effects depends not only on the number of

delocalized electrons but also on the square of the ring size<sup>20</sup> and on the degree of the perfection of electron delocalization. While condensed polycyclic aromatic systems are larger in size, they can be regarded as being a combination of the smaller component rings rather than reflecting the large ring  $\pi$  periphery.

Recently, Schleyer *et al.* have proposed the use of the negative of the magnetic shieldings computed, e.g., at the ring center, referred to as "nucleus-independent chemical shift (NICS), as a simple criterion for aromaticity.<sup>14</sup> NICS, as an indicator of aromaticity, agrees well with the energetic, geometric, and magnetic criteria in five-membered heterocycles, and also has the advantages of being less dependent on ring size and not requiring an increment system. Moreover, NICS is an effective probe of the individual rings in polycyclic systems.

We now employ the diamagnetic susceptibility exaltation ( $\Lambda$ ) criterion of aromaticity to characterize the magnetic properties of **1-9** and NICS to analyze the aromaticity of the individual rings. Like NICS, the  $\text{Li}^+$  chemical shifts of lithium cation complexes with anions **1-3** and neutral **7-9** systems are used to assess the aromaticity of the individual rings. We also have computed singlet-triplet differences of cations **4-6**.

## Computational Methods

Geometries were optimized at RHF/6-31G\*, RMP2(fc)/6-31G\* ab initio, and the B3LYP/6-31G\* (in some cases at B3LYP/6-311+G\*\*) density functional levels with the Gaussian 94 program package.<sup>21</sup> Single-point energies were also computed at BLYP/6-311+G\* with the B3LYP/6-31G\* geometries. The calculated total energies are given in the Supporting Information. The magnetic susceptibilities  $\chi_{\text{tot}}$  and the magnetic susceptibility anisotropies  $\chi_{\text{anis}}$  were calculated with the IGLO<sup>22</sup> method and basis set II for the parent cyclopentadienyl system as well as the DZ basis set for the indenyl and the fluorenyl systems. The Li chemical shifts were calculated at IGLO/DZ//B3LYP/6-31G\* relative to the naked lithium cation as standard. The magnetic susceptibility exaltations ( $\Lambda$ ) were evaluated from the difference between each  $\chi_{\text{tot}}$  and the "normal" values deduced from increments for hypothetical polyene systems without cyclic delocalization obtained from calculations on a set of small molecules. The nucleus-independent chemical shifts (NICS<sup>14</sup>) in the ring centers were calculated at GIAO-SCF/6-31G\* with the Gaussian 94 program package.

To compare the aromaticity and antiaromaticity of these planar carbocations (**4-6**), we employed the orbital deletion procedure (ODP),<sup>23</sup> which requires only a slight modification of the HF method implemented in Gaussian 94. ODP deletes (deactivates) the p atomic orbitals (AOs), e.g., on the formally charged carbon in a carbocation. Subsequent optimization (here at HF/6-311G\*\*) results in a localized wave function  $\Psi^{\text{Loc}}$ ; the corresponding total energy  $E(\Psi^{\text{Loc}})$  excludes conjugation or hyperconjugation effects.<sup>24</sup> The usual HF optimization (also at HF/6-311G\*\*) with all AOs yields the delocalized wave function  $\Psi^{\text{Del}}$  and its corresponding total energy  $E(\Psi^{\text{Del}})$ . The difference between  $E(\Psi^{\text{Loc}})$  and  $E(\Psi^{\text{Del}})$  is defined as the delocalization

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**Table 1.** The Calculated Magnetic Susceptibilities ( $\chi_{\text{tot}}$ ), Anisotropies ( $\chi_{\text{anis}}$ , ppm cgs), Magnetic Susceptibility Exaltations ( $\Lambda$ , ppm cgs), and Nucleus Independent Chemical Shifts (NICS, ppm)<sup>a</sup> for Anions **1–3**, as Well as  $\text{Li}^+$  Chemical Shifts ( $\delta\text{Li}^+$ , ppm)<sup>b</sup> Compared with Their Iso- $\pi$ -Electronic Aromatic Hydrocarbons and **7–9**

	$\chi_{\text{tot}}$	$\chi_{\text{anis}}$	$\Lambda$	NICS(5)	NICS(6)	$\delta\text{Li}^+(5)$	$\delta\text{Li}^+(6)$
<b>1</b>	-67.7	-45.8	-17.2	-19.4		-6.9	
<b>2</b>	-124.3	-111.7	-31.9	-19.5	-12.5	-9.6	-9.6
<b>3</b>	-175.6	-174.5	-49.3	-16.4	-12.4	-10.7	-9.4
benzene	-68.1	-62.9	-13.4		-11.5		-6.6
naphthalene	-123.6	-130.3	-28.2		-11.4		
anthracene	-179.1	-204.8	-49.8		-14.3, <sup>c</sup> -9.6 <sup>d</sup>		
<b>7</b>	-51.0	-31.7	-2.4	-4.2		-0.6	
<b>8</b>	-106.9	-88.4	-17.2	-1.4	-11.3	-3.4	-8.1
<b>9</b>	-155.4	-141.0	-31.8	+0.5	-10.7	-2.5	-7.9

<sup>a</sup> NICS(5) and NICS(6) mean the GIAO-SCF/6-31G\*\*/B3LYP/6-31G\* calculated NICS value in the center of the five- and six-membered rings, respectively. <sup>b</sup>  $\delta\text{Li}^+(5)$  and  $\delta\text{Li}^+(6)$  mean the calculated  $\delta\text{Li}^+$  value for  $\text{Li}^+$  over the  $\pi$ -faces of the five- and the six-membered rings, respectively. <sup>c</sup> In the central ring center. <sup>d</sup> In the outer ring center.

