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Dications of 3-Phenylindenylidenefluorenes: Evaluation of Antiaromaticity of Indenyl and Fluorenyl Cations by Magnetic Measures

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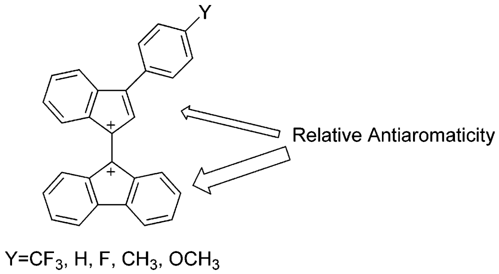

Dications of *p*-substituted 3-phenylindenylidenefluorenes were prepared to examine the response of the resulting indenyl and fluorenyl cationic systems to magnetic measures of antiaromaticity. All measures, ^{1}H NMR shifts, nucleus independent chemical shifts (NICS(1)$_{zz}$), and magnetic susceptibility exaltation, Λ, supported the antiaromaticity of the dications **3a**−**f**$^{2+}$. The ^{1}H NMR shifts and NICS(1)$_{zz}$ showed that the indenyl ring system was less antiaromatic than the fluorenyl ring system, contrary to the antiaromaticity of indenyl monocations compared to fluorenyl monocations. The presence of a phenyl substituent in the 3-position was able to stabilize the indenylidene cation through resonance, decreasing its antiaromaticity, but even in the absence of the 3-phenyl substituent, the indenyl system of indenylidenefluorene dications was less antiaromatic than the fluorenyl system. The decreased antiaromaticity of the 3-phenylindenylidenefluorene dications over the unsubstituted indenylidenefluorene dication was supported by (anti)aromatic (de)stabilization energy calculations, ASE.

Introduction

Although aromaticity is part of the lexicon of organic chemistry and has played an important role in the understanding of the behavior of a large number of compounds, there is no general agreement on those characteristics of a molecule that allow it to be considered as aromatic. Basically, the criteria that have been used to assess aromaticity of molecules and other species are based on characteristics of benzene and fall into three categories, energetic, structural, and magnetic. Characteristics associated with the energetic criteria reflect the observation that delocalized aromatic species are more stable than localized reference systems. Among the methods used to evaluate this stability is calculation of aromatic stabilization energy, ASE. ASE is evaluated through reactions in which the species to be evaluated is “prepared” via isodesmic-type reactions, where the reactants and products are matched in terms of number and type of atoms and bonds, and where strain energy is matched in all species.[1,2] Structural criteria attempt to evaluate the amount of delocalization through bond length alternation. One approach to the evaluation of delocalization is the harmonic oscillator measure of aromaticity, HOMA, which examines the deviation of each bond length from the average bond length for a system.[3,4] Finally, the magnetic criteria look for evidence

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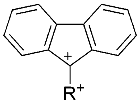
of a ring current by considering ^{1}H NMR chemical shift,[5] magnetic susceptibility exaltation (Λ),[6−8] and nucleus independent chemical shift (NICS).[9,10]

While these criteria generally show good agreement in a qualitative sense, for some systems, they differ in their quantitative assessment of aromaticity. If they are indeed measuring the same phenomenon, there should be agreement between all criteria. One problem with the use of these criteria lies in the fact that the criteria, when applied to aromatic species, have a relatively small range of values. Thus small errors in measurements can obscure relationships between the criteria. We have approached the evaluation of the different criteria used to assess aromaticity by looking at how the criteria assess antiaromaticity, which would expand the range of values examined. We have discovered a suite of fluorenylidene dications, **1**, in which the fluorenyl system is antiaromatic by magnetic criteria, ^{1}H NMR shifts, NICS, and Λ, and by energetic criteria, ASE.[11−20] There was a linear relationship between magnetic and energetic measures of antiaromaticity, refuting the contention that these properties are orthogonal, at least in the fluorenyl system.[20] Structural criteria, via the examination of bond length alternation through HOMA calculations, were insensitive to changes in R$^+$ in **1**, which prevented its relationship to magnetic and energetic criteria from being examined.[16] We have begun to use these systems to examine relationships between antiaromaticity and aromaticity.[21]



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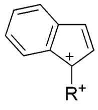

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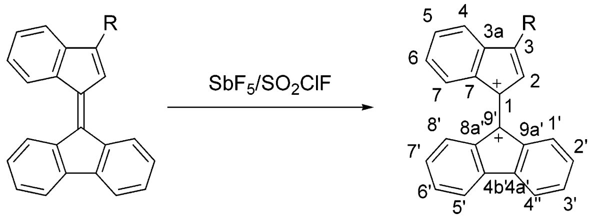
We were anxious to extend these studies to indenylidene dications, **2**, because indenyl cations were shown to be more antiaromatic than fluorenyl cations.[22] Presumably, the three criteria used to evaluate aromaticity/antiaromaticity would be more sensitive in systems that are more antiaromatic, allowing a more precise evaluation of relationships. In addition, NICS calculations, which assess the aromaticity/antiaromaticity of individual rings in a polycyclic aromatic/antiaromatic system, showed the five-membered ring of the fluorenyl ring system to possess greater antiaromaticity than the six-membered rings,[15,17,20] but the absence of protons on the five-membered ring prevented direct experimental assessment of antiaromaticity. The indenyl system of **2** allows that assessment. Finally, while HOMA analysis of the fluorenyl system showed little responsiveness to changes in R$^+$, the indenyl system of **2** would have more ability to undergo bond deformation because it has less benzannulation.

