Dications of Fluorenylidenes. Use of Magnetic Properties To Evaluate the Antiaromaticity of the Dication of Tetrabenzo[5.5]fulvalene and Substituted Fluorenyl Cations

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Abstract: The NICS values of the dication of tetrabenzo[5.5]fulvalene (**1**) show substantial antiaromaticity. Substituted fluorenyl cations possess antiaromatic five-membered rings but the calculated antiaromaticity (NICS) of the six-membered rings depends on the calculational level. Through calculation of magnetic susceptibility exaltation (Λ), **1** is antiaromatic while fluorenyl cations are not. The paratropic shift seen in the ^{1}H NMR spectra of **1** and the substituted fluorenyl cations is linearly related to NICS (six-membered ring) and to Λ. NICS values suggest that electron delocalization in the fluorenyl cations occurs to maintain the aromaticity of the benzene subunits and to localize the positive charge in the five-membered ring. In contrast, electron delocalization in **1** results in delocalization of a positive charge throughout each fluorenyl system.

While the antiaromatic character of the cyclopentadienyl cation is well recognized,[1] that of the fluorenyl cation has been the subject of controversy. Early solvolysis studies of fluorenyl derivatives attributed their low chemical reactivity to the instability of the 12 π-electron fluorenyl cation, which was assumed to be antiaromatic.[2−4] More recent studies continued the controversy, with a study disputing the claim that fluorenyl cations were antiaromatic based on pK_R values[5] and a subsequent study supporting the antiaromaticity of a doubly destabilized fluorenyl cation[6] based on the strong rate retardation to solvolysis of its tosylate precursor.

The criteria by which aromaticity and antiaromaticity are evaluated fall into the following three general categories, energetic, structural, and magnetic.[7,8] Of these, magnetic criteria appear to be most reliable predictors of aromaticity and antiaromaticity.[9] Magnetic criteria are based on the existence of a ring current which, while experimentally unobservable, can be measured indirectly through the chemical shift of the protons,[10] the magnetic susceptibility exaltation (Λ)[11−14] and

anisotropy, as well as evaluated through the calculated nucleus independent chemical shift (NICS).[15] Of the three manifestations, diamagnetic susceptibility exaltation appears to be the most reliable.[16]

Recently, Schleyer et al.[17] have attempted to set the controversy of the antiaromaticity of the fluorenyl cation to rest through use of high level ab initio and density functional theory computations to assess the aromaticity and antiaromaticity of the cations and anions derived from cyclopentadiene, indene, and fluorene. Using IGLO-calculated magnetic susceptibility exaltations (Λ) and the GIAO-calculated nucleus-independent chemical shifts (NICS), they determined that the cyclopentadienyl and indenyl cations were as antiaromatic as cyclobutadiene and benzocyclobutadiene, respectively. However, the fluorenyl cation was deemed nonaromatic by assessment of magnetic susceptibility exaltation ($\Lambda = -0.6$) and a very small value for the NICS of the six-membered ring.

We have been interested in this controversy because of our ongoing examination of the dications of tetrabenzo[5.5]fulvalene,[18,19] as well as other dications which contain the fluorenyl cation.[20,21] The dication of tetrabenzo[5.5]fulvalene (**1**) is essentially two fluorenyl cations linked by a single bond. The ^{1}H NMR shift of **1** shows a substantial upfield chemical shift, compared to its acyclic analogue, the tetraphenyl ethylene dication (**2**) (Table 1). Such an upfield (paratropic) shift has been considered evidence of antiaromaticity.[22] We have carefully

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Table 1. Comparison of ¹H NMR Chemical Shifts for Fluorenyl Cation with Diphenylmethyl Cation

	c	d	e	f	av		o	m	p	av	$\Delta\delta_{av}$
1	5.33± 0.02	5.16± 0.01	5.77± 0.02	4.97± 0.02	5.31	**2**	8.55	8.55	9.07	8.65	−3.35
3a	7.50	7.10	7.82	6.95	7.34	**4a**	8.17	7.28	8.28	7.84	−0.50
3b	7.62	7.04	7.62	7.04	7.33	**4b**	7.96	7.53	8.12	7.82	−0.49
3c	7.65	7.25	7.55	7.25	7.43	**4c**	7.56	7.74	8.12	7.74	−0.32
3d	7.90	7.60	7.90	7.60	7.75	**4d**	8.12	7.82	8.15	8.01	−0.26

examined all other factors (hybridization, charge density, medium effects) and have concluded that the upfield shift of **1** is due to the existence of an antiaromatic ring current. Substituted fluorenyl cations **3a−d** show a much smaller upfield shift in comparison to the corresponding substituted diphenyl methyl cations, **4a−d** (Table 1).