**Table 2.** The Calculated Magnetic Susceptibilities ( $\chi_{\text{tot}}$ ), Anisotropies ( $\chi_{\text{anis}}$ , ppm cgs), Magnetic Susceptibility Exaltations ( $\Lambda$ , ppm cgs), and Nucleus Independent Chemical Shifts (NICS, ppm)<sup>a</sup> for Cations **4–6** Compared with Their Iso- $\pi$ -Electronic Aromatic Hydrocarbons

	$\chi_{\text{tot}}$	$\chi_{\text{anis}}$	$\Lambda$	NICS(5)	NICS(6)
<b>4</b>	-1.6	58.1	32.6	54.1	
<b>5</b>	-51.5	7.0	18.4	34.5	8.6
<b>6</b>	-104.4	-54.7	-0.6	24.7	1.9
cyclobutadiene <sup>b</sup>	-18.4	28.7	18.0	(28.8) <sup>c</sup>	
benzocyclobutadiene <sup>b</sup>	-65.9	-17.8	9.0	(21.5) <sup>c</sup>	-4.2
biphenylene <sup>b</sup>	-116.7	-70.5	-7.9	(18.2) <sup>c</sup>	-6.5

<sup>a</sup> NICS(5) and NICS(6) mean the GIAO-SCF/6-31G\*\*/B3LYP/6-31G\* calculated NICS value in the centers of the five- and the six-membered rings, respectively. <sup>b</sup> Taken from ref 19. <sup>c</sup> In the four-membered ring center.

energy (DE). The stabilization energy (SE) is the DE difference between the cyclic and linear (noncyclic) conjugated carbocations. Thus, an aromatic carbocation is stabilized and has a negative SE, while an antiaromatic carbocation with a positive SE is destabilized. The differences in geometric, energetic, and magnetic properties between the localized (after ODP) and delocalized molecules quantify the aromaticity and antiaromaticity effects in these cations. For this special purpose, the NICS are computed at GIAO-SCF/6-311G\*\*/RHF/6-311G\*\* for both the parent **4–6** cations and **4\*–6\*** cations after ODP.

## Results and Discussion

The calculated magnetic properties are given in Tables 1 and 2. The B3LYP/6-31G\* and MP2/6-31G\* (in parentheses) C–C bond lengths are shown in Figure 1.

The  $(4n + 2)$   $\pi$  electron cyclopentadienyl (**1**), indenyl (**2**), and fluorenyl (**3**) anions are, as expected, aromatic.<sup>11</sup> Their large magnetic susceptibility exaltations,  $\Lambda$ , of -17.2, -31.9, and -49.3, may be compared with calculated  $\Lambda$  values for analogous neutral systems, e.g., benzene (-13.4), naphthalene (-28.2), and anthracene (-49.8), respectively. The magnetic susceptibility differences ( $\Delta\chi_{\text{tot}}$ ) between anions **1–3** and their neutral **7–9** counterparts (-16.7, -17.4, and -20.2, respectively) show strongly enhanced diamagnetic ring current effects in the anions. The same conclusions are shown by the large negative NICS values for both the five- and the six-membered rings.

In addition to their NICS and magnetic susceptibilities, the aromaticity of **1–3** is also revealed by their geometries as shown in Figure 1. Of course, **1** is fully delocalized with only one C–C bond length (1.413 Å), but **2** and **3** have significantly equalized bond lengths. The average bond lengths, 1.407 ± 0.007 Å in **2** and 1.406 ± 0.011 Å in **3**, are close to the

naphthalene (1.402 ± 0.019 Å) and anthracene (1.404 ± 0.021 Å) values.<sup>25</sup> The geometric criteria are thus fulfilled for **1–3**.

Arguments for the possible aromatic character of cyclopentadiene (**7**) due to the pseudo  $2\pi$   $\text{CH}_2$  hyperconjugative contribution have been proposed.<sup>26</sup> However, our present analysis shows **7** to have neither special stabilization, bond length equalization, nor significant magnetic susceptibility exaltation compared with a wide set of five-membered heterocycles.<sup>15</sup> At best, the aromaticity of cyclopentadiene is borderline. This conclusion is also indicated by its NICS value (-4.2), only 21% of the cyclopentadienyl anion NICS value (-19.4) (Table 1) (Small NICS values can result from local contributions from the CH and  $\sigma$  CC bonds<sup>26</sup>).

As shown in Figure 1, B3LYP gives somewhat more localized structures than MP2 for the neutral systems **7–9**. For example, the C<sub>1</sub>–C<sub>2</sub> and C<sub>2</sub>–C<sub>3</sub> bond lengths at Becke3LYP are longer and shorter than those at MP2—their differences are 0.158 (Becke3LYP) and 0.147 Å (MP2). The B3LYP values are closer to the gas-phase experimental data for **7** than MP2.<sup>27</sup>

Indene (**8**) and fluorene (**9**), with  $\Lambda$  of -17.2 and -31.8 ppm cgs, respectively, are aromatic. However, no significant hyperconjugative effects for the methylene group (which might contribute to the aromaticity) are found, since the difference (-14.8 ppm cgs) between the  $\Lambda$  of **7** and **8** is close to the difference (-14.6 ppm cgs) between **8** and **9**. This indicates the six-membered-ring contribution to be constant!<sup>13b</sup> Likewise, the NICS values for the six-membered rings in **8** (-11.3) and in **9** (-10.7) are close to the benzene NICS (-11.5). On the other hand, the NICS(5) value in the center of the five-membered ring decreases in magnitude slightly from **7** to **9**, e.g., -4.2 for **7**, -1.4 for **8**, and +0.5 for **9**. This may be ascribed to the in-plane deshielding effect of the benzene rings.