We chose to begin our examinations with the preparation of dications of indenylidenefluorenes, **3**, reasoning that the presence of the fluorenyl system would give us an internal calibration of antiaromaticity. Because the indenylidene system was anticipated to be more antiaromatic than the fluorenylidene system, in analogy to the greater antiaromaticity of the indenyl cation over the fluorenyl cation,[22] we began with the preparation of 3-phenyl-substituted indenylidenefluorene dications, assuming that the phenyl substituent would help to stabilize the indenylidene system. In addition, varying the electronic nature of substituents on the phenyl ring would provide a slight alteration of the electronic nature of the indenyl system and an additional probe of antiaromaticity. In this paper, we report the characterization of these indenylidenefluorene dications through use of the magnetic criteria, ^{1}H NMR shifts, Λ, and NICS. A second paper will evaluate the antiaromaticity of the indenyl and fluorenyl systems of **3^{2+}** via energetic and structural criteria.



3, a, R=p-C$_6$H$_4$CF$_3$
b, R=p-C$_6$H$_5$
c, R=p-C$_6$H$_4$F
d, R=p-C$_6$H$_4$CH$_3$
e, R=p-C$_6$H$_4$OCH$_3$
f, R=H

3^{2+}, a, R=p-C$_6$H$_4$CF$_3$
b, R=p-C$_6$H$_5$
c, R=p-C$_6$H$_4$F
d, R=p-C$_6$H$_4$CH$_3$
e, R=p-C$_6$H$_4$OCH$_3$
f, R=H

Results and Discussion

^{1}H NMR Shifts. Oxidation with an excess of SbF$_5$ in SO$_2$ClF at −78 °C gave formation of dications of **3a**−**d**. Oxidation of **3e** was unsuccessful, presumably because complexation of the methoxy substituent by the Lewis acid SbF$_5$ made it sufficiently electron deficient that the resulting dication was too unstable to be observed. We had anticipated that oxidation of **3d** would be facile, but the ^{1}H NMR spectra of **3d^{2+}** were very poorly resolved, making assignments very unreliable. We have seen poor resolution in other fluorenylidene dications with methyl substituents,[13] but have no explanation for the deterioration in the quality of the NMR spectra for these methyl-substituted derivatives. For that reason, we have included only data from **3a**−**c^{2+}** in our discussion of experimental chemical shifts. We were unable, after multiple attempts, to obtain the ^{13}C spectra of the dications, so assignments of the ^{1}H NMR

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TABLE 1. Experimental Proton Shifts for 3a−c^{2+} [a] (in ppm) Relative to TMS

	3a^{2+} [b]	**3a**$^{2+}$ [b]	**3a**$^{2+}$ [c]	**3b**$^{2+}$ [d]	**3c**$^{2+}$ [b]
Indenyl system					
H-2	5.67 ± 0.01	5.50 ± 0.04	5.59 ± 0.10	5.70 ± 0.10	6.03 ± 0.04
H-4	6.49 ± 0.01	6.31 ± 0.04	6.40 ± 0.11	6.54 ± 0.06	6.71 ± 0.01
H-5	5.85 ± 0.01	5.77 ± 0.08	5.81 ± 0.07	5.91 ± 0.05	6.14 ± 0.02
H-6	6.17 ± 0.01	5.97 ± 0.08	6.07 ± 0.13	6.12 ± 0.04	6.38 ± 0.04
H-7	5.55 ± 0.01	5.38 ± 0.04	5.47 ± 0.11	5.61 ± 0.06	5.85 ± 0.01
avg	5.95 ± 0.01	5.79 ± 0.05	5.86 ± 0.10	5.98 ± 0.06	6.21 ± 0.03
Fluorenyl system					
H-1,8	5.63 ± 0.01	5.47 ± 0.04	5.55 ± 0.10	5.61 ± 0.06	5.79 ± 0.01
H-2,7	5.24 ± 0.01	5.07 ± 0.04	5.16 ± 0.10	5.17 ± 0.06	5.35 ± 0.01
H-3,6	5.85 ± 0.01	5.77 ± 0.08	5.81 ± 0.07	5.77 ± 0.06	5.96 ± 0.01
H-4,5	5.15 ± 0.01	4.99 ± 0.04	5.07 ± 0.10	5.09 ± 0.02	5.30 ± 0.01
avg	5.43 ± 0.01	5.32 ± 0.05	5.40 ± 0.10	5.43 ± 0.05	5.60 ± 0.01
Phenyl					
o	7.26 ± 0.01	7.09 ± 0.04	7.18 ± 0.10	7.11 ± 0.07, 7.30 ± 0.07	7.71 ± 0.02, 7.45 ± 0.01
m	6.95 ± 0.01	6.77 ± 0.04	6.86 ± 0.10	6.66 ± 0.05	6.52 ± 0.01
p				7.30 ± 0.02	

[a] Spectra are reported at −40 °C in SO_2ClF with acetone-d_6 and TMS in a capillary tube in the sample as external references. The number of spectra used to obtain the data reported are listed below. In all cases, at least 5 NMR samples were prepared, but the dication preparation was quite variable, with some samples giving no usable data, even though the method of preparation and reagents used appeared to be identical. [b] Two runs. [c] Average of four runs. [d] Three runs.