1   **2**

3   **4**

a, Y=Cl
b, Y=CH₃
c, Y=C₆H₅
d, Y=OH

a, Y=Cl
b, Y=CH₃
c, Y=C₆H₅
d, Y=OH
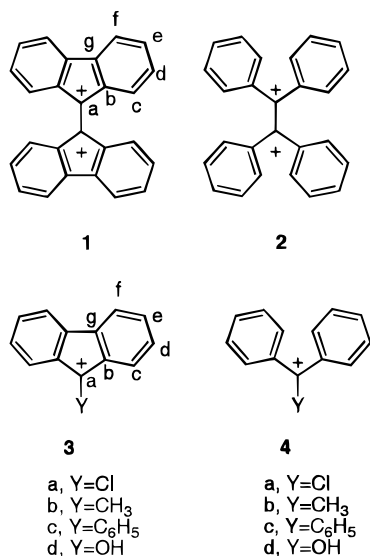
As our experimental evidence for antiaromaticity rests solely on the paratropic shift observed, we report in this paper our evaluation of antiaromaticity via the use of ab initio and density functional calculations to evaluate the magnetic susceptibility exaltation and NICS for **1** and for **3a−d**. In addition, the relationship between the chemical shift differences between **1** and **3a−d** and their analogues, **2** and **4a−d** in Table 1 ($\Delta\delta_{av}$) and the calculated values for magnetic susceptibility exaltation and NICS were examined. This represents the first use of NICS in conjunction with experimental data to determine the antiaromaticity of a set of cations.

Computational Methods

Geometries were optimized at RHF/6-31G(d) ab initio and B3LYP/6-31G(d) density functional theory levels with the Gaussian 94 package (Figure 1 for **2** and **3b**).[23] The calculated absolute energies of **1** and **3a−d** are given in the Supporting Information as well as the coordinates of their optimized geometries and frequencies.[24] 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 in Gaussian 94. The magnetic susceptibilities χ_{tot} were calculated with

B3LYP/6-31G(d) optimization of **1**

B3LYP/6-31G(d) optimization of **3b**

Figure 1. Structures from geometry optimization at B3LPY/6-31G-(d) for **1** and **2b**.

the IGLO[25,26] method and basis sets DZ and II for all systems. The DZ basis set was constructed from the Huzinaga[27] (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 ($\eta = 1.0$) and a p-set ($\eta = 0.65$) for H. Basis II was constructed from the Huzinaga[27] (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. The magnetic susceptibility exaltations (Λ) were evaluated from the difference between each χ_{tot} and the "normal" values deduced from increments for hypothetical polyene systems without cyclic delocalization obtained from calculations on a set of small molecules.[28,29]

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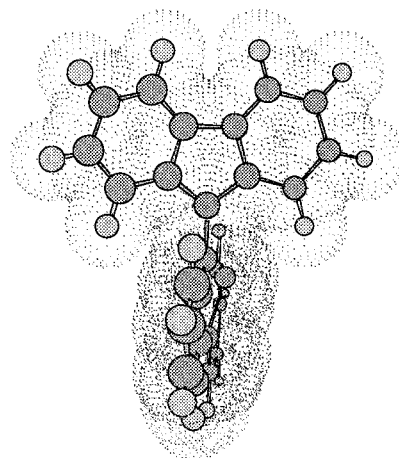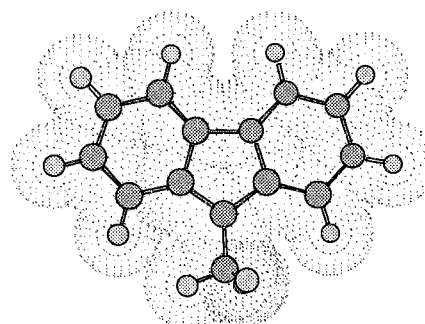
(24) We were unable to find the minimum for **3b**. Frequency calculations at the B3LYP/6-31G(d) level of the optimized structure of the lowest energy which we could find revealed that the structure was not a minimum on the potential energy surface and that the single imaginary frequency was associated with rotation of the methyl group. Optimization of several other geometries resulted in structures with slightly higher energies than the one reported in the Supporting Information; however, the calculated values of NICS and magnetic susceptibility exaltation were very similar to those for the structure with the lowest calculated energy. Thus small changes in geometry of this type have very little effect on the magnitude of either NICS or the magnetic susceptibility exaltation.

