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Dications of Fluorenylidenes. Contribution of Magnetic and Structural Effects to the Antiaromaticity of Fluorenylidene Dications with Cyclic Substituents

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The antiaromaticity of fluorenylidene dications **1−5**, which contain cyclic cationic substituents, has been examined using magnetic criteria, NICS and magnetic susceptibility, and by structural criteria, HOMA. The magnetic criteria, including proton chemical shifts, strongly support the antiaromaticity of the fluorenyl ring system of these dications. HOMA values are a very insensitive measure of structural effects in polycyclic ring systems because they reflect the inability of the fused ring systems to respond to changes in aromaticity/antiaromaticity. Finally, in these systems, the interaction between the ring systems appears to occur primarily through a type of hyperconjugation, as demonstrated by a decrease in the bond lengths for the bonds connecting the ring systems. In conjunction with the evaluation of magnetic effects, the quality of the calculation of ^{1}H and ^{13}C NMR shifts was assessed by comparison with experimental data. The calculation of ^{13}C NMR shifts was excellent in all methods examined, but the quality of ^{1}H NMR shifts was substantially poorer in calculations using the IGLO method, basis set DZ or II. The CSGT method gives a superior correlation between experimental and calculated ^{1}H NMR shifts.

The understanding of the unique property of molecules such as benzene, which we call aromaticity, has focused the attention of generations of chemists and created the impetus for the synthesis of a number of interesting nonbenzenoid aromatic compounds.[1] As the molecules became more removed from benzene, the need to define aromaticity, particularly in terms of properties that could be measured, became more intense.[2,3] The characteristics of aromatic compounds fall into three general categories: energetic, structural, and magnetic.[4,5] The energetic criterion is based on the observation that benzene is thermodynamically more stable than its open-chain analogues, which requires that the appropriate open-chain analogue be defined. Assessment of aromaticity based on structural properties returns to the structure of benzene for the definition of those properties. Thus planarity and lack of bond length alternation are the primary descriptors of this property. The harmonic oscillator model of aromaticity (HOMA)[6−8] allows evaluation of the deviation of bond lengths in a species from the optimal bond length of benzene, considering both the increase in bond length alternation (a geometric contri-

bution to dearomatization) and the deviation from the mean bond length (an energetic contribution).[9] Magnetic criteria are based on the existence of a ring current that, while experimentally unobservable, can be measured indirectly through the chemical shift of the protons,[10] the magnetic susceptibility exaltation (Λ), and anisotropy,[11−14] as well as evaluated through the calculated nucleus independent chemical shift (NICS, vide infra).[15] The question of whether these criteria can be quantitatively related, i.e., whether conclusions drawn about relative aromaticity agree under all the criteria, is under vigorous debate.[16,17] Even the most recent article, which was intended to "present an authoritative assessment of all of this work"[16] ends with the authors divided in their conclusions. Authors Cyrañski, Krygowski, and Katritzky stress that for a system to be considered fully aromatic, it must follow all the main criteria, while Schleyer suggests that the special behavior associated with induced ring currents is most closely related to the cyclic electron delocalization that characterizes aromatic species.

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If the situation with aromatic compounds is not clearly defined, the situation with antiaromatic compounds is even more uncertain, in part because the instability predicted for antiaromatic species has prevented the characterization of a sufficient number of species to allow an understanding of antiaromaticity to be developed. We have discovered that dications of fluorenylidenes, **1**–**6**, formed by oxidation of their olefin precursors with SbF_5 in SO_2ClF, possess appreciable antiaromaticity,[18–21] as evidenced by the substantial paratropic ^{1}H NMR shift of the fluorenyl ring. Magnetic susceptibility exaltations[12,15] and nucleus independent shifts for **1a** and **6** and 9-substituted fluorenyl monocations confirmed the antiaromaticity of the fluorenylidene dications,[22,23] in contrast to the lack of antiaromaticity of the fluorenyl monocation.[24,25]

We have recently determined that antiaromaticity for **6**, as evaluated through NICS calculations, is directly related to the electron-withdrawing ability of the substituent, with the most electron-withdrawing substituent resulting in the most antiaromatic dication, when the fluorenyl cationic portion of the molecule is considered.[23] In this paper, we have extended those calculations to **1**–**5**, allowing an evaluation of the effect of geometry on the transmission of substituent effects. We include also an evaluation of magnetic susceptibility exaltation calculated by a variety of methods. Finally, we discuss the efficacy of structural effects, through HOMA calculations, in evaluation of aromaticity/antiaromaticity.