TABLE 2. Calculated Proton Shifts for 3a−f^{2+} [a,b] (in ppm) versus TMS

substituent	**3a**$^{2+}$	**3b**$^{2+}$	**3c**$^{2+}$	**3d**$^{2+}$	**3e**$^{2+}$	**3f**$^{2+}$
Indenyl system						
H-2	5.66 (6.16)	5.82 (6.37)	5.81 (6.41)	6.03	6.03	4.04
H-3						6.48
H-4	6.93 (7.12)	7.14 (7.30)	7.13 (7.33)	7.38	7.33	5.78
H-5	6.90 (6.73)	6.95 (6.87)	7.00 (6.93)	7.12	7.16	5.65
H-6	7.20 (7.07)	7.18 (7.18)	7.23 (7.22)	7.34	7.33	5.98
H-7	6.41 (6.36)	6.38 (6.55)	6.44 (6.61)	6.54	6.67	4.89
Fluorenyl system						
H-1,8	5.77 (6.29)	5.82 (6.39)	5.82 (6.40)	5.89	6.00	4.40
H-2,7	5.83 (6.04)	5.88 (6.10)	5.90 (6.13)	5.92	6.01	4.72
H-3,6	6.67 (6.75)	6.66 (6.79)	6.78 (6.81)	6.70	6.81	5.50
H-4,5	5.77 (6.02)	5.81 (6.12)	5.83 (6.14)	5.86	6.01	4.28
Phenyl						
o	7.61 (8.10)	7.67 (8.02)	7.84 (8.22)	7.57	7.61	
m	7.85 (7.87)	7.83 (7.84)	7.34 (7.39)	7.59	6.98	
p		8.54 (8.47)				
CH_3/OCH_3				2.81	4.34	

[a] ^1H NMR shifts for **3a**−**c**$^{2+}$ were calculated with and without solvent using the GIAO method, B3LYP/6-31G(d)//B3LYP/6-31G(d). Shifts calculated with solvent (DMSO) via the PCM method are shown in parentheses. ^1H NMR shifts for **3d**−**f**$^{2+}$ were calculated without solvent. [b] For the methyl group and the fluorenyl system, the shifts recorded are the average of the shifts calculated for the three protons of the methyl group and for the comparable protons of the fluorenyl system (e.g., H-1′ and H-8′). Because these protons appeared as single peaks in the experimental spectra, it seemed reasonable to average the shifts calculated for a static structure.

spectra were made via COSY spectra, augmented by spectra calculated using the GIAO method (vide supra) rather than with the use of HMBC or HMQC data.

The experimental ^1H NMR shifts for **3a**−**c**$^{2+}$ are given in Table 1, and the calculated ^1H NMR shifts for **3a**−**e**$^{2+}$ are in Table 2, along with the average shifts for the indenyl and fluorenyl ring systems. The data for **3a**$^{2+}$ fall into two groups, as shown in the table. Because we had no basis for determining which group had “better” data, we averaged the two data sets, giving a greater standard deviation for that dication than for the other dications reported. Looking at the experimental data first, the *p*-substituent on the phenyl in the 3-position was able to affect the antiaromaticity of the dication, with the following order of paratropicity/antiaromaticity, $CF_3 > H > F$. We have seen[12−14,16,18,20] that the greater the electron-withdrawing ability of the substituent, the greater the antiaromaticity of the dication. The ability of substituents to modulate aromaticity was shown by Fowler et al.[23] for substituted pentafulvalenes in which the ring current changes from paratropic to diatropic as the substituent changes from an electron-withdrawing substituent to an electron-donating one. These magnetic effects were complemented by the geometrical evidence of aromaticity in which the pentafulvalene substituted with the best electron-donating group also has the least bond length alternation. The effect in **3**$^{2+}$ is, in general, greater on the protons of the indenyl system, as would be expected because of the location of the phenyl substituent.

The ^1H NMR shifts in the absence of solvent (vide supra) were calculated using the GIAO method in Gaussian 03[24] with the DFT method B3LYP using basis set 6-31G(d), B3LYP/6-31G(d), on geometries calculated at the same level, B3LYP/6-31G(d). We have found that calculations at this level on other fluorenylidene dications[15,17,20] give chemical shifts that show a good linear correlation with experimental shifts, with $r^2 \sim 0.95$. However, a similar plot for **3a**−**c**$^{2+}$ gave $r^2 = 0.82$. When the correlation for protons on the indenyl and fluorenyl systems only are considered, r^2 drops to 0.64; see Supporting Information for the plots of experimental versus calculated shifts. An

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examination of the individual shifts shows that the experimental shifts that deviate most strongly from the calculated shifts are for protons H-2 on the indenyl system and H-1′,H-8′ on the fluorenyl system. If those protons are removed from the correlation, r^2 rises to 0.89.