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Results and Discussion

NICS Calculations, Choice of Calculational Level. Although the work of Schleyer et al.[17] calculated the nucleus-independent chemical shifts at the GIAO-RHF/6-31G(d) level, we began our investigations with calculations at both the ab initio and density functional theory (DFT) level because we had access to the experimental ^{13}C chemical shifts for **1** and **3a**−**d** and could "check" the quality of the calculations by comparison with experimental data. The ^{13}C chemical shifts calculated at the RHF/6-31G(d) level and at the B3LYP/6-31G(d) level are given in Table 2, along with the experimental chemical shifts. Because solvent and counterion are not included in these calculations, it is not surprising that the calculated (gas phase) values deviate from the experimental values. If we assume that the effect of solvent manifests itself in a similar way for all carbons, we can assess the quality of the calculations by looking at the internal consistency of the calculated values in comparison to the experimental values. If the difference between the experimental and calculated chemical shift (Δ, $\delta_{exp} - \delta_{calcd}$) is similar for each carbon of the fluorenyl system, the calculated shift would be considered "good". The measure of the deviation of $\delta_{exp} - \delta_{calcd}$ between each carbon is reported as the standard deviation in Table 2. Thus, for **1**, the difference between experimental and calculated shifts at the RHF/6-31G(d) level range from −10 to 17, with a standard deviation of 9, while the differences at the B3LYP/6-31G(d) level range from 8 to 13, with a standard deviation of 2. By this measure, the chemical shifts calculated at the B3LYP/6-31G(d) level are better than at the RHF/6-31G(d) level for **1**. There is reasonable improvement at the B3LYP/6-31G(d) level for **3a**−**b** and **3d** and poorer performance for **3c**.

Calculations at the density functional theory level give slightly smaller (less deshielded) chemical shifts in the absence of solvent. In addition to revealing that the calculated chemical shift is smaller than the experimental one at the density functional theory level, the only other apparent trend is that at the density functional theory level, the greatest deviation between calculated and experimental shifts is for carbon a. Carbon a is also the carbon with the greatest downfield shift, presumably the one with the greatest concentration of positive charge, and therefore the carbon which could benefit the most from interaction with the solvent/counterion, which is not reflected in our calculations.

NICS Calculations. Because of the consistency between calculated and experimental chemical shifts shown at the B3LYP/6-31G(d) level, we assume that the magnetic properties calculated at that level to assess antiaromaticity are slightly more reliable than those calculated at the RHF/6-31G(d) level. For purposes of examination however, we have calculated the nucleus-independent chemical shifts (NICS) for **1** and **3a**−**d** at both the RHF/6-31G(d) level and the B3LYP/6-31G(d) level. Those values are shown in Table 3. It is immediately obvious that the magnitude and sign of the NICS value depends greatly on the calculational method. Thus comparisons between NICS values *must* be made at the same calculational level and method. The NICS values calculated using density functional theory are more positive than those at the Hartree−Fock level, with larger positive values indicating greater antiaromaticity. For both ab initio and density functional theory calculations, the greatest amount of antiaromatic character lies in the five-membered ring

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Table 2. Experimental and Calculated ^{13}C NMR Chemical Shifts for **1** and **3a**−**d**, GIAO-SCF/6-31G(d)//B3LYP/6-31G(d) and GIAO-B3LYP/6-31G(d)//B3LYP/6-31G(d)