Relationship between Experimental and Calculated Chemical Shift. There are several measures of ring current that are available through calculation, including magnetic susceptibility, used to calculate magnetic susceptibility exaltation, and nucleus independent chemical shift. Magnetic susceptibility exaltation refers to an absolute susceptibility that is different than that expected on the basis of an incremental system.[11] The nucleus independent chemical shift (NICS)[15] is based on the observation that protons in the center of an aromatic ring system experience a dramatic upfield shift because of the effect of the ring current.[26,27] By computing magnetic shieldings at ring centers, effectively putting a dummy atom in the center of the ring system to "sense" the effect of the ring current, one can evaluate both the aromatic or antiaromatic character through the sign of the shielding, with aromatic species possessing negative NICS, as well as the relative magnitude of the aromaticity/antiaromaticity through the size of the shielding. Because the local contributions of the σ bonds[28–30] might

a, Y=CF$_3$
b, Y=Br
c, Y=Cl
d, Y=H
e, Y=F
f, Y=CH$_3$
g, Y=OCH$_3$
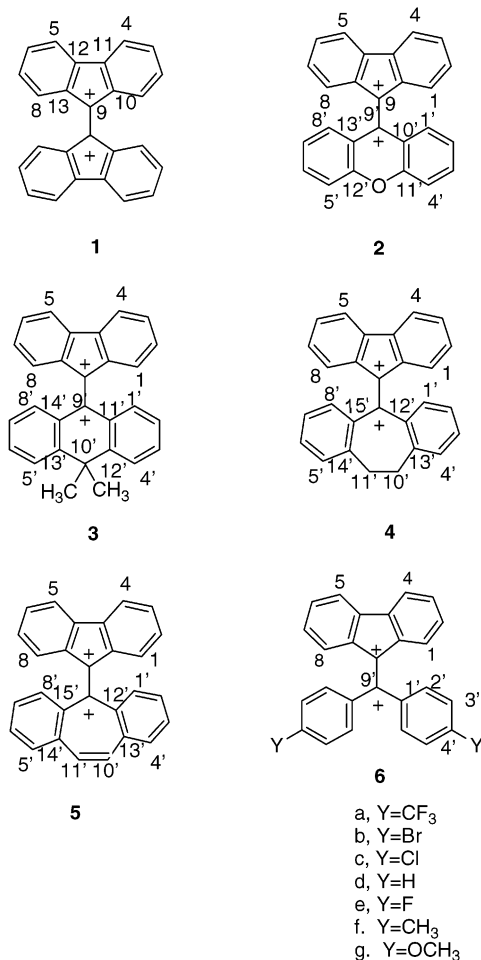
affect the magnetic shieldings, NICS values are normally calculated in the plane of the ring and at a distance, usually 1 Å, above the plane of the ring. NICS is usually calculated with the GIAO method in the Gaussian suite of programs.[31,32] Magnetic susceptibility is most commonly calculated using the IGLO program;[33] however, the

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CSGT method in Gaussian has also been used to evaluation magnetic susceptibility.[34-41]

The magnitude of chemical shifts, NICS, or magnetic susceptibility is dependent upon the basis set used for the calculation,[22,42,43] and it seemed prudent to begin with a comparison of the experimental NMR shifts for those dications for which measurements exist and their calculated shifts. The experimental chemical shifts for **1–5** have been reported[19] and were compared with the ^{13}C shifts calculated with five different methods and/or basis sets, GIAO at the RHF level with basis set 6-312G(d), with the density functional theory method using the B3LYP functionals with the 6-312G(d) basis set, via the CSGT method using B3LYP functionals with the 6-312G-(d) basis set, and from the IGLO[33] method with basis sets DZ and II. The results of all calculations are reported in Supporting Information, as well as the correlation coefficients r^2 for comparison of experimental shifts with the calculated ^{13}C and ^{1}H NMR shifts for each method and for each dication. As expected, all methods show a linear relationship between experimental and calculated ^{13}C NMR shifts, but the quality of that correlation varies with the method, with best correlation for CSGT calculations using the density functional theory method, with a range of r^2 from 0.927 to 0.998 for individual systems and 0.988 for all systems. A good correlation between experimental ^{13}C NMR shifts and shifts calculated with density functional theory for aliphatic cations has been reported recently.[44]

The agreement between the experimental and calculated proton shifts for **1–5**[19] is not quite as good, as is apparent from the correlation coefficients reported in Supporting Information. Because proton shifts cover a smaller range than do carbon shifts, it has been assumed that the accuracy with which shifts can be calculated would be insufficient for proton shifts.[45] However, this also means that proton shifts are a more sensitive measure of the quality of the calculations. It is apparent that the correlations suggest that NICS calculated using density functional theory are slightly more reliable than values calculated using ab initio methods. The proton shifts calculated with density functional theory methods were also closest to the experimental values, with the ratio of $\delta_{exp}/\delta_{calc}$ of 0.86.