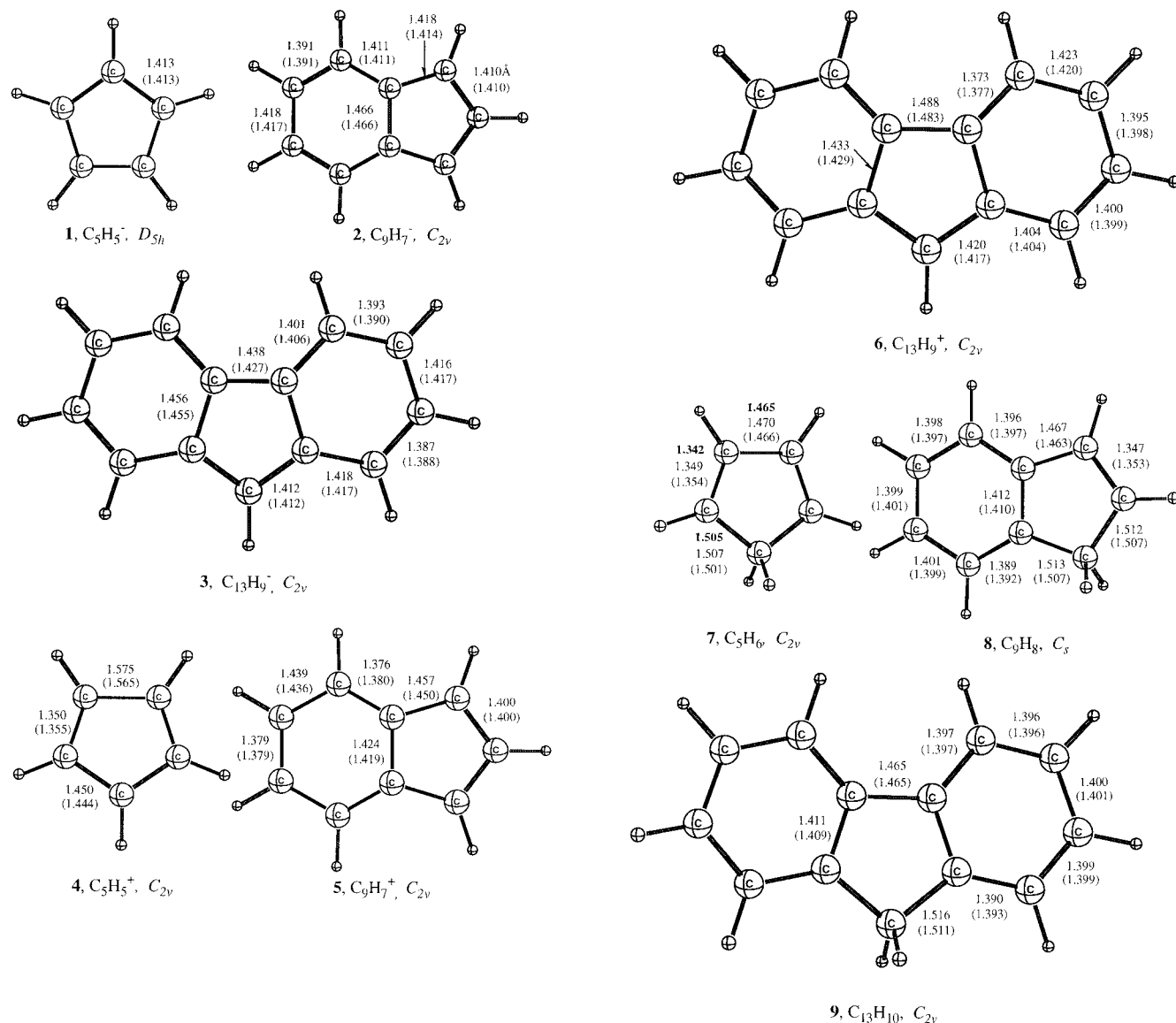
The antiaromatic character of the  $4n$   $\pi$  electron singlet cyclopentadienyl (**4**) and indenyl (**5**) cations is also shown by their paramagnetic magnetic susceptibility exaltations,  $\Lambda$ , of +32.6 and +18.4, the positive  $\chi_{\text{anis}}$  of +58.1 for (**4**) and +7.0 for (**5**), and the magnetic susceptibility difference between these cations (**4**, **5**) and their neutral compounds (**7**, **8**), which are opposite in sign to those of their corresponding anions (**1–3**). These  $\Lambda$  values, comparable with those for  $D_{2h}$  cyclobutadiene (+18.0) and  $C_{2v}$  benzocyclobutadiene (+9.0), are ascribed to paramagnetic ring current effects.<sup>14</sup> In addition, the positive NICS in the geometric centers for **4** (+54.1) and for **5** for the five- (+34.5) and six-membered (+8.6) rings reveal the antiaromatic character (Table 2). Furthermore, the bond length

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(24) In order to delete specific basis functions in the molecular orbitals, their one-electron integrals are set to very high positive values (e.g. 5000 au) and zeros are assigned to their overlap integrals with all other basis functions. Consequently, the molecular orbital coefficients of these functions in the occupied molecular orbitals become negligible and they do not contribute to the molecular energy.



**Figure 1.** B3LYP/6-31G\* and MP2/6-31G\* (in parentheses) bond lengths (in Å) for 1–9 (the gas-phase values for 7 are given in bold).

alternation in **4** of 0.225 Å is quite large and close to the cyclobutadiene value (0.221 Å).

In contrast, the 12  $\pi$  electron fluorenyl cation (**6**) with its counterbalancing 4  $\pi$ -electron five-membered-ring and two 6  $\pi$ -electron six-membered-ring moieties has essentially no magnetic susceptibility exaltation [ $\Lambda = -0.6$ ]. On this basis, the fluorenyl cation can be considered to be *nonaromatic*! This agrees with Novak *et al.*'s<sup>10</sup> conclusions based largely on energetic evidence and the  $pK_R$  values compared with the other corresponding carbocations. The compensation of diamagnetic six ring and paramagnetic five ring, which results in the non-aromaticity of the fluorenyl cation (**6**), also is found in **5**. But the paramagnetic dominates over the diamagnetic contribution; the net effect is paramagnetic, and **5** is still *antiaromatic*. Compensation is also reflected by the calculated NICS(5) and NICS(6) values given in Table 2. Similarly, we found benzocyclobutadiene to be moderately antiaromatic, but biphenylene to be moderately aromatic.<sup>14</sup>