	exp	SCF/-6-31G(d)	diff	B3LYP/-6-31G(d)	diff
			1		
a	189	199	−10	178	11
b	146	129	17	134	12
c	145	144	1	132	13
d	136	124	12	126	10
e	159	162	−3	151	8
f	130	122	8	121	9
g	152	148	4	143	9
st dev Δ			9		2
			3a		
a	218	224	−6	202	16
b	141	127	14	130	11
c	134	141	−7	128	6
d	133	123	10	123	10
e	150	154	−4	143	7
f	126	117	9	115	11
g	147	146	1	139	8
st dev Δ			8		3
			3b		
a	228	229	−1	206	22
b	144	129	15	132	12
c	141	141	0	129	12
d	133	123	10	122	11
e	152	154	−2	142	10
f	126	117	9	115	11
g	151	148	3	140	11
CH_3	19	12	7	10	9
st dev Δ			7		4
			3c		
a	224	213	11	187	37
b	144	127	17	129	15
c	141	140	1	130	11
d	135	122	13	121	14
e	153	147	6	137	16
f	127	117	10	115	12
g	151	146	5	139	12
i	138	120	18	120	18
o	136	132	4	122	14
m	131	123	8	120	11
p	141	143	−2	133	8
st dev Δ			5		9
			3d		
a	206	204	2	185	21
b	131	116	15	118	13
c	134	133	1	122	12
d	133	123	10	121	12
e	147	149	−2	138	9
f	125	118	7	115	10
g	149	145	4	138	11
st dev Δ			6		3

Table 3. The Calculated Nucleus Independent Chemical Shifts (NICS) for **1** and **3a**−**d**

	SCF/6-31G(d)		B3LYP/6-31G(d)	
	five-membered ring	six-membered ring	five-membered ring	six-membered ring
1	24.5	20.9	28.9	14.3
3a	20.8	−0.2	24.2	6.2
3b	21.2	−0.8	25.5	6.2
3c	18.2	−2.1	20.9	3.7
3d	15.3	−3.6	17.5	1.3

of **1** and **3a**−**d**, as shown by the greater positive value calculated for NICS.

At the RHF/6-31G(d) level, the NICS values for the six-membered ring show a steady decrease in antiaromatic character/

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increase in aromatic character, which is consistent with the decreasing difference between **1** and **2** and between **3a**−**d** and **4a**−**d** shown in Table 1. Of greater interest is the distribution of the NICS values between the five- and six-membered rings for **1** compared to **3a**−**d**. All of the antiaromaticity of **3a**−**d** is found in the five-membered ring, while in **1** there is additional antiaromaticity in the six-membered ring where there was none or slight (local) antiaromaticity in **3**.

In contrast, NICS calculated at the B3LYP/6-31G(d) level, also shown in Table 3, show that while the five-membered rings of **3a**−**d** possess a substantial amount of antiaromatic character, the six-membered rings are also antiaromatic. Again, the degree of antiaromatic character decreases as the chemical shift differences decrease as shown in Table 1. At this level, the calculated NICS values for the six-membered ring of **1** shows a substantial amount of antiaromaticity, consistent with the large chemical shift difference between **1** and **2** shown in Table 1.

Because the ^{1}H chemical shift differences between **1** and **3a**−**d** and reference compounds **2** and **4a**−**d** ($\Delta\delta$) appear to vary in a consistent manner with the NICS values for the six-membered rings, we examined a plot of ^{1}H chemical shifts ($\Delta\delta$, $\Delta(\delta_{1,3a-d} - \delta_{2,4a-d})$) vs NICS values for the six-membered ring. As mentioned previously, ^{1}H chemical shifts are affected by a number of effects. In the case of **1**, protons on carbons c and d feel the effect of the fluorenyl ring system attached at carbon a.[18,19] That same effect is not present in **2**. To evaluate the chemical shifts on the same basis, we plotted the chemical shift difference between the average shift of protons on carbons e and f of **1** and **3a**−**d** and the average shift of all protons on **2** and **4a**−**d** ($\Delta\delta$) vs the NICS value for the six-membered ring calculated at the B3LYP/6-31G(d) level. The correlation coefficient is adequate to show a roughly linear relationship, with $R = 0.940$. The analogous plot of chemical shift difference vs NICS value calculated at the RHF/6-31G(d) level shows a better linear relationship, with a correlation coefficient of 0.998.

Magnetic Susceptibility Exaltation, Choice of Basis Set. Magnetic susceptibilities are often calculated using the IGLO program of Kutzelnigg and Schindler,[26,30] which also calculates chemical shifts. Again, we can assess the "quality" of the calculational level by comparison with experimental chemical shifts. We report the ^{13}C NMR shifts of **1** and **3a**−**d** calculated on geometries optimized at the B3LYP/6-31G(d) level using IGLO/DZ and IGLO/II in Table 4, along with the experimental chemical shifts. We again calculated the difference (Δ, $\delta_{exp} - \delta_{calcd}$) between the experimental values and those calculated with basis sets DZ and II for each ^{13}C NMR shift of **1** and **3a**−**d** and evaluated the "accuracy" of the calculation for each basis set via the standard deviations of Δ. Those standard deviations are also reported in Table 4 and show that basis set II is very slightly better than basis set DZ in terms of the agreement of the calculated values with experiment.