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TABLE 1. Experimental and Calculated [1]H Proton Shifts for 1–5

proton	exptl shift	CSGT, B3LYP/6-31G(d)	IGLO, II
1			
H-1	5.33	3.29	7.38
H-8	5.33	3.29	7.39
H-2,7	5.16	3.46	6.28
H-3,6	5.77	4.11	8.53
H-4,5	4.97	2.77	6.31
r^2		0.874	0.922
2			
H-1,8	4.86	2.75	6.78
H-2,7	5.06	3.38	6.20
H-3,6	5.86	4.32	8.58
H-4,5	5.21	3.17	6.51
H-1′,8′	7.58	6.30	8.30
H-2′,7′	7.09	6.03	7.95
H-3′,6′	7.59	6.39	9.59
H-4′,5′	7.27	5.68	8.19
r^2		0.978	0.672
3			
H-1,8	5.13	3.08	7.06
H-2,7	5.18	3.61	6.23
H-3,6	5.94	4.39	8.55
H-4,5	5.31	3.26	6.52
H-1′,8′	7.73	6.42	8.31
H-2′,7′	7.02	5.70	7.50
H-3′,6′	7.29	6.0	9.60
H-4′,5′	7.06	5.82	7.68
CH₃	0.70	1.13	1.40
r^2		0.895	0.882
4			
H-1,8	5.16	3.15	6.99
H-2,7	5.25	3.65	6.22
H-3,6	5.99	4.38	8.53
H-4,5	5.38	3.26	6.52
H-1′,8′	7.87	6.53	8.39
H-2′,7′	6.79	5.56	7.24
H-3′,6′	7.21	5.83	9.60
H-4′,5′	6.63	5.08	7.13
H-11′,12′,α	5.16	3.15	2.74
H-11′,12′,β	5.25	3.65	2.79
r^2		0.960	0.839
5			
H-1,8	5.01	2.92	6.86
H-2,7	5.24	3.62	6.21
H-3,6	6.10	4.47	8.58
H-4,5	5.57	3.45	6.7
H-1′,8′	8.58	7.48	8.81
H-2′,7′	7.58	6.48	8.59
H-3′,6′	7.69	6.48	9.55
H-4′,5′	7.77	6.17	8.54
H-11′,12′	8.28	6.30	9.36
r^2		0.958	0.706
r^2 (all)		0.933	0.792

The correlations for shifts calculated by the IGLO method are particularly poor. This suggests that calculation of magnetic susceptibility would be appreciably better by the CSGT method, at least in these systems, than by IGLO methods; we will use results from the CSGT method in evaluation of the magnetic properties of **1–5**. However, because IGLO methods are more commonly used,[46] it is appropriate to examine the differences in the calculational results more carefully. Table 1 contains the experimental proton shifts for **1–5** and the shifts calculated by the CSGT method (B3LYP/6-31G-(d)) and by the IGLO method, basis set II. It is obvious

(45) A search of *Chemical Abstracts* reveals 459 references to calculations of magnetic properties by IGLO and only 46 references to CSGT calculations.
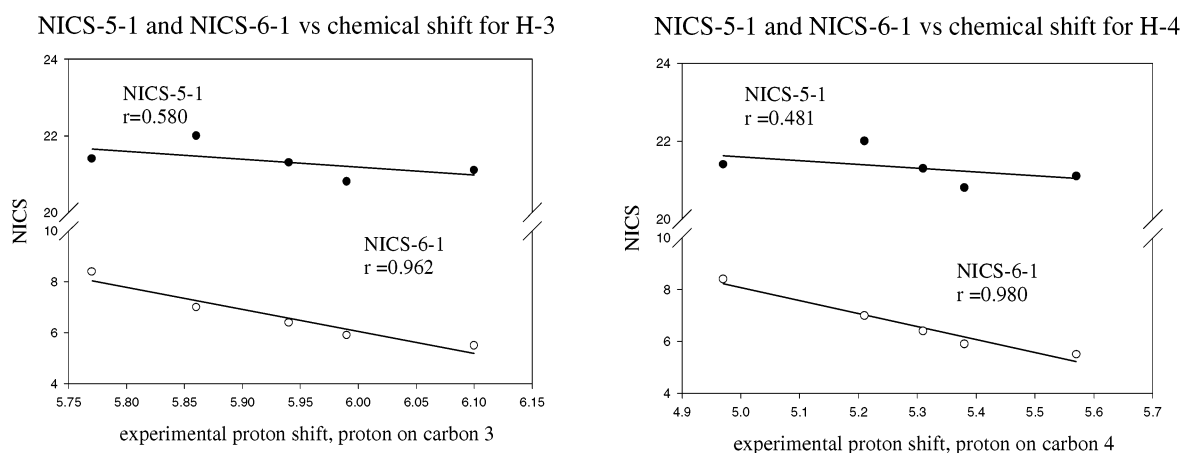
NICS-5-1 and NICS-6-1 vs chemical shift for H-3