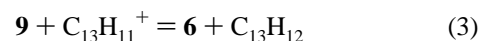
In addition to the magnetic properties, we have also evaluated the energetic effect of **4**–**6** using the isodesmic equations (eqs 1–3) in which the cations of 1,4-pentadienyl (C<sub>2v</sub>, C<sub>5</sub>H<sub>7</sub><sup>+</sup>), 1-phenylallyl (C<sub>s</sub>, C<sub>9</sub>H<sub>9</sub><sup>+</sup>) and diphenylmethyl (C<sub>2</sub>, C<sub>13</sub>H<sub>11</sub><sup>+</sup>), and 1,4-pentadiene (C<sub>2</sub>, C<sub>5</sub>H<sub>8</sub>) and 3-phenylpropylene (C<sub>1</sub>, C<sub>9</sub>H<sub>10</sub>) as well as diphenylmethane (C<sub>2</sub>, C<sub>13</sub>H<sub>12</sub>) are used as

**Table 3.** Calculated Reaction Energies ( $\Delta H$ , in kcal/mol)<sup>a</sup> for **4**–**6** at Various Computational Levels Based on the Isodesmic Eqs 1–3

level	$\Delta H(4)$	$\Delta H(5)$	$\Delta H(6)$
HF/6-31G*	35.7	18.5	9.8
B3LYP/6-31G*	42.5	20.3	10.8
B3LYP/6-311+G* <sup>b</sup>	42.0	20.0	10.4

<sup>a</sup>  $\Delta H > 0$  means destabilization. <sup>b</sup> Using the B3LYP/6-31G\* geometries.

reference molecules.



At B3LYP/6-311+G\*/B3LYP/6-31G\*, the singlet cyclopentadienyl cation (**4**) is destabilized by 42.0 kcal/mol (Table 3). This destabilization (20.0 kcal/mol) is reduced in the indenyl cation (**5**), and the stabilization contribution of the annelated benzene ring is 22.0 kcal/mol. Due to the two annelated benzene rings, **6** has a destabilization of only 10.4 kcal/mol,

**Table 4.** HF/6-311G\*\* Delocalization Energy (DE, kcal/mol) and NICS (in ppm) Values<sup>a</sup>

systems	DE <sup>b</sup>	NICS(5) <sup>c</sup>	NICS(6) <sup>c</sup>
benzene			-10.4
<b>4 (4*)</b>	-30.7	+47.0 (+2.2)	
<b>10 (10*)</b>	-52.5		
<b>11 (11*)</b>	-76.1		
<b>12 (12*)</b>	-61.5		
<b>13 (13*)</b>	-74.4		
<b>14 (14*)</b>	-36.8		
<b>15 (15*)</b>	-55.6		
<b>16 (16*)</b>	-57.1		
<b>5 (5*)</b>	-45.1	+28.4 (+2.7)	+8.1 (-8.4)
<b>6 (6*)</b>	-49.1	+21.6 (+2.6)	+1.8 (-8.2)

<sup>a</sup> At GIAO-SCF/6-311G\*\* with the HF/6-311G\*\* geometries; NICS(5) values for the five-membered rings and NICS(6) values for the six-membered rings. <sup>b</sup> Energy difference between the delocalized and localized (after ODP) systems. <sup>c</sup> NICS values for the localized systems (after ODP) are given in parentheses.

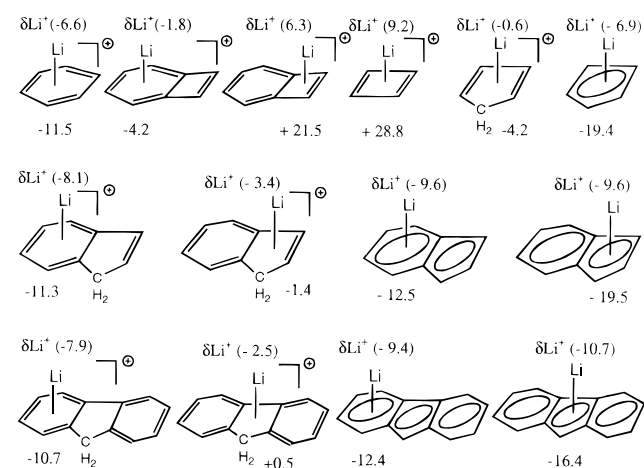
and this result agrees well with the MINDO/3 (10.1 kcal/mol)<sup>9</sup> and the HF/6-31G\*\*/3-21G (10.0 kcal/mol)<sup>10</sup> calculations.

### Results with the Orbital Deletion Procedure

The aromaticity or antiaromaticity of cations **4–6** has been characterized by the orbital deletion procedure (ODP). The ODP calculated energies and NICS (GIAO-SCF/6-311G\*\*//HF/6-311G\*\*) values are given in Table 4, and the geometries are shown in Figure 2. At HF/6-311G\*\*, the considerable bond length alternation of the *cis*-butadiene moiety in **4**, 0.218 Å, is larger than the 0.178 Å obtained for **4\*** after orbital deletion. The corresponding bond length difference is 0.156 Å in cyclopentadiene. The highly antiaromatic character in **4**, in contrast with the non-aromaticity of **4\***, also is indicated by the NICS values, e.g., +47.0 ppm for **4**, but only +2.2 ppm for **4\***.

Even though **4** is highly antiaromatic, it is also delocalized. The delocalization energy (DE) is -30.7 kcal/mol. Antiaromaticity reduces delocalization, but does not eliminate it completely. To what extent is **4** destabilized relative to an acyclic standard? We have computed the delocalization energy (DE) of *all-trans*-1,3-pentadienyl cation (**10**) in which the formally positive center in the ODP treatment was located at the C<sub>1</sub> position; this gives a C<sub>s</sub> symmetrical localized cation with a conjugated butadiene moiety (**10\***). The DE difference between the cyclic and linear (noncyclic) conjugated cations is also defined as the stabilization energy (SE). As expected from chemical intuition and compared with the calculated DE for **10** (-52.5 kcal/mol), antiaromatic **4** is destabilized by 21.8 kcal/mol. In contrast, aromatic carbocations not only have large DE's but also are stabilized relative to acyclic standards. For example, the tropylium ion (**11**, DE = -74.9 kcal/mol) is stabilized by -14.6 kcal/mol compared with the DE (-61.5 kcal/mol) for the *all-trans*-1,3,5-heptatrienyl cation (**12**, the positive charge is fixed at C1 in the ODP calculation). A similar result also is found for the cyclopropenyl cation (**13**). Compared with the DE (-36.8 kcal/mol) of the allyl cation (**14**), the cyclopropenyl cation **13** (DE = -74.4 kcal/mol) is stabilized by -37.6 kcal/mol (Table 4).

