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Dications of Fluorenylidenes. The Relationship between Redox Potentials and Antiaromaticity for Meta- and Para-Substituted Diphenylmethylidenefluorenes

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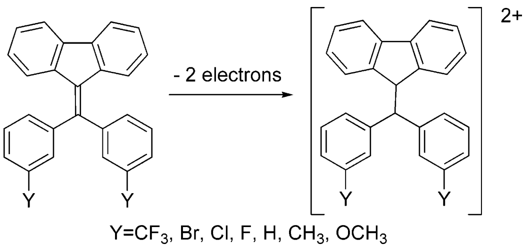

Electrochemical oxidation of meta-substituted diphenylmethylidenefluorenes (**3a**−**g**) results in the formation of fluorenylidene dications that are shown to be antiaromatic through calculation of the nucleus independent chemical shift (NICS) for the 5- and 6-membered rings of the fluorenyl system. There is a strong linear correlation between the redox potential for the dication and both the calculated NICS and σ_m. Redox potentials for formation of dications of analogously substituted tetraphenylethylenes shows that, with the exception of the *p*-methyl derivative, the redox potentials for these dications are less positive than for formation of the dications of **3a**−**g** and for dications of *p*-subtituted diphenylmethylidenefluorenes, **2a**−**g**. The greater instability of dications of **2a**−**g** and **3a**−**g** compared to the reference system implies their antiaromaticity, which is supported by the positive NICS values. The redox potentials for formation of the dications of meta-substituted diphenylmethylidenes (**3a**−**g**) are more positive than for the formation of dications of para-substituted diphenylmethylidenes (**2a**−**g**), indicating their greater thermodynamic instability. The NICS values for dications of **3a**−**g** are more antiaromatic than for dications of **2a**−**g**, which is consistent with their greater instability of the dications of **3a**−**g**. Although the substituted diphenylmethyl systems are not able to interact with the fluorenyl system through resonance because of their geometry, they are able to moderate the antiaromaticity of the fluorenyl cationic system. Two models have been suggested for this interaction, σ to p donation and the ability of the charge on the substituted ring system to affect delocalization. Examination of bond lengths shows very limited variation, which argues against σ to p donation in these systems. A strong correlation between NICS and σ constants suggests that factors that affect the magnitude of the charge on the benzylic (α) carbon of the diphenylmethyl cation affect the antiaromaticity of the fluorenyl cation. Calculated atomic charges on carbons 1−8 and 10−13 show an increase in positive charge, and therefore greater delocalization of charge in the fluorenyl system, with increasing electronegativity of the substituent. The change in the amount of positive charge correlated strongly with NICS, supporting the model in which the amount of delocalization of charge is related to the antiaromaticity of the species. Thus, both aromatic and antiaromatic species are characterized by extensive delocalization of electron density.

Introduction

Aromaticity is one of the fundamental concepts of organic chemistry; however, there is widespread disagreement about how it is manifested.[1−3] In general, the criteria used to characterize aromaticity fall into three categories that are derived from properties of benzene: *magnetic*, *structural*, and *energetic*.[4,5] Briefly, *magnetic* criteria focus on the consequences of the existence of a ring current, which include magnetic susceptibility ex-

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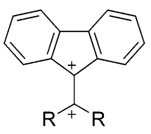
altation (Λ),[6] nucleus-independent chemical shift (NICS),[7] and diatropic shift of protons on the periphery of an aromatic ring system.[8,9] An antiaromatic system would show values of NICS, Λ, and potentially chemical shift that are opposite in sign to those of an aromatic system.[10] *Structural* criteria include lack of bond length alternation and can be evaluated through the harmonic oscillator model of aromaticity (HOMA).[11−13] While some authors believe that antiaromatic species are characterized by bond length alternation,[10,14] there is growing evidence that both aromatic and antiaromatic species are characterized by a lack of bond length alternation.[15] *Energetic* criteria are based on the greater stability of an aromatic system over a comparable system with localized bonds. Antiaromatic systems would show a greater thermodynamic instability compared to an appropriate reference system.