These calculations are done in the gas phase, and the experimental data are for cations in solution, in which interaction with the solvent would be expected to contribute stabilization to the cation, possibly affecting some protons more than others, depending on the association of the solvent with particular regions of the dication. While counterions undoubtedly also play a role, research by Eliasson et al. suggests that this association is relatively minor.[25] One of the ways in which solvent can be included in computations is the PCM method in Gaussian 03. We performed the GIAO calculations via this method, using DMSO as the model for SO_2ClF, at B3LYP/6-31G(d)//B3LYP/6-31G(d). ^1H NMR shifts calculated in this manner gave an improvement of r^2 from 0.63 to 0.87. In our previous examination of fluorenylidene dications **1**,[16−18,20] we did not observe a particularly poor correlation for H-1′/H-8′; however, it might be that the electronic nature of the indenyl system requires greater stabilization from the solvent. If the solvent is most closely associated with the region of the indenyl system near H-2, the solvent may also affect H-1′/8′, which are relatively close. When H-2 and H-1′/8′ are removed from the data set, plots of shifts calculated with solvent have r^2 equal to 0.89, while for shifts calculated without solvent, $r^2 = 0.95$. Thus both methods of calculation of ^1H NMR shifts give values with reasonable to good agreement with the experimental shifts.

As was true for the dication of tetrabenzo[5.5]fulvalene,[15] the upfield experimental and calculated chemical shifts show that both the indenyl and the fluorenyl ring systems of **3**$^{2+}$ are antiaromatic. In addition, they demonstrate that the fluorenyl system is more antiaromatic than the indenyl system, and that electron-withdrawing substituents on the phenyl ring in the 3-position of the indenyl system increase the antiaromaticity of **3**$^{2+}$ as evaluated through an increased paratropic shift.

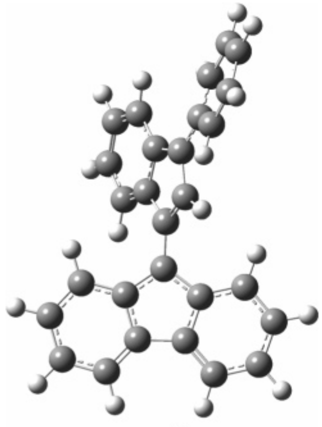
Nucleus Independent Chemical Shifts. A second measure of antiaromaticity is through the GIAO calculation of the nucleus independent chemical shift for a ghost atom placed in the center of a ring.[9,10] Concerns about the effect of the σ-electrons resulted in the suggestion that the ghost atom be placed 1 Å above the center of the ring.[10] Very recently, Schleyer et al.[26] have modified that to suggest that the value of the shielding tensor most appropriate for evaluation of a ring current in the π-system would be that which is perpendicular to the planar ring. Furthermore, while the best measurement of that tensor would be one in which localized molecular orbital (LMO) or canonical molecular orbital (CMO) dissection would allow selection of only π-contributions to the tensor ($NICS_{\pi zz}$), the effect of σ-electron density on the shielding tensor 1 Å above the center of the ring is sufficiently small so that this shielding tensor, $NICS(1)_{zz}$, can be used as an effective probe of aromaticity/antiaromaticity. A particular advantage of using the shielding tensor perpendicular to the plane of the ring is that the magnitudes of the NICS values are greater, allowing more effective evaluation of aromaticity/antiaromaticity, particularly, in similar systems. A positive value for NICS is associated with antiaromaticity. Its magnitude is dependent on the basis set and on the method used.[15] NICS values have no experimental equivalent, but because both the NICS and the proton chemical shifts are calculated by the same method, the agreement of calculated and experimental proton shifts helps give validity to the NICS values.

TABLE 3. Nucleus Independent Chemical Shifts, $NICS(1)_{zz}$, for 3a−f^{2+} [a] (vide supra)

	Indenyl ring system		Fluorenyl ring system		Phenyl rings
	NICS-5-1	NICS-6-1	NICS-5-1	NICS-6-1	NICS-6-1
3a^{2+}	44.61	7.18	70.25	26.88	−16.95
3b^{2+}	41.71	5.06	69.15	25.71	−15.66
3c^{2+}	39.04	2.86	68.84	25.21	−12.88
3d^{2+}	34.81	−1.62	67.50	23.78	−13.24
3e^{2+}	29.49	−4.38	64.34	20.09	−9.67
3f^{2+}	89.98	48.71	95.98	61.49	
indenyl cation	92.15	43.35			
fluorenyl cation			67.75	20.05	

[a] $NICS(1)_{zz}$ calculated 1 Å above the center of each ring in the indenyl and fluorenyl systems using the GIAO method with the B3LYP/6-31G(d) level on geometries optimized at the B3LYP/6-31G(d) level. The values reported are for the shielding tensor perpendicular to the plane of the ring. NICS values were calculated for the indenyl, fluorenyl, and phenyl rings individually, with the ring system under examination placed in the *XY* plane. NICS values for the five-membered rings are indicated as NICS-5-1, those for the six-membered rings as NICS-6-1.