The ODP can be used in conjunction with NICS to analyze the delocalization effects in the indenyl (**5**) and fluorenyl (**6**) cations. The GIAO-SCF/6-311G\*\*//HF/6-311G\*\* calculated NICS values of +8.1 and +28.4 for the six- and the five-membered ring in **5** indicate both rings to be antiaromatic. Due to compensation of the aromatic and antiaromatic character, the values are smaller in magnitude than those of the corresponding monocyclic rings, e.g., benzene (-10.4) and **4** (+47.0). However, the NICS sum of the individual rings in **5** is close to

**Scheme 2.** Comparison of the  $\delta\text{Li}^+$  (IGLO/DZ//B3LYP/6-31G\*) and NICS (in ppm) Values<sup>a</sup>

<sup>a</sup> Computed in the absence of the lithiums.

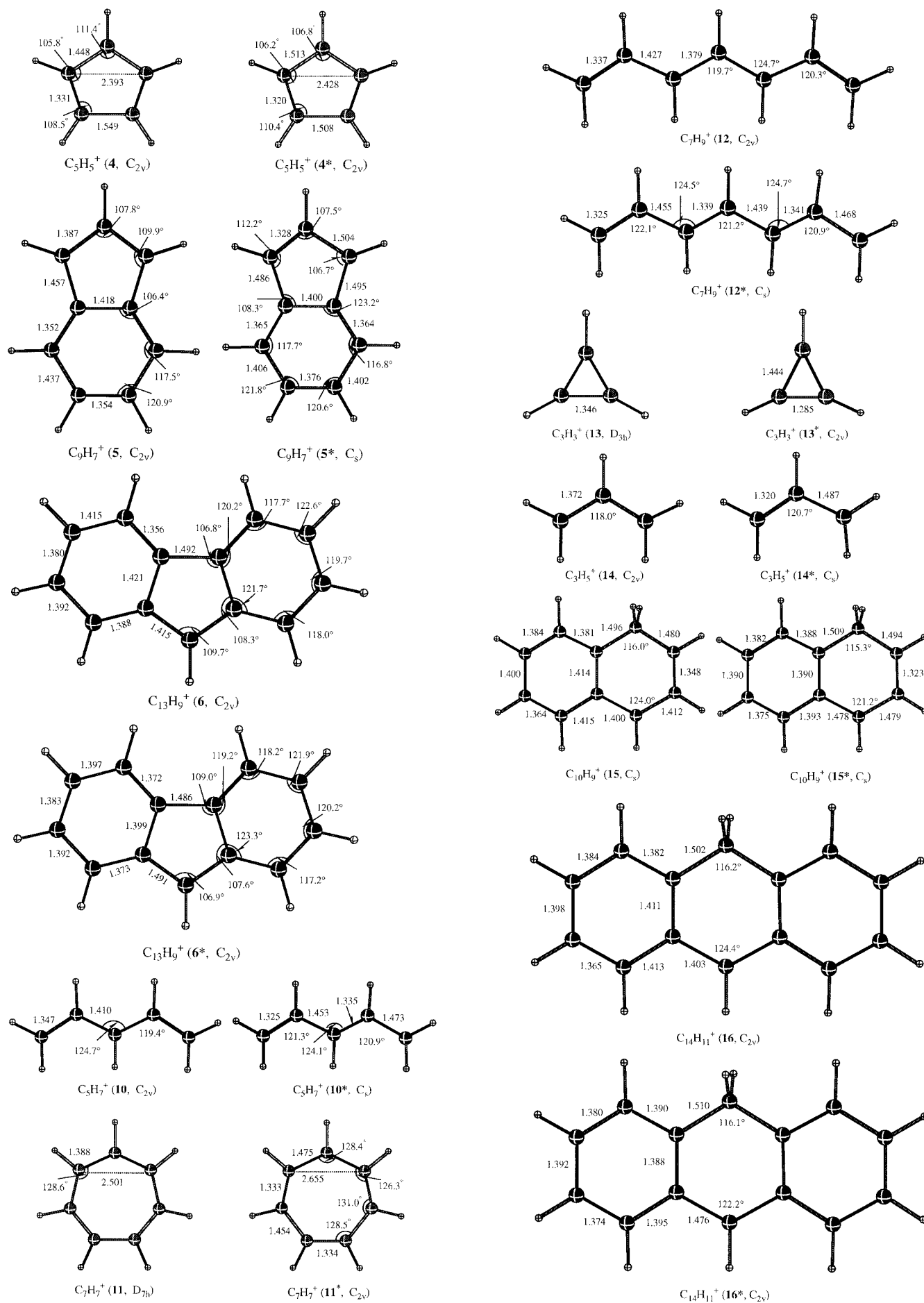
the sum of the monocyclic rings. After ODP, the symmetry is reduced from C<sub>2v</sub> (**5**) to C<sub>s</sub> (**5\***), and the C–C bond length alternation of the six-membered rings also is decreased. The NICS values (-8.4 for the six-membered ring and +2.7 for the five-membered ring) for **5\*** are close to the values of benzene and **4\***. At HF/6-311G\*\*, **5** is 45.0 kcal/mol more stable than **5\*** (Table 4). Compared with **4**, **5** has a large DE due to the annelation of the six-membered ring. But is **5** stabilized? Do the aromatic and antiaromatic character compensate energetically? For evaluating the SE of the indenyl cation (**5**), we have used 1-protonated naphthalene (**15**) as an approximate reference molecule. At HF/6-311G\*\*, **15** has a large DE of -55.6 kcal/mol. On the basis of **15**, **5** is destabilized by 10.5 kcal/mol.