NICS-5-1 and NICS-6-1 vs chemical shift for H-4

FIGURE 1. Comparison of calculated NICS values with experimental proton shifts.

TABLE 2. Nucleus Independent Chemical Shift Values for Cyclic Dications[a,b]

| compd | fluorenyl system | | nonfluorenyl system | |
	NICS-5	NICS-6	NICS-x center ring	NICS-6 benzene
1	30.1 (21.4)	14.3 (8.4)		
2	31.0 (22.0)	12.6 (7.0)	−9.2 (−8.7)	−7.1 (−11.0)
3	30.0 (21.1)	11.6 (6.1)	0.8 (−2.7)	−5.6 (−8.8)
4	29.6 (20.8)	11.3 (5.9)	3.0 (2.5)	−3.8 (−7.1)
5	29.9 (21.1)	10.8 (5.5)	−6.8 (−8.9)	−10.1 (−12.4)

[a] NICS values at 1 Å above plane of ring are in parentheses.
[b] B3LYP/6-31G(d) on geometries optimized at B3LYP/6-31G(d)

that both methods do not calculate the magnitude of the chemical shift correctly; with the CSGT method underestimating the shift by an average of 1.7 ppm, a paratropic shift, while the IGLO method overestimates it by an average of 1.2 ppm, giving an enhanced diatropic shift.

Use of NICS To Evaluate Antiaromaticity. The nucleus independent chemical shifts (NICS) were calculated for each ring of **1−5** and are reported in Table 2. As mentioned above, NICS were calculated both within the plane of the ring system and 1 Å above, NICS-5-1 and NICS-6-1, to reduce the effect of local contributions of the σ bonds to the magnetic shielding. Examination of NICS for the fluorenyl systems shows that both the five- and six-membered rings have appreciable antiaromaticity, with a greater degree of antiaromaticity in the five- rather than the six-membered rings.

Validation of the quality of the NICS calculations comes from a comparison of those values with the experimentally determined ¹H chemical shifts. We have shown in previous work[19] that the chemical shift of protons on carbons 1 and 2 are affected by not only the ring current of the fluorenyl system but also the nature of the cationic ring system on carbon 9. Specifically, because the ring systems of **1−5** are almost perpendicular, the protons on carbon 1 and, to a lesser extent carbon 2, are positioned over the center of the opposing ring system. When that ring system is aromatic, **2** and **5**, those protons are shifted slightly upfield; when that ring system is antiaromatic, as in **1**, the protons are shifted slightly downfield. Thus, these protons do not serve as a useful probe of the antiaromaticity of the fluorenyl system. The plots of the shifts of protons on carbons 3

and carbons 4 respectively vs NICS-5-1 and NICS-6-1 of the fluorenyl ring systems are shown in Figure 1. It is apparent that the antiaromaticity of the fluorenyl cation
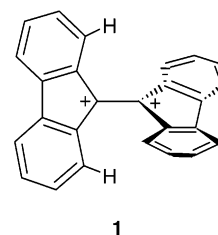
1

is affected by the nature of the substituent on carbon 9 of the fluorenyl system, the "opposing ring system", with the most antiaromatic substituent creating the most antiaromatic fluorenyl system and the most aromatic substituent creating the least antiaromatic fluorenyl system. The correlations between chemical shift and NICS values are good, with the best correlation occurring between the proton shifts and the NICS values for the six-membered ring. As has been seen in other systems,[23] the changes in NICS-6-1 are not mirrored exactly by changes in NICS-5-1.

NICS calculations for the opposing ring systems are also given in Table 2 and serve to validate the use of NICS in these systems. As would be expected, the xanthylium and dibenzotropylium ring systems show appreciable aromaticity, both in the aromatic center ring and in the benzannulated rings. Similarly, the NICS values for the dibenzannulated cyclohexyl and cycloheptyl ring systems show a lack of aromaticity in the center rings and reasonable aromaticity in the benzannulated ring systems.