While there appears to be little dissension about the three criteria, there is a great deal of discussion about whether the criteria evaluate the same property, that is, are the criteria related or orthogonal? To date, the evaluation of these criteria has been primarily with aromatic systems. Antiaromatic systems, such as the fluorenyl cation, could allow an alternative approach. By evaluating the criteria in systems whose antiaromaticity should make them as far removed from benzene and its aromaticity as possible, differences in the responses of the criteria should be enhanced. However, there is some dispute about the antiaromaticity of the fluorenyl cation.[16−21] We have entered this discussion through a suite of fluorenylidene dications **1**[22−29] that demonstrate antiaromatic behavior. These dications are characterized by a cationic fluorenyl system that is antiaromatic and a second cationic system that can be modified to systematically "adjust" the antiaromaticity of the fluorenyl ring system. Thus, by a series of rational changes, it is possible to evaluate the antiaromaticity of the fluorenyl cation via the three criteria and to see the relationship between the criteria.



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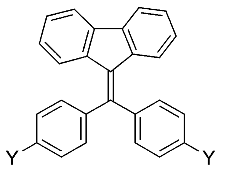
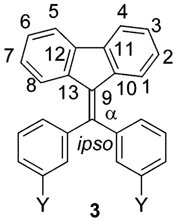
One problem with the assessment of aromaticity/antiaromaticity is that many of the criteria involve calculated rather than measured quantities. Although there is growing acceptance of the results of calculations, many chemists are more comfortable when those results are supported by experimental data. A particular problem exists in the assessment of the stability of a molecule or species because the choice of a reference system can be contentious.

We have been interested in using the redox potential for formation of fluorenylidene dications as a measure of their stability. That is, the more positive the potential for formation of the dication, the greater its instability. We demonstrated this approach with the oxidation of a series of para-substituted diphenylmethylidenefluorenes, **2**, which demonstrated a linear relationship between the antiaromaticity of their dications, as evaluated by NICS calculations and paratropic ^{1}H NMR shifts, and redox potential for formation of the dications, with species with the greatest positive potential showing the largest degree of antiaromaticity.[27] We here report the extension of that work to meta-substituted diphenylmethylidenefluorenes, **3**. Because the manner in which the antiaromaticity of fluorenylidene dications is moderated by substituents



2

a. Y=CF_3
b. Y=Br
c. Y=Cl
d. Y=F
e. Y=H
f. Y=CH_3
g. Y=OCH_3



3

a. Y=CF_3
b. Y=Br
c. Y=Cl
d. Y=F
e. Y=H
f. Y=CH_3
g. Y=OCH_3

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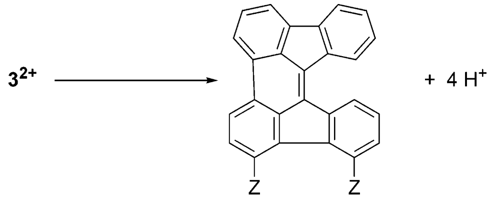
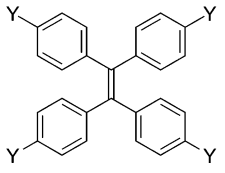
was difficult to determine in the para series (**2**) in which the substituent could operate through a combination of inductive/field and resonance effects, the examination of meta-substituted diphenylmethylidenefluorene dications would allow the effect to be restricted to inductive/field effects only. Our intent was to utilize both the paratropicity of the ^{1}H NMR shifts for the dications and NICS calculations to evaluate magnetic properties, but unfortunately, the dications cyclized so rapidly, see below, that it was impossible to measure their proton spectra. This was also true for the unsubstituted diphenylmethylidenefluorene dication.[25] Thus, our comparison of magnetic and energetic criteria will rest on the calculated NICS values along with redox potentials.



A second limitation of our evaluation of the antiaromaticity of para-substituted diphenylmethylidenefluorene dications was the choice of reference system used in the evaluation of the decreased stability of **2**. We utilized tetrakis-4-substituted phenylethylenes, **4**, as the precursor to the dications. The effect of the substituent is overstated because it appears four times in the reference system as compared to twice in **2**. We report here the redox potentials for oxidation of **5** and **6** in which the effects of the substituents are more appropriately balanced with those of the diphenylmethylidenefluorene systems.



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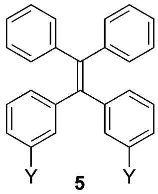

5
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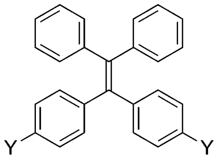
b. Y=Br
c. Y=Cl
d. Y=F
e. Y=H
f. Y=CH_3
g. Y=OCH_3



6
a. Y=CF_3
b. Y=Br
c. Y=Cl
d. Y=F
e. Y=H
f. Y=CH_3
g. Y=OCH_3