Similar conclusions are reached for the fluorenyl cation (**6**). Due to the two annelated six-membered rings in **6**, the compensation effect is greater than in **5**—note the nonaromatic six-membered ring (NICS = +1.8) and the less antiaromatic five-membered ring [NICS = +21.6 compared with the NICS of benzene (-10.4) and **4** (+47.0)]. After ODP, the situation changes dramatically. The six-membered ring (NICS = -8.2) in **6\*** is still aromatic and the five-membered ring (NICS = +2.6) nonaromatic as compared with values for benzene and for **4\*** (NICS = +2.2). At HF/6-311G\*\*, **6** is 49.1 kcal/mol more stable than **6\***. Compared with the DE (-57.1) of the C(10)-protonated anthracene (**16**) as reference, **6** is destabilized by 8.0 kcal/mol. This destabilization of **6** is within the 5.7–10.0-kcal/mol range found from the pK<sub>R</sub> and HF/6-31G\*\*/3-21G computations.<sup>10</sup>

### $\pi$ -Complexes with Li<sup>+</sup> Cation

In addition to magnetic susceptibility exaltations, the computed Li<sup>+</sup> chemical shifts in the monocyclic and polycyclic neutral or anionic compounds complexed with Li cations have been used to characterize the aromaticity of individual rings; examples are shown in Scheme 2.<sup>17</sup> This method is very similar in principle to our NICS criterion. For example, the Li<sup>+</sup> upfield shifts, computed to be -6.9 in C<sub>5v</sub> cyclopentadienyl lithium (the measured value is -8.6 in THF at 25 °C<sup>28</sup>) and -6.6 in the C<sub>6v</sub> benzene-Li<sup>+</sup> complex, confirm the presence of strong diamagnetic ring current in these 4n + 2  $\pi$  electron annulenes. In non-aromatic systems,  $\delta\text{Li}^+$  data have only a small range ( $\pm 2$  ppm relative to the experimental Li<sup>+</sup> shift standard). This probe has even been used to demonstrate the aromaticity of a

(28) (a) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776–8789. (b) For a review, see: Bauer, W. *Lithium Chemistry, A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; John Wiley & Sons, Inc.: New York, 1995; Chapter 5, pp 125–172.



**Figure 2.** HF/6-311G\*\* geometries for the parent cyclopentadienyl (4), indenyl (5) and fluorenyl (6) cations, and 4\*–6\* after ODP analysis, compared with 1,3-pentadienyl cation (10), tropylium (11) and 1,3,5-heptatrienyl cations (12), cyclopropenyl (13) and allyl cations (14), protonated naphthalene (15) and anthracene (16), as well as their localized counterparts (10\*–16\*) after ODP.

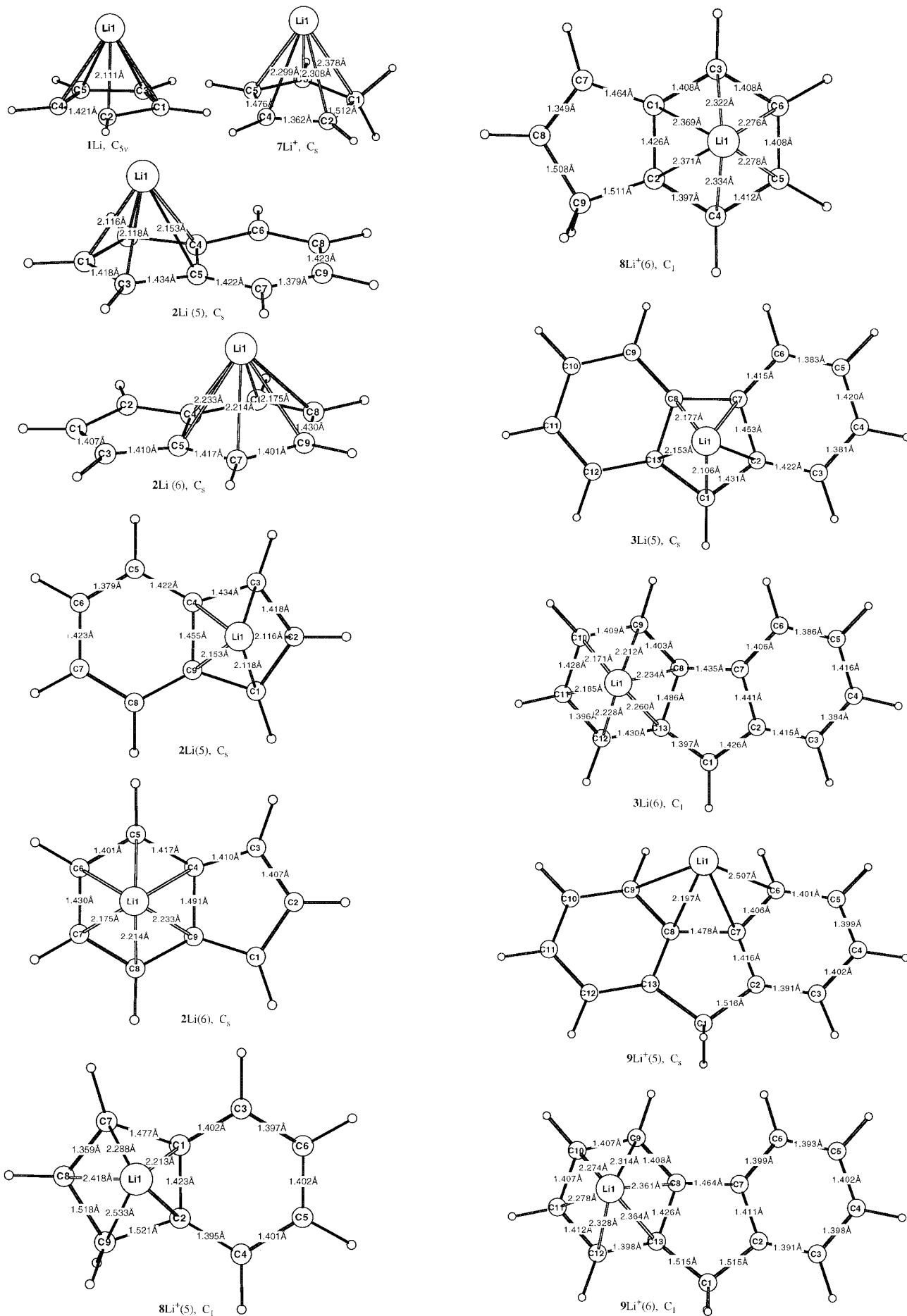


Figure 3. B3LYP/6-31G\* geometries for the Li<sup>+</sup> complexes with the anion systems 1–3 and the neutral systems 7–9.