Use of Magnetic Susceptibility Exaltation (Λ) To Evaluate Antiaromaticity. Magnetic susceptibility exaltation is evaluated through the difference between the calculated susceptibility χ_{tot} and the "normal" values deduced from increments for hypothetical polyene systems without cyclic delocalization. The increments were obtained by calculation using IGLO, basis set II, and CSGT, B3LYP/6-31G(d), on localized cations whose geometries were optimized at the B3LYP/6-31G(d) level. In the case of **1−5**, the localized reference systems were constructed in two ways. In the first approach, the

TABLE 3. IGLO/II and CSGT/B3LYP/6-31G(d) Calculated Magnetic Susceptibilities (ppm cgs), Increment Values[a]

increment	precursor	χ, II basis	increment[a]	χ, **6−10** Σ of increments	χ, CSGT basis	increment[a]	χ, **6−10** Σ of increments
$(>C-C<)^{2+}$	tetramethylethylene dication	−55.44	6.56[b,c]		−35.46	4.42	
$(>C=C<)$	2,3-dimethyl butene	−74.09	−12.09[b,c]		−50.07	−10.19	
cis −CH=CH−	*cis*-2-butene	−47.57	−16.57[c]		−31.89	−11.95	
−O−	dimethyl ether	−34.50	−4.50		−23.02	−3.08	
$-C(CH_3)_2-$	neopentane	−69.78	−38.78		−45.21	−25.27	
$-CH_2CH_2-$	butane	−58.80	−27.80		−36.25	−16.31	
6-(2 methyls)	**6**	−99.85	−68.85	−83.90	−32.04	−12.10	−63.76
7-(2 methyls)	**7**	−185.68	−154.68	−88.40	−114.01	−94.07	−66.84
8-(2 methyls)	**8**	−155.18	−124.18	−96.34	−102.54	−82.60	−71.91
9-(2 methyls)	**9**	−178.01	−147.01	−122.65	−116.77	−96.83	−89.03
10-(2 methyls)	**10**	−187.38	−156.38	−100.47	−124.57	−104.63	−75.71

[a] Increment values derived from calculated magnetic susceptibility for each precursor minus the magnetic susceptibility for ethane (−31.00/IGLO; −19.94/CSGT) [b] Values for these increments are determined by subtracting four methyl groups, twice the magnetic susceptibility of ethane, from the susceptibility of the parent species. [c] Zyweitz, T. K.; Jaio, H.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1998**, *63*, 3417−3422.

increments for each set of bonds were summed to give χ_{tot} for the localized reference system. This masked the differences in the contribution of the fluorenyl system because the magnetic susceptibility of the fluorenyl system in **5**, for example, which was anticipated to reflect antiaromatic behavior, would be offset by the magnetic susceptibility of the tropylium system, which would be opposite in sign. To allow the differences in the fluorenyl systems to be most obvious, a second set of reference systems were constructed using the calculated magnetic susceptibility of the intact substituent, **7−11**, and the localized increments for calculation of the fluorenyl system. Because the calculated magnetic susceptibility
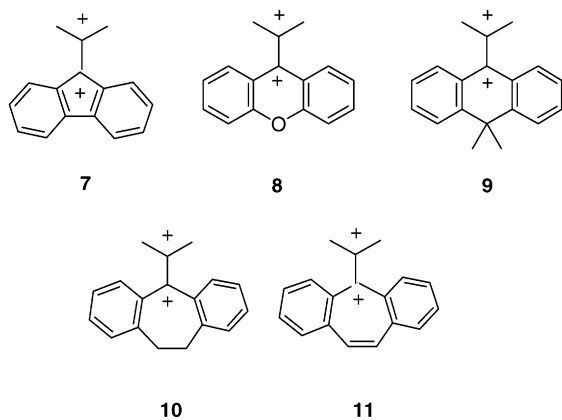
of the "intact" increments would include their contribution to the magnetic susceptibility of the dication, the difference between χ_{tot} for the dication and χ_{tot} from summation of increments by this method would reflect the magnetic susceptibility exaltation of the fluorenyl system alone. The increments, and the cations or dications from which the increments were derived, are listed in Table 3.