NICS values are calculated for ghost atoms placed above and below the plane of the ring. The optimized geometry for **3**$^{2+}$ shows that the fluorenyl and indenyl ring systems have a dihedral angle of approximately 130°, as shown below for **3b**$^{2+}$.



3b^{2+}

The NICS values for ghost atoms placed on either side of each ring are slightly different because the environments on each side are slightly different. All NICS values for **3a−e**$^{2+}$ are given in the Supporting Information, while the averaged NICS values for each ring are given in Table 3, along with the values for the indenyl and fluorenyl monocations. The values clearly indicate that the dications are antiaromatic and that the magnitude of the antiaromaticity is affected by the substituent on the phenyl ring, with electron-withdrawing substituents resulting in the greatest antiaromaticity. The $NICS(1)_{zz}$ values suggest that the aromaticity of the substituted phenyl ring decreases from **3a**$^{2+}$ to **3e**$^{2+}$, consistent with a decrease in electron density through stabilization of the indenyl cation. The $NICS(1)_{zz}$ values

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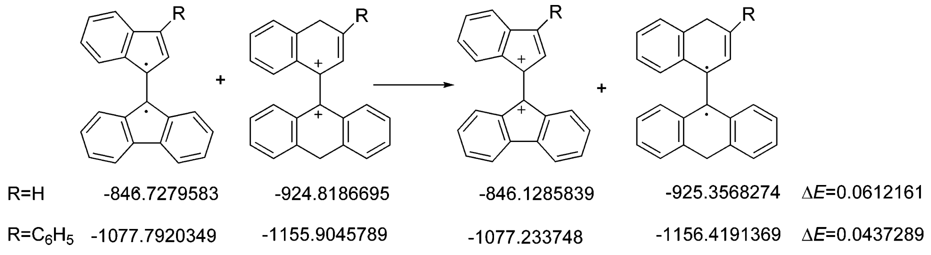
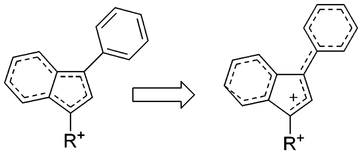


FIGURE 1. Reaction scheme for calculation of (anti)aromatic (de)stabilization energy for $\mathbf{3b}^{2+}$ and $\mathbf{3f}^{2+}$. Energies in hartrees were calculated for structures optimized at the B3LYP/6-31g(d) level.

also support the conclusion from the ^{1}H NMR shifts that the fluorenyl system is more antiaromatic than the indenyl system in $\mathbf{3}^{2+}$.

Effect of the 3-Phenyl Substituent on the Antiaromaticity of the Indenyl Ring in $\mathbf{3}^{2+}$. Our premise in examining indenylidenefluorene dications was based on the assumption that indenyl systems would be more antiaromatic than fluorenyl systems; however, this appears not to be true for $\mathbf{3}^{2+}$. Did we overcompensate with the addition of a phenyl substituent in the 3-position? That is, did the ability of the phenyl substituent to stabilize the positive charge cause a change in the pattern of delocalization so that the system behaved more like an allylic cation and a benzene ring, as in **4**, as opposed to the complete delocalization shown in **5**?



5 **4**

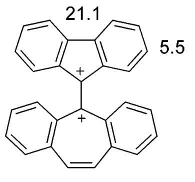
The NICS(1)$_{zz}$ values for the indenyl system indicate that the system is still antiaromatic, so the resonance hybrid is a composite of **4** and **5**. In addition, the dihedral angles for the phenyl rings with the indenyl systems of $\mathbf{3a}-\mathbf{e}^{2+}$, given in the Supporting Information, are approximately 160°. If **4** was the only resonance form, the dihedral angle would be closer to 180°. If we were to be able to examine the unsubstituted analogue of $\mathbf{3}^{2+}$, $\mathbf{3f}^{2+}$, would the indenyl system be more antiaromatic? We have been unable to observe $\mathbf{3f}^{2+}$ experimentally yet, but the calculated NICS(1)$_{zz}$ values are given in Table 3. It is apparent that the absence of the phenyl substituent has a dramatic effect on the antiaromaticity of the indenyl system, but it is still not as antiaromatic as the fluorenyl system. The reason for the diminished antiaromaticity of the indenyl system over the fluorenyl system may lie with the ability of the singly benzannulated five-membered ring of the indenyl system to distort more effectively than the doubly benzannulated ring of the fluorenyl system. That is under investigation in our laboratories and will be discussed in a second paper examining the structural and energetic measures of antiaromaticity of these systems.