**Table 5.** The Computed Complexation Energies ( $E_{\text{comp}}$ , kcal/mol) at B3LYP/6-311+G\*\*/B3LYP/6-31G\* + ZPE (HF/6-31G\*)<sup>a</sup>

complex(5) <sup>b</sup>	$E_{\text{comp}}(5)^c$	complex(6) <sup>d</sup>	$E_{\text{comp}}(6)^e$
1Li(5)	-168.6		
7Li(5)	-33.1		
2Li(5)	-153.8	2Li(6)	-146.1
8Li(5)	-34.7	8Li(6)	-42.3
3Li(5)	-142.6	3Li(6)	-138.0
9Li(5)	-36.4	9Li(6)	-43.1

<sup>a</sup> On the basis of  $R^- + Li^+ \rightarrow RLi$  for the anions 1–3 and  $R-H + Li^+ \rightarrow RHLi^+$  for the neutral species 7–9. <sup>b</sup> For  $Li^+$  over the faces of the five-membered rings. <sup>c</sup> Complexation energies for  $Li^+$  over the faces of the five-membered rings. <sup>d</sup> For  $Li^+$  over the face of the six-membered rings. <sup>e</sup> Complexation energies for  $Li^+$  over the faces of the six-membered rings.

**Table 6.** Computed Singlet–Triplet Energy Separations ( $\Delta E_{\text{ST}}$ , kcal/mol) for the Cyclopentadienyl (4), Indenyl (5) and Fluorenyl (6) Cations

systems	$\Delta E_{\text{ST}}$
4 $\rightarrow$ 4T	-9.9 <sup>a</sup> (-9.8) <sup>b</sup>
5 $\rightarrow$ 5T	+9.2 <sup>c</sup>
6 $\rightarrow$ 6T	+14.9 <sup>c</sup>

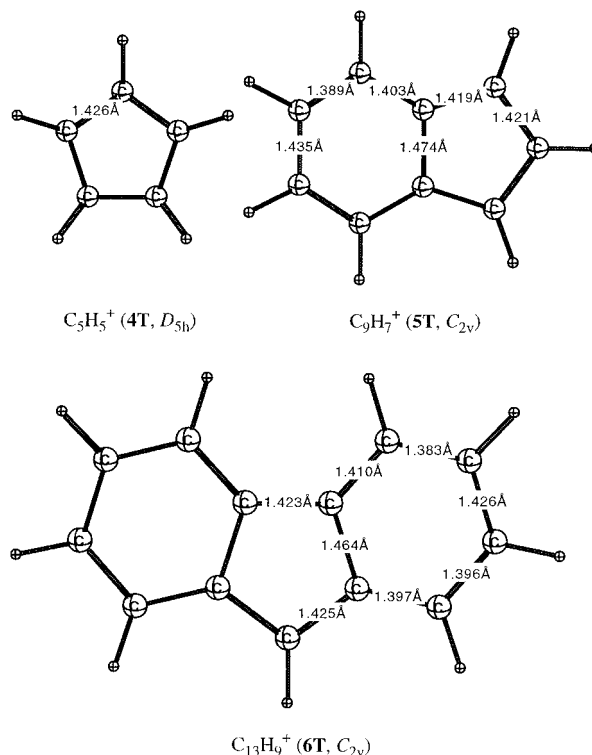
<sup>a</sup> At B3LYP/6-311+G\*\* + ZPE (B3LYP/6-311+G\*\*). <sup>b</sup> At B3LYP/6-311+G\*\*/B3LYP/6-31G\* + ZPE (B3LYP/6-311+G\*\*). <sup>c</sup> At B3LYP/6-311+G\*\*/B3LYP/6-31G\* + ZPE (HF/6-31G\*).

set of pericyclic transition states.<sup>19</sup> In antiaromatic compounds, a  $Li^+$  downfield shift of +9.2 ppm was computed for the  $C_{2v}$  cyclobutadiene– $Li^+$  complex. In the benzocyclobutadiene– $Li^+$  complexes, the computed  $Li^+$  chemical shifts of only -1.8 ppm for  $Li^+$  cation over the six-membered ring and +6.3 ppm for  $Li^+$  over the four-membered ring are reduced significantly as compared with their monocyclic counterparts. The same relationships are shown by the calculated NICS values for the individual rings, e.g., -4.2 for the six-membered ring and +21.5 for the four-membered ring (Scheme 2).

Besides the cyclopentadienyl anion,  $Li^+$  can coordinate with both the five- and the six-membered-ring  $\pi$ -faces of indene (8) and fluorene (9), as well as with their anions (2 and 3). As shown in Figure 3, the  $Li$ –C distances in the anion (1–3)–complex systems, due to the stronger electrostatic interactions, are shorter than those in the neutral (7–9)–complexes. These stronger interactions are reflected by the complexation energies, for example, computed to be 168.6 kcal/mol for  $C_5H_5Li$  (1Li,  $C_{5v}$ ) but only 33.1 kcal/mol for  $C_5H_6Li^+$  (7Li<sup>+</sup>,  $C_s$ ) (Table 5).

The  $Li^+$  cation does not coordinate centrally to the non-aromatic five-membered ring in fluorene, but to C(6,7,8,9) (Figure 3). The calculated complexation energies are 33.1, 34.7, and 36.4 kcal/mol for 7, 8, and 9.