The calculated χ_{tot} for dications **1−5** and their magnetic susceptibility exaltation, Λ, calculated using each of the two reference systems are listed in Table 4. It is apparent that the trends shown by NICS calculations for **1−5** are not demonstrated in the values for Λ calculated by summation of increments derived from individual bonds. However, when the reference system that included increments from **7−11** was used, the CSGT calculations show a general trend of decreasing antiaromaticity from **1−5**

TABLE 4. Magnetic Susceptibility Exaltation from IGLO and CSGT Calculations

	χ, IGLO	Λ from Σ of increments	Λ using increments from **6−10**	χ, CSGT	Λ from Σ of increments	Λ using increments from **6−10**
1	−152.66	21.7	6.65	−36.25	95.69	44.03
2	−213.00	−26.2	32.14	−121.67	13.36	40.58
3	−234.30	−21.19	3.17	−129.00	28.21	36.01
4	−215.35	−13.19	5.48	−110.94	37.32	37.68
5	−242.97	−52.04	3.87	−137.35	6.55	35.45

suggested by NICS calculations. With the exception of **2**, which contains a heteroatom, the IGLO calculations also show a similar trend. The comparison of calculated with experimental proton shifts for **2** in Table 1 also show that the shifts calculated by the IGLO method are poorer than those calculated for other systems and those calculated by the CSGT method.

If the exaltation for **2** is not included, both the IGLO and CSGT methods indicate that the fluorenyl cationic system is antiaromatic in **1** and **3−5**. The IGLO calculations for Λ calculated from individual increments shows that, when the substituent is aromatic (**5**) or contains two benzene rings (**3** and **4**) the aromaticity of the substituent is greater than the antiaromaticity of the fluorenyl system, and the species as a whole is aromatic. When Λ is calculated for the isolated fluorenyl system, the values that range from 6.65 to 3.87 ppm cgs indicate that the ring system is antiaromatic. Substituted fluorenyl monocations were shown to possess Λ of −4.30 to −11.24 ppm csg[22] and were considered to be not antiaromatic.[25]

CSGT calculations of Λ appear to overstate the case for antiaromaticity. By analogy with the IGLO calculations, we would expect the values of Λ calculated from the summation of increments to show the dominance of the contribution from the aromatic systems of **2−5** and to be negative. In contrast, Λ calculated from the increment system are positive, indicating the dominance of the contribution from the antiaromatic fluorenyl systems. The calculation of Λ for isolated fluorenyl systems, with values ranging from 44.03 to 35.45 ppm cgs, indicates appreciable antiaromaticity in the fluorenyl systems. For reference, the magnetic susceptibility exaltation for benzene, calculated by the CSGT method, is −15.1 ppm cgs.[34] The enhanced antiaromaticity/paratropicity from these calculations was also evident in the calculation of the proton shifts, which were substantially upfield from

the experimental shifts. Until there is a larger body of calculations of Λ and ^{1}H NMR shifts by the CSGT method, which can serve to put some context to the meaning of the magnitude of the values, we are best served by using the values to indicate trends.

As stated previously, the values of Λ calculated by either method, with the exception of **2** by the IGLO method, show a general decrease that parallels both the calculation of antiaromaticity by NICS and the change in the shifts of protons 3 and 4. The correlation coefficient r^2 is approximately 0.902 for Λ calculated by either method vs the experimental proton shift. Again, the degree of antiaromaticity is shown to be affected by the nature of the substituent on carbon 9.

Evaluation of Bond Lengths as a Measure of Antiaromaticity. Among the properties of potentially aromatic compounds that can be evaluated experimentally are the C–C bond lengths that in benzene are equal and intermediate in length between single and double bonds. Thus, an increase in bond length and a deviation from the optimal length found in benzene are considered as evidence of a decrease of aromaticity.[6] The harmonic oscillator model of aromaticity (HOMA)[7,8] examines the deviation of bond lengths from the optimal bond length found in benzene as shown:

$$HOMO = 1 - \frac{\alpha}{n}\Sigma(R_{opt} - R_i)^2$$

where n is the number of bonds taken in the summation and α is an empirical constant chosen to give HOMA = 0 for the hypothetical Kekulé structure of cyclohexatriene (where the bond lengths for CC bonds are equal to the bond lengths in an acyclic polyene, 1,3-butadiene) and HOMA = 1 for the system in which the CC bond lengths are all equal to the optimal length, i.e., benzene for hydrocarbon systems. The quantity R_{opt} is 1.388 Å for CC bonds, R_{av} stands for the average bond length, and R_i is the individual bond length.