TABLE 4. Calculated Values of Magnetic Susceptibility, Χ, and Magnetic Susceptibility Exaltation, Λ, for 3a−f$^{2+\,a}$

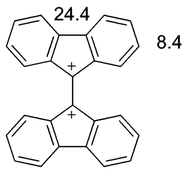
	Χ	Λ
$\mathbf{3a}^{2+}$	−118.22	57.95
$\mathbf{3b}^{2+}$	−92.27	59.17
$\mathbf{3c}^{2+}$	−102.16	55.47
$\mathbf{3d}^{2+}$	−102.76	55.41
$\mathbf{3e}^{2+}$	−115.76	48.67
$\mathbf{3f}^{2+}$	11.46	121.28

[a] Magnetic susceptibility calculated with the CSGT method, B3LYP/6-31G(d), on geometries calculated at B3LYP/6-31G(d).

The increase in the antiaromaticity of the indenyl system with the removal of the phenyl substituent is not surprising, but the increase in the antiaromaticity of the fluorenyl system is larger than might be expected since the indenyl and fluorenyl ring systems are not planar. We have observed that changing the R substituent on **1** affects the antiaromaticity of the fluorenyl system. As the substituent R$^+$ becomes more antiaromatic, the antiaromaticity of the fluorenyl system becomes greater. This effect is shown for $\mathbf{7}^{2+}$ and $\mathbf{8}^{2+}$, with the NICS(1) values shown by the appropriate ring system.[27] While the effect of changing the R substituent from the dibenzotropylium cation to the fluorenyl cation is not large, the trend is consistent with that observed for $\mathbf{3a}-\mathbf{e}^{2+}$ and $\mathbf{3f}^{2+}$.



$\mathbf{7}^{2+}$



$\mathbf{8}^{2+}$

Magnetic Susceptibility Exaltation. The final method we considered for evaluation of aromaticity/antiaromaticity using magnetic criteria is the determination of the magnetic susceptibility exaltation, Λ. The method relies on the observation that, while the magnetic susceptibility of most compounds/species is a summation of the magnetic susceptibility of the individual atoms and bonds, in the case of an aromatic molecule, the presence of a ring current gives additional magnetic susceptibility, an exaltation. A molecule is aromatic when $\Lambda < 0$ and antiaromatic when $\Lambda > 0$. The magnetic susceptibility exaltation is determined by comparing the calculated magnetic susceptibility of a species to that of a reference system in which increments representing the localized bonds are summed; see Supporting Information for additional details of the calculations. Table 4 contains the calculated values of magnetic susceptibility, Χ, and Λ for $\mathbf{3a}-\mathbf{f}^{2+}$, calculated with the CSGT method. Magnetic susceptibilities can also be calculated with the IGLO method,[28] but we have found that the correlation of experimental chemical shifts with those calculated using the CSGT method is better[20] than chemical shifts calculated with the IGLO method. The values of Λ indicate that $\mathbf{3}^{2+}$ are antiaromatic. The decrease in Λ with decrease in the electron-withdrawing ability of the

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(27) The NICS values reported here are NICS(1), not NICS(1)$_{zz}$; see ref 19.

(28) Kutzelnigg, W.; Schindler, M.; Fleischer, U. *NMR, Basic Principles and Progress*; Springer-Verlag: Berlin, Germany, 1990.

substituent in general follows the trends seen both with the NICS(1)$_{zz}$ calculations and ^{1}H NMR shifts. As was true for NICS, **3f**$^{2+}$ is substantially more antiaromatic than **3a**−**e**$^{2+}$.

Although the primary focus of this paper is on the use of magnetic properties to evaluate antiaromaticity, it is appropriate to briefly consider how other measures of aromaticity/antiaromaticity, such as those using the energetic criteria, evaluate the relative antiaromaticity of the phenyl-substituted dications of indenylidenefluorene, such as **3b**$^{2+}$ and **3f**$^{2+}$. The aromatic stabilization energy for formation of **3b**$^{2+}$ and for **3f**$^{2+}$ was calculated by the isodesmic reaction scheme shown in Figure 1. We have found that radical species are appropriate species in the isodesmic reaction schemes used to evaluate the destabilization of the fluorenyl cation.[1] The energy difference shown was calculated by subtracting the energies of the reactants from the energies of the products. Thus the larger and more positive ΔE, the less stable the species examined. The (anti)aromatic (de)stabilization energy for **3b**$^{2+}$ was 27.44 kcal/mol; that of **3f**$^{2+}$ was 38.41 kcal/mol. Thus **3f**$^{2+}$ is less stable than **3b**$^{2+}$, consistent with its greater magnetic susceptibility exaltation and larger, more positive NICS(1)$_{zz}$ values.