As discussed above, the calculated Li NMR chemical shifts of  $Li^+$  complexes can be used to probe the aromaticity of not only monocyclic but also individual rings in polycyclic systems. As given in Table 1 and shown in Scheme 2, the  $\delta Li^+$  values for  $Li^+$  over the five ( $C_5H_5Li$ )- and six ( $C_6H_6Li^+$ )-membered aromatic rings are all significantly negative in contrast to the  $Li^+$  over the antiaromatic cyclobutadiene ring. As in our NICS analysis, the diamagnetic and paramagnetic compensations also are shown by the calculated  $\delta Li^+$ . For example, the  $\delta Li^+$  values for the six-membered ( $\delta Li^+ = -1.8$ ) and four-membered ( $\delta Li^+ = +6.3$ ) rings in benzocyclobutadiene are smaller in magnitude than the values for benzene ( $\delta Li^+ = -6.6$ ) and cyclobutadiene ( $\delta Li^+ = +9.2$ ). In the indene (8)– $Li^+$  complex, the  $\delta Li^+$  for  $Li^+$  over the six-membered aromatic rings (-8.1) is much larger than that of  $Li^+$  over the five-membered non-aromatic ring (-3.4). In the indenyllithium (2Li) complex,  $\delta Li^+$  (-9.6) is the same for  $Li^+$  over the five- and six-membered aromatic

**Figure 4.** B3LYP/6-31G\* geometries for the triplet cyclopentadienyl (4T), indenyl (5T), and fluorenyl (6T) cations.

rings. Similar results are found for the fluorene and fluorenyl-lithium complexes.

### Singlet–Triplet Splittings ( $\Delta E_{\text{ST}}$ )

Simple Hückel theory and recent more sophisticated ab initio computations suggest the cyclopentadienyl cation to have a  $D_{5h}$  symmetric triplet ground state.<sup>7</sup> This agrees with the observed ESR spectra.<sup>6</sup> Due to Jahn–Teller distortion, two  $C_{2v}$  singlet states also are predicted; one has a *cis*-butadiene moiety and is an energy minimum, and the other, a combination of an allyl cation and an ethylene, is a transition state. Both are nearly isoenergetic.<sup>7</sup> The triplet state of the cyclopentadienyl cation was computed to be 8.7 kcal/mol lower in energy than the singlet ground state at QCISD(T)/6-31G\*\*//MP2/6-31G\*. We present here density functional theory computations for the singlet–triplet splitting ( $\Delta E_{\text{ST}}$ ) for the indenyl and fluorenyl cations compared with the cyclopentadienyl cation.

At B3LYP/6-311+G\*\*, as at MP2/6-31G\*,<sup>7</sup> both the singlet (4) and triplet cyclopentadienyl (4T) cations are minima. The B3LYP/6-311+G\*\* lowest frequencies are 263  $cm^{-1}$  for 4 and 397  $cm^{-1}$  for 4T. As given in Table 6, the calculated energy differences between 4 and 4T are 9.8 kcal/mol (B3LYP/6-311+G\*\* + ZPE (B3LYP/6-311+G\*\*)) and 9.9 kcal/mol (B3LYP/6-311+G\*\*/B3LYP/6-31G\* + ZPE (B3LYP/6-311+G\*\*)); these are close to the QCISD(T) result (8.7 kcal/mol).<sup>7</sup> Thus, the B3LYP/6-311+G\*\*/B3LYP/6-31G\* calculations on the larger indenyl and fluorenyl cations should be reliable. In addition, the B3LYP/6-311+G\*\* C–C bond length of 1.426 Å for 4T is nearly the same as that at B3LYP/6-31G\* (Figure 4), so that reoptimization with the larger basis set should add negligible refinement.

At Becke3LYP/6-31G\*, both the  $C_{2v}$  symmetric triplet indenyl (5T) and fluorenyl (6T) cations are minima. In contrast with the cyclopentadienyl cation, the singlet indenyl cation is 9.2 kcal/mol and the fluorenyl cation is 14.9 kcal/mol more stable than their triplet states (B3LYP/6-311+G\*\*/B3LYP/6-31G\* + ZPE (HF/6-31G\*)). Hence, the triplets do not compete



with the singlet indenyl and fluorenyl cations energetically. Geometrically, the  $C_{2v}$  allyl cation–ethylene form of the singlet cyclopentadienyl cation is stabilized by one annelated benzene ring in the indenyl cation (**5**), and the singlet  $C_5H_5^+$  form with a *cis*-butadiene moiety is stabilized by two annelated benzene rings in the fluorenyl cation.

### Conclusions

On the basis of the magnetic criteria of aromaticity (magnetic susceptibility exaltation ( $\Lambda_{tot}$ ), magnetic susceptibility anisotropies ( $\chi_{anis}$ ), and nucleus-independent chemical shifts, NICS), the cyclopentadienyl (**1**), indenyl (**2**) and fluorenyl (**3**) anions are aromatic, and the singlet cyclopentadienyl (**4**) and indenyl (**5**) cations are antiaromatic. Due to the essentially complete diamagnetic and paramagnetic compensation, the fluorenyl cation (**6**) is *non-aromatic* by the calculated magnetic susceptibility exaltation. By the NICS criterion the benzene rings are almost non-aromatic and the five-membered ring is still antiaromatic, while by isodesmic reaction **6** is destabilized by 10.4 kcal/mol and by ODP by 8.0 kcal/mol. The latter is in agreement with the  $pK_R^+$  measurements and the MINDO/3 as well as HF/6-31G\*\*/3-21G calculations.<sup>9,10</sup> These compensation effects are supported generally by using the orbital deletion procedure (ODP), which “deactivates” the p orbital at the formally charged carbon center. Both aromatic and antiaromatic

systems have large delocalization energies (DE), but the former are stabilized and the latter destabilized relative to non-aromatic systems. In contrast to the cyclopentadienyl cation, which has a triplet ground state, the singlet indenyl and fluorenyl cations are 9.2 and 14.9 kcal/mol lower in energy than their triplet states. Either of the Jahn–Teller distorted forms of the singlet cyclopentadienyl cation can be stabilized considerably by the appropriately placed benzene ring(s).

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**Supporting Information Available:** Tables of computed total energies (hartrees) for compounds **1–9** at various computational levels (3 pages). See any current masthead page for ordering and Internet access instructions.

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