It is possible to separate the equation to examine the effect of changes in the average bond length, which is presumed to be a term reflecting the energy cost of distortions from the optimal length and denoted EN, and to examine the effect of increased bond length alternation, which is considered a term reflecting geometry, GEO, as shown

$$HOMO = 1 - \left[\alpha(R_{opt} - R_{av})^2 + \frac{\alpha}{n}\Sigma(R_{av} - R_i)^2\right] = 1 - EN - GEO$$

Although experimental data for the bond lengths of these dications is probably impossible to obtain, satisfactory agreement between experimental data and geometry optimizations at the density functional theory level (B3LYP/6-31G(d)) for other systems suggests that examination of these systems through their calculated geometries would be appropriate.[47–40] The calculated HOMA values, and those for the GEO and EN terms, for

TABLE 5. HOMA Values for 1–5

| | GEO | EN | HOMA | 5-ring | | | 6-ring | | |
				GEO	EN	HOMA	GEO	EN	HOMA
fluorenyl system									
1	0.18	0.18	0.64	0.10	0.76	0.14	0.10	0.08	0.83
2	0.18	0.17	0.65	0.20	0.48	0.32	0.10	0.08	0.82
3	0.18	0.17	0.65	0.20	0.48	0.32	0.10	0.08	0.82
4	0.18	0.17	0.65	0.20	0.50	0.30	0.07	0.08	0.85
5	0.18	0.17	0.65	0.21	0.49	0.30	0.09	0.07	0.84
fluorenyl cation	0.19	0.15	0.66	0.17	0.66	0.17	0.10	0.07	0.83

the fluorenyl systems of **1–5** are listed in Table 5 along with the values for the fluorenyl cation.[23]

Selected calculated bond lengths can be found in Supporting Information. In addition, the values have been further dissected into those relating to each ring system. The HOMA values for the six-membered rings suggests that there is very little variation in either the degree of bond length alternation (GEO term) or the deviation from the optimal bond length (EN term) as a function of variation in the "opposing ring system". However, the five-membered ring of the fluorenyl system of **1** is markedly different from those of the other dications examined, both in terms of bond length alternation and in terms of deviation from optimal bond length. The lack of bond length alternation shown through the GEO term is overwhelmed by the term reflecting deviation from optimal bond length, EN, giving a HOMA value that is substantially smaller than those of the other systems. However, the overall HOMA values for **1–5** show very little variance, suggesting that HOMA in polycyclic aromatic ring systems is a very insensitive measure of aromaticity/antiaromaticity. In addition, the values for the fluorenyl cation, which has been suggested to possess little antiaromaticity,[22,24,25] are quite similar to those of **1–5**, again suggesting that this measure of aromaticity/antiaromaticity is very insensitive.

A greater concern lies in the comparison of these values with those from other systems. For example, the HOMA value for these systems is larger than that calculated for the external rings of anthracene, which has HOMA of 0.512.[50] This would suggest that these rings of anthracene are less aromatic than these dications **1-5**, but the calculated NICS value is −9.6, indicating aromaticity.[51] Benzannulation of the fluorenyl system has a marked affect on the ability of the system to alter its geometry in a manner that might be related to aromaticity/antiaromaticity. For this reason, we think that caution must be used in conclusions drawn about relative aromaticity/antiaromaticity in systems that contain substantial benzannulation.

Substituent Effect on the Antiaromaticity of the Fluorenyl Cation. The magnetic evidence supports the antiaromaticity of the fluorenyl cationic system of **1–5**. The remaining question involves how the substituent is able to affect the antiaromaticity of the fluorenyl system.

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(51) The NICS values reported in this article are done with a basis set that is known to overestimate aromaticity, but the proton chemical shifts for anthracene, 7.98 and 7.44 ppm, certainly do not indicate antiaromaticity.

TABLE 6. Experimental ^{13}C NMR Shifts as a Measure of Electron Delocalization[a]

carbon	1	2	3a	4	5	av	SD
1,8	145	146	146	146	145	146	0.55
2,7	136	136	136	136	135	136	0.45
3,6	159	159	158	157	157	158	1.00
4,5	130	130	129	129	129	129	0.55
9	189	197	202	207	211	201	8.61
10,13	146	147	148	148	147	147	0.84
11,12	152	152	151	151	151	151	0.55

[a] Reference 19.

TABLE 7. Calculated Bond Lengths, Angles, and Dihedral Angles for 1−5

	bond length 9−9′	bond length 9′−10′ for 2 and analogously for other species	dihedral angle 10−9−9′−10′
1	1.461	1.433	118.93
2	1.467	1.414	90.00
3	1.485	1.423	90.00
4	1.500	1.431	100.77
5	1.504	1.430	90.00
1-90	1.467	1.430	90.23

The optimized geometries of **1−5**, see Supporting Information, show that the two ring systems have a large twist angle, vide supra, which would prevent the normal types of interaction through resonance. We have suggested two models for interaction. In the first, electron density from one system is donated into the π system of the other, σ to p donation.[18] Evidence for this donation comes from a

σ to p donation,
benzene rings not shown for clarity
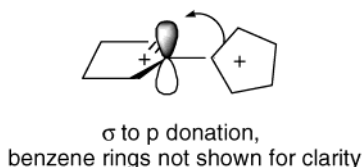
consideration of the ^{13}C shifts for C-9 of **1**, 189 ppm, which are substantially shielded, compared to the same carbon of the fluorenyl monocations, 218 to 224 ppm. Alternatively, the magnitude of the positive charge on the atom attached to C-9 of the fluorenyl system may act to force greater delocalization of charge in the fluorenyl system.[22] The delocalization of charge onto the six-membered rings of **1** was substantially greater than the delocalization of charge onto the analogous rings of substituted fluorenyl monocations, as measured by ^{13}C NMR shifts.