Summary

The dications of **3a**−**c**$^{2+}$ have been characterized experimentally via their ^{1}H NMR shifts, which show satisfactory agreement with calculated ^{1}H NMR shifts when those calculations include the effect of solvent. The agreement is markedly poorer for protons H-2 of the indenyl system and H-1/8 of the fluorenyl system in the absence of solvent in the calculations. There is good agreement between experimental and calculated chemical shifts for the remaining protons of the system, giving support to the NICS values calculated by the same method and allowing extension of the examination of antiaromaticity to **3d**,**e**$^{2+}$. The chemical shifts and NICS values both show that the indenyl system is less antiaromatic than the fluorenyl system. The presence of a phenyl substituent in the 3-position of the indenyl ring is responsible for a decrease in the antiaromaticity of that ring system, but even when the phenyl substituent is absent, the indenyl system of **3f**$^{2+}$ is less antiaromatic than the fluorenyl system. The greater antiaromaticity of **3f**$^{2+}$ over **3b**$^{2+}$ was supported by ASE calculations.

Experimental Section

The olefin precursors to **3a**−**e** were synthesized by Peterson olefination of the appropriate substituted 3-phenylindene with fluorenone, as described below for the synthesis of **3a**. Experimental details for the synthesis of the appropriate 3-phenylindenes and ^{1}H NMR data for **3a**−**e** and for **3a**−**d**$^{2+}$ can be found in the Supporting Information.

3-(*p*-Trifluoromethylphenyl)-9-(1*H*-indenylidene)-9*H*-fluorene, 3a. To 1-(4-trifluoromethylphenyl)indene (0.559 g, 2.20 mmol) in 30 mL of dry THF at −78 °C was added 2.02 mL of *n*-butyllithium (3.23 mmol), giving a dark red solution. After 10 min, trimethylsilyl chloride (0.50 mL, 6.4 mmol) was added to the reaction mixture. The reaction mixture turned a slightly lighter shade of deep red. After 10 min, *n*-butyllithium (2.02 mL, 3.23 mmol) was added, and the reaction mixture returned to the deeper red color. After 10 min, 9-fluorenone (0.39 g, 2.20 mmol) in 10 mL of dry THF was added to the reaction mixture. The mixture was allowed to stir overnight, warming to room temperature, and was a deep maroon color the next morning. The reaction mixture was quenched with water and extracted with 2 × 40 mL of ether and 2 × 40 mL of water. The solvent was removed under a vacuum, giving a dark maroon oil. The oil was crystallized in 2-propanol, yielding a dark maroon powdery solid. Recrystallization from isopropyl alcohol gave 0.39 g of product (42% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.22 (t, 1H, H-6), 7.24 (t, 1H, H-7′), 7.28 (t, 1H, H-5), 7.31 (t, 1H, H-6′), 7.33 (t, 2H, H-2′ and H-3′), 7.41 (s, 1H, H-2), 7.52 (d, J = 6.5 Hz, 1H, H-4), 7.66 (d, J = 6.9 Hz, 2H, H-1′ and H-4′), 7.72 (d, J = 8.2 Hz, 2H, H-o), 7.83 (d, J = 7.8 Hz, 2H, H-m), 7.95 (d, J = 7.3 Hz, 1H, H-5′), 8.37 (d, J = 6.9 Hz, 1H, H-8′), 8.47 (d, J = 7.8 Hz, 1H, H-7). Anal. Calcd for $C_{29}H_{17}F_3$: C, 82.45; H, 4.06; F, 13.49. Found: C, 82.34; H, 4.15; F, 13.02.

3-(Phenyl)-9-(1*H*-indenylidene)-9*H*-fluorene, 3b. Same procedure as for **3a**, with the following exceptions: purification was achieved by flash column and then recrystallization in petroleum ether, and instead of 10 min intervals between each addition, 5 min intervals were used. Yield: 0.27 g (37%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.25 (t, 2H, H-6 and H-7′), 7.27 (t, 1H, H-5), 7.33 (t, 1H, H-6′), 7.34 (t, 2H, H-2′,3′), 7.40 (s, 1H, H-2), 7.43 (t, 1H, H-p), 7.51 (d, 2H, H-m), 7.61 (d, 1H, H-4), 7.69 (d, 2H, H-1′.4′), 7.78 (d, 2H, H-o), 8.02 (d, 1H, H-5′), 8.40 (d, 1H, H-8′), 8.52 (d, 1H, H-7). Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 95.03; H, 5.07.

3-(*p*-Fluorophenyl)-9-(1*H*-indenylidene)-9*H*-fluorene, 3c. Yield: 0.525 g (46.2%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.19 (t, 2H, H-6 and H-7′), 7.26 (d, 2H, H-m), 7.27 (t, 1H, H-5), 7.32 (t, 1H, H-6′), 7.34 (t, 2H, H-2′,3′), 7.35 (s, 1H, H-2), 7.54 (d, 1H, H-4), 7.69 (d, 2H, H-1′,4′), 7.74 (d of d, 2H, H-o), 8.00 (d, 1H, H-5′), 8.39 (d, 1H, H-8′), 8.50 (d, 1H, H-7). Anal. Calcd for $C_{28}H_{17}F$: C, 90.30; H, 4.60; F, 5.10. Found: C, 84.51; H, 5.52.