Using simple resonance theory, one can determine those carbons which would be expected to possess a partial positive charge. When one looks at the difference between calculated and experimental shifts, those carbons which would be partially positively charged (carbons a, c, e, and g) show a calculated shift which is further downfield than in the experimental spectra, with the opposite effect shown for the carbons not bearing positive charges. This suggests that IGLO calculations may overstate the localization of charge in a delocalized system, as manifested in the ^{13}C chemical shifts. In general, the greatest deviation from experimental chemical shifts was for carbon a.

Calculation of Magnetic Susceptibility Exaltation. Magnetic susceptibility exaltation is evaluated through the difference

Table 4. Experimental and Calculated (IGLO) ^{13}C NMR Chemical Shifts for **1** and **3a**−**d**

	exp	IGLO(DZ)	diff	IGLO(II)	diff
1					
a	189	203	−14	210	−21
b	146	131	15	137	9
c	145	155	−10	154	−9
d	136	133	3	134	2
e	159	172	−13	172	−13
f	130	130	0	130	0
g	152	153	−1	157	−5
st dev Δ			10		9
3a					
a	218	248	−30	237	−19
b	141	132	9	136	5
c	134	152	−18	150	−16
d	133	132	1	132	1
e	150	164	−15	163	−14
f	126	126	0	125	0
g	147	149	−2	154	−7
st dev Δ			14		9
3b					
a	228	241	−13	244	−16
b	144	132	12	138	6
c	141	150	−9	149	−8
d	133	132	1	132	1
e	152	162	−10	162	−10
f	126	126	1	125	1
g	151	151	0	156	−4
CH$_3$	19	18	1	14	5
st dev Δ			9		7
3c					
a	224	221	3	225	−1
b	144	130	14	136	8
c	141	150	−9	150	−9
d	135	132	3	132	3
e	153	158	−5	157	−4
f	127	126	1	125	2
g	151	151	0	155	−4
i	138	124	14	130	8
o	136	141	−5	142	−6
m	131	131	0	133	−2
p	141	154	−13	154	−13
st dev Δ − fl ring			7		5
3d					
a	206	223	−17	217	−11
b	131	121	10	125	6
c	134	144	−10	143	−9
d	133	132	1	132	1
e	147	159	−12	159	−12
f	125	127	−2	127	−2
g	149	150	−1	155	−6
st dev Δ			10		6

between the calculated χ_{tot} and the "normal" values deduced from increments for hypothetical polyene systems without cyclic delocalization. The "normal values" were obtained by calculation using basis sets DZ and II on localized cations whose geometries were optimized at the B3LYP/6-31G(d) level. The increments, and the cations or dications from which the increments were derived, are listed in Table 5 and the calculated magnetic susceptibility (χ_{tot}) and magnetic susceptibility exaltation (Λ) for **1** and **3a**−**d** are listed in Table 6. Positive values for Λ reflect antiaromatic character; negative values reflect aromaticity. Calculation of $|\chi_{tot}|$ is basis set dependent for **1** and **3a**−**d** and for the increment values in Table 5 and is smaller for basis set II than for DZ.[30] The calculated values of Λ are

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Table 5. IGLO/DZ and IGLO/II Calculated Magnetic Susceptibilities (ppm cgs), Increment Values[a]

increment	precursor	increment value	precursor, DZ basis	increment value	precursor, II basis
>CH$^+$	2-propyl cation	4.17, lit.[b]	−31.43	2.34	−28.66
>CCl$^+$	2-chloropropyl cation	−12.13	−47.73	−13.79	−44.79
>COH$^+$	2-hydroxypropyl cation	−7.5	−43.1	−7.76	−38.76
>CPh$^+$	2-phenylpropyl cation	−64.43	−100.03	−57.66	−88.66
>CCH$_3^+$	*tert*-butyl cation	−8.96	−44.56	−9.9	−40.9
(>C−C<)$^{2+}$	tetramethylethylene dictation	9.98[b]	−61.22	6.56	−55.44
(>C=C<)	2,3-dimethylbutene	−14.2,[c] lit. −13.8[b]	−85.4	−12.09	−74.09
cis-CH=CH−	*cis*-2-butene	−19.3,[c] lit. −19.3[b]	−54.9	−16.57	−47.57

[a] Increment values derived from calculated magnetic susceptibility for each precursor minus the magnetic susceptibility for ethane (−35.6/DZ bisis set; −31.01/II basis set). [b] Zyweitzx, T. K.; Jaio, H.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1998**, *63*, 3417−3422. [c] Increment values = precursor − 2 × ethane.