Table 6 gives the experimental ^{13}C NMR shifts for the fluorenyl systems of **1−5** along with the average shift for each type of carbon and the variance in those values as measured by their standard deviation. It is apparent that, with the exception of the shift of C-9, there is very little variation in the extent of charge delocalization in these systems as a result of the nature of the substituent on C-9. The variation in the charge delocalization in the six-membered rings is less than that in the five-membered rings. If the charge delocalization were directly related to the degree of antiaromaticity in these systems, then these results contradict the conclusions from the NICS calculations that show a greater variation in the antiaromaticity of the six-membered rings than that found in the five-membered rings. It appears that, in this set of compounds, the substituents do not communicate substantially with the fluorenyl ring through moderation of the charge delocalization.

If σ to p donation were occurring, there would be obvious changes in geometry. In particular, the bond distance between C9 and C9′ would shorten while that of C9′−C10′ for **2** and analogous bonds for **1** and **3−5** would lengthen. That is, the C9−C9′ bond in **1**, which has the greatest σ to p donation based on the ^{13}C NMR shift of C9, should be the shortest, while the bonds between C9′−C10′ should be the longest. The calculated

geometries give partial confirmation of this donation. Table 7 gives the calculated bond lengths, angles, and dihedral angles for the optimized geometries of **1−5**. The bond between the two systems, C9−C9′, lengthens from **1** to **5** as would be expected with a decrease in hyperconjugation. Because the dihedral angle between the two ring systems of **1** is fairly different from those of the other ring systems, we partially optimized the geometry of **1**, keeping the dihedral angle fixed at 90°. The results in Table 7 show that there is minimal effect of the dihedral angle on the calculated bond lengths and angles. The bond lengths of C9′−10′ for **2** and the analogous bonds for **1** and **3−5** do not show the expected lengthening; however, their presence in a polycyclic ring system would undoubtedly limit their ability to distort in response to hyperconjugation.

Conclusion

The antiaromaticity of fluorenylidene dications **1−5** has been examined using magnetic criteria, NICS and magnetic susceptibility, and by structural criteria, HOMA. The magnetic criteria, including proton chemical shifts, strongly support the antiaromaticity of the fluorenyl ring system of these dications. HOMA values in polycyclic ring systems reflect the inability of the fused ring systems to respond to changes in aromaticity/antiaromaticity and are a very insensitive measure of these effects. Finally, in these systems, the interaction between the ring systems appears to occur primarily through a type of hyperconjugation, as demonstrated by a decrease in the bond lengths for the bonds connecting the ring systems. The third criterion of aromaticity/antiaromaticity, the stability of the species, is currently under investigation in our laboratories.

Calculational Details

Geometries were optimized at B3LYP/6-31G(d) density functional theory levels with the Gaussian 94 and 98 program packages.[31,32] The nucleus independent chemical shifts (NICS[15]) in the ring centers were calculated at RHF/6-31G(d) and B3LYP/6-31G(d) using the GIAO approach with Gaussian 94 or 98. The magnetic susceptibilities were calculated with the IGLO,[33,52] method and basis sets DZ and II for all systems and by CSGT calculated as implemented in Gaussian 98. The DZ basis set was constructed from the Huzinaga[53] (7s3p) set for carbon and the (3s/2s) set for hydrogen, contracting it to (4111/21) and augmenting it by a d-set for C ($\eta = 1.0$)

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and a p-set ($\eta = 0.65$) for H. Basis II was constructed from the Huzinaga[53] (9s5p) set for carbon and the (5s) set for hydrogen, contracting it to (51111/2111) and augmenting it by a d-set for C ($\eta = 1.0$) and a p-set ($\eta = 0.65$) for H.

Supporting Information Available: Experimental and calculated ^{13}C and ^{1}H chemical shifts; correlation coefficients for comparison of experimental and calculated ^{13}C and ^{1}H NMR chemical shifts; calculated bond lengths, angles, and selected dihedral angles for **1**−**5**; calculated symmetries, total energies, and [x,y,z] coordinates for **1**−**5** and **7**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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