3-(*p*-Methylphenyl)-9-(1*H*-indenylidene)-9*H*-fluorene, 3d. Same procedure as for **3a**, with the following exceptions: purification was achieved by column separation and recrystallization in pentane. Yield: 0.35 g (48.4%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.42 (s, 3H, CH$_3$), 7.22 (t, 2H, H-6,7′), 7.23 (d, 2H, H-m), 7.27 (t, 1H, H-5), 7.31 (t, 2H, H-2′,3′), 7.32 (t, 1H, H-6′), 7.35 (s, 1H, H-2), 7.58 (d, 1H, H-4), 7.68 (d, 4H, H-1′,4′,o), 8.00 (d, 1H, H-5′), 8.37 (d, 1H, H-8′), 8.49 (d, 1H, H-7). Anal. Calcd for $C_{29}H_{20}$: C, 94.53; H, 5.47. Found: C, 94.05; H, 5.33.

3-(*p*-Methoxyphenyl)-9-(1*H*-indenylidene)-9*H*-fluorene, 3e. Same procedure as for **3a** with the following exceptions: instead of 10 min intervals between each addition, 2 h intervals were used. Yield: 0.78 g (46%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.90 (s, 3H, CH$_3$), 7.02 (d, J = 8.9 Hz, 2H, H-m), 7.23 (t, 2H, H-6,7′), 7.27 (t, 1H, H-5), 7.30 (s, 1H, H-2), 7.31 (t, 2H, H-2′,3′), 7.32 (t, 1H, H-6′), 7.58 (d, J = 7.5 Hz, 1H, H-4), 7.68 (d, J = 7.0 Hz, 2H, H-1′,8′), 7.72 (d, J = 8.4 Hz, 2H, H-o), 8.01 (d, J = 7.0 Hz, 1H, H-5′), 8.37 (d, J = 7.5 Hz, 1H, H-8′), 8.49 (d, J = 7.5 Hz, 1H, H-7). Anal. Calcd for $C_{29}H_{27}O$: C, 90.60; H, 5.24. Found: C, 87.23; H, 5.36.

Preparation of Dications by Chemical Oxidation. SbF$_5$ (∼0.7 mL, ∼9 mmol) was added to a graduated centrifuge tube in a drybox, and the tube was capped with a septum and placed in an ice bath. SO$_2$ClF[29] (1.3 mL) at −78 °C was transferred by cannula into the centrifuge tube. The contents were mixed on a vortex stirrer until homogeneous, and the solution was cooled to −78 °C. The neutral precursor (∼3 mmol) was added in small portions, followed by vortex mixing and cooling to −78 °C. Samples for NMR analysis were kept at −78 °C until needed and transferred by chilled pipet into a chilled NMR tube. A capillary tube with acetone-d_6 was then inserted into the NMR tube to serve as an external standard and deuterium lock. At the conclusion of NMR studies, samples were quenched with 20 mL of saturated K$_2$CO$_3$ in methanol at −78 °C. The resulting mixture was extracted with CH$_2$Cl$_2$ and solvent removed under vacuum. The majority of the isolated solid was starting material, with 60−80% recovery of starting material.

Computational Methods. Geometries were optimized at B3LYP/6-31G(d) density functional theory levels with the Gaussian 98[30]

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(29) Reddy, V. P.; Bellew, D. R.; Prakash, G. K. S. *J. Fluorine Chem.* **1992**, *56*, 195−197.

and 03[24] program packages. The chemical shifts were calculated at B3LYP/6-31G(d) using the GIAO approach with the Gaussian 98 or 03 program packages on the optimized geometries. The nucleus independent chemical shifts (NICS$(1)_{zz}$)[9,26] were obtained from the chemical shift tensor perpendicular to the ring for a dummy atom placed 1 Å above the center of each ring. Magnetic susceptibilities were calculated with the CSGT method in the Gaussian 98 package on optimized geometries.

Acknowledgment. We thank the Welch Foundation, Grant W-794, and the National Science Foundation, Grant CHE-0242227, for support of this work.

Supporting Information Available: Plot of calculated versus experimental shifts: without solvent, for all protons, for indenyl/fluorenyl systems, with solvent for indenyl/fluorenyl systems; NICS$(1)_{zz}$ for all rings of **3a**−**f**$^{2+}$, dihedral angles between ring systems and between the phenyl and indenyl systems for **3a**−**e**$^{2+}$, increments for magnetic susceptibility exaltation calculations; plots of average ^{1}H NMR shifts versus Λ and $\sum$NICS$(1)_{zz}$ for **3a**−**f**$^{2+}$; plots of average ^{1}H NMR shifts versus $\sum$NICS$(1)_{zz}$ for fluorenyl and indenyl systems of **3a**−**e**$^{2+}$, including the effect of ring size and radius; plots of average ^{1}H NMR shifts versus $\sum$NICS$(1)_{zz}$ for indenyl systems of **3a**−**e**$^{2+}$, including the effect of ring size and radius; experimental preparation of 3-phenylindenes; ^{1}H NMR spectra for **3a**−**e**; ^{1}H NMR spectra of **3a**−**d**$^{2+}$, calculated total energies, and [x,y,z] coordinates for **3a**−**e**$^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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