Table 6. The Calculated Magnetic Susceptibilities (χ_{tot}) and Magnetic Susceptibility Exaltations (Λ) for **1** and **3a−d**

	DZ		II	
	χ_{tot}	Λ	χ_{tot}	Λ
1	−194.23	6.99	−152.66	21.7
3a	−131.07	−13.34	−109.30	−5.05
3b	−125.18	−10.62	−104.66	−4.30
3c	−186.63	−16.60	−157.69	−9.57
3d	−130.01	−16.91	−109.46	−11.24

more positive for basis set II than for basis set DZ. Since the values of χ_{tot} calculated at the II basis set are normally closer to experimental values,[30] the interpretation of the differences in Λ calculated with different basis sets would be that calculations with the DZ basis set overestimate aromaticity. It is conceivable that calculations with larger basis sets would give exaltations showing even lesser aromaticity/greater antiaromaticity. Because the magnitude of the exaltation depends on the basis set used, *it is inappropriate to compare magnetic susceptibility exaltations calculated using different basis sets.*

By use of either basis set, **1** is shown to possess appreciable antiaromaticity while the fluorenyl cations **3a−d** are all aromatic. As noted above, basis set II gives values for Λ which are more antiaromatic/less aromatic than those calculated with the DZ basis set. Values of Λ for **3a−d** are more aromatic than those calculated for the unsubstituted fluorenyl cation, −0.6, with basis set DZ. It is not surprising that the exaltation of fluorenyl cations that contain potentially electron-donating substituents reflects a greater aromaticity than that of the unsubstituted fluorenyl cation. There is a roughly linear correlation between the calculated exaltation and substituent constants which reflect inductive effects, such as σ^l_X[31] and ι;[32] the correlation becomes much better if the exaltation for the chloro-substituted fluorenyl cation **3a** is removed. Because chlorine is the only second row element in the compounds studied, this may reflect the need for a larger basis set. Magnetic susceptibilities of compounds containing chlorine have shown greater deviations from experimental values than the susceptibilities of compounds which do not contain chlorine when basis set II is used.[30]

The relationship between the experimentally determined measure of antiaromaticity, paratropic shift, and Λ was examined. As described above for the comparison of paratropic shift and NICS, the paratropic shift of **1** and **3a−d** was determined on the basis of the difference between the shift of protons e and f on the fluorenyl system and the average shift of the phenyl

protons in **2** and **4a−d**. Those shifts were plotted vs Λ. As was true for the NICS values, there is a linear relationship between the experimentally determined chemical shift difference and the calculated Λ.

Evaluation of the Antiaromaticities of 1 and 3a−d. Both the calculation of magnetic susceptibility exaltation and NICS calculations confirm the substantial antiaromatic character of **1** proposed on the basis of its large paratropic shift.[18,19] Using the DZ basis set, the magnetic susceptibility exaltation for **1** is 6.9, and 21.7 with basis set II. These values can be compared to values of 32.6 (basis set II) for the cyclopentadienyl cation, 18.4 (basis set DZ) for the indenyl cation, and −0.6 (basis set DZ) for the unsubstituted fluorenyl cation.[17] Benzocyclobutadiene has a calculated magnetic susceptibility exaltation of 9.0.[15] By this measure, **1** is intermediate in antiaromaticity between the indenyl cation and the unsubstituted fluorenyl cation and fairly similar to benzocyclobutadiene. Although comparisons are frequently made between molecules and ions with different ring sizes, the dependence of magnetic susceptibility on ring size[15] makes comparison with nonfluorenyl systems problematic, so the comparison with the indenyl cation and benzocyclobutadiene should be used as an approximate comparison of the degree of antiaromaticity.

The NICS at the ring centers (SCF/6-31G(d)) can be compared with the corresponding values for the cyclopentadienyl, indenyl, and fluorenyl cations,[17] in which the NICS for the five-membered ring was found to be 54.1, 34.5, and 24.7, respectively, while that of the six-membered rings of the indenyl and fluorenyl cations were 8.6 and 1.9. By these calculations, the antiaromaticity of the five-membered ring of **1** is substantial and most comparable to that of the five-membered ring of the fluorenyl cation. More interestingly, the antiaromaticity of the six-membered ring of **1** is substantially greater than that of the corresponding rings of the indenyl cation which is considered antiaromatic. Benzocyclobutadiene, which has a similar magnetic susceptibility exaltation, has NICS of 21.5 (four-membered ring) and −4.2 (six-membered ring).[15]

Schleyer et al.[17] have discussed the degree of antiaromaticity of the indenyl and fluorenyl cations in terms of compensation of the "diamagnetic six ring and paramagnetic five ring" and have concluded that for the indenyl cation the paramagnetic dominates over the diamagnetic contribution; the net effect is paramagnetic and the indenyl cation is still antiaromatic. For the fluorenyl cation, the counterbalance of two diamagnetic rings and one paramagnetic ring resulted in a *non*aromatic species. Similar conclusions were advanced for benzocyclobutadiene and dibenzocyclobutadiene (biphenylene). The NICS for **1** reveal that the six-membered ring is not diamagnetic, that it possesses

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(32) Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1007−1010.

appreciable paratropicity, resulting in the overall antiaromatic character of **1**.

Evaluation of the antiaromaticity of **3a**−**d** is more problematic. The calculation of magnetic susceptibility exaltation, proposed by Scheyler as the "only measurable property which is *uniquely* associated with aromaticity",[16] for **3a**−**d** reveals that all four fluorenyl cations are aromatic; however, the basis set dependence of Λ suggests that small basis sets tend to overestimate aromaticity, vide supra. While there is slightly better agreement between calculated and experimental ^{13}C chemical shifts using basis II, both basis sets show effectively the same trends in Λ. The dependence of Λ on basis set suggests that Λ be used to evaluate aromaticity and antiaromaticity in a relative, rather than absolute sense, for "small" values of Λ.

While the NICS calculations at either RHF/6-31G(d) or B3LYP/6-31G(d) for the five-membered rings of all systems reveals substantial antiaromatic character, the six-membered rings are antiaromatic by DFT calculations but nonaromatic or slightly aromatic for NICS calculations at the RHF/6-31G(d) level. A comparison of the magnitude of the NICS calculations for both five- and six-membered rings shows that calculations at the DFT level are ∼5 ppm more positive (antiaromatic). For rings that are only slightly aromatic by Hartree−Fock calculations, this is enough to give calculated values that are antiaromatic in density functional theory calculations. The dependence of the sign of the NICS value on the calculational method used suggests that NICS values be used to evaluate aromaticity and antiaromaticity in a relative, rather than an absolute sense, for NICS values which are ±5.

As noted above, Schleyer et al.[17] describe the parent fluorenyl cation as a 4 π-electron five-membered ring whose paramagnetic contribution is dominated by the diamagnetic contribution of two 6 π-electron six-membered rings, resulting in a system which is nonaromatic. Our calculations at this level allow us to come to a similar conclusion about the lack of antiaromaticity in substituted fluorenyl cations. Since the magnitude of the NICS values for both the five- and six-membered rings of the substituted fluorenyl cations is less positive than for the unsubstituted fluorenyl cation, the effect of the substituent is to decrease the antiaromaticity of each ring. This effect is also seen in calculated values of Λ. Furthermore, as was true for values of Λ, the more electron-donating the substituent through induction, the greater the decrease in antiaromatic character. Analogously, a strongly electron-withdrawing substituent would be expected to increase the antiaromaticity of the fluorenyl cation, as suggested recently by Tidwell et al.[6] The fluorenyl cations examined here can reasonably be considered to be nonantiaromatic.

It remains to address the reasons for the difference in the antiaromaticity of the fluorenyl cation in **1** compared to the aromaticity/nonaromaticity of **3a**−**d**. It appears that the presence of a positively charged substituent on C-9 of the fluorenyl cation is crucial for the antiaromaticity of the fluorenyl cation and we have observed this in other systems.[18−21] The calculations, particularly of NICS, give additional information. The assessment of aromaticity/antiaromaticity in polycyclic systems often involves a consideration of the pattern of delocalization of electron density.[33,34] For the fluorenyl monocations, the difference between the signs of the NICS in the five- and six-membered rings suggests that the delocalization of electron density occurs to maintain the aromaticity of the six-membered

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(34) Minsky, A.; Meyer, A. Y.; Hafner, K.; Rabinovitz, M. *J. Am. Chem. Soc.* **1983**, *105*, 3975−3981.

Table 7. Comparison of [13]C Chemical Shifts of **1** with **3a**−**d**

	1	3a	3b	3c	3d	av δ for 3a−d	st dev
a	189	218.2	228	224.2	205.5	219.0	8.5
b	146	141.3	144.3	143.8	131.4	140.2	5.2
c	145	134.3	141	141.4	134.1	137.7	3.5
d	136	133.3	133	134.6	132.5	133.4	0.8
e	159	149.5	152.4	153.4	146.8	150.5	2.6
f	130	125.9	126.4	126.8	125.3	126.1	0.6
g	152	147.1	151.4	151.4	149.1	149.8	1.8
av	148	145	148	148	142	146	3.1
av of carbons b−g	145	139	141	142	137	140	2.5
av of carbons c−f	143	136	138	139	135	137	2.0

benzene ring. The NICS calculations suggest that the delocalization of electron density in **1** is very different from that in the unsubstituted fluorenyl cation with the six-membered ring accepting greater delocalization and therefore a greater amount of the antiaromaticity of the system. Confirmation of this suggestion comes from an examination of the experimental chemical shifts of the fluorenyl ring system of **1** and **3a**−**d**. It is more difficult to include carbon a in this comparison because its shift is the most variable. However, the average shift of carbons b−g for **3a**−**d** can be compared to the shift of the corresponding carbons of **1**. Those values are reported in Table 7. For all carbons, the shift of the carbons of **1** are greater than a standard deviation larger than the shifts of the corresponding carbons of **3a**−**d**, suggesting that the positive charge is delocalized more effectively into the six-membered rings of **1**. Another way to sort out these differences is to consider only the carbons unique to the six-membered rings, carbons c−f. Comparison of either the shifts of the individual carbons c−f or their average shift of **3a**−**d** with **1** reveals that the downfield shift apparent in the six-membered ring of **1** is even greater, with the average shift of carbons c−f in **1** at least two standard deviations larger than the average shift for the same carbons in **3a**−**d**.

Summary

Calculation of magnetic susceptibility exaltation, Λ, as well as NICS for both five- and six-membered rings of **1** demonstrate substantial antiaromaticity, which is consistent with the paratropic shift observed in its ^{1}H NMR spectrum. We have observed similar paratropic shifts in a family (**5**) of derivatives of **1** which

5
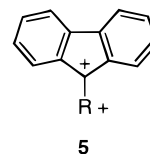
can be considered as fluorenyl cations with cationic substituents.[18−21] The Λ and NICS values for these systems are currently under investigation to confirm that **5** does represent a new set of antiaromatic cations.

Fluorenyl cations **3a**−**d**, on the other hand, do not appear to be antiaromatic, on the basis of calculation of Λ as well as NICS for both five- and six-membered rings, even though they demonstrate a small paratropic shift compared to reference cations. They are less antiaromatic than the parent fluorenyl cation, with the diminution of antiaromaticity related to the electron-donating ability of the substituent.

The NICS calculations suggest that the difference in the antiaromaticity of these systems lies in the pattern of delocalization of the electron density of the π-system. For **1**, with a

positively charged substituent, the electron density of the π-system is delocalized more completely to the six-membered ring than in **3a−d.** Substituted fluorenyl cations **3a−d** in contrast show a delocalization pattern in which the aromaticity of the six-membered ring is preserved. Experimental confirmation of the difference in the delocalization patterns comes from a comparison of the ^{13}C NMR shifts for **1** with those of **3a−d**. The chemical shifts for carbons b−g of **1** are substantially further downfield than those of **3a−d**, suggesting greater delocalization of positive charge into the six-membered ring of **1**.

Of equal importance, the calculated measures of antiaromaticity, Λ and NICS, have been shown to be linearly related to the magnitude of the paratropic shift of the fluorenyl protons of **1** and **3a−d**. This represents the first documentation of the relationship between these calculated measures of antiaromaticity and the paratropic shift observed in the ^{1}H NMR spectrum. This relationship can therefore be used to validate the use of paratropic shifts in the determination of antiaromaticity, after careful examination of the other factors, which affect chemical shifts.

Supporting Information Available: Zero point energies for **1** and **3a,c,d**; optimized geometries and frequencies for **1**, **3a−d** (PDF). This material is available free of charge via the Internet at http://www.pubs.acs.org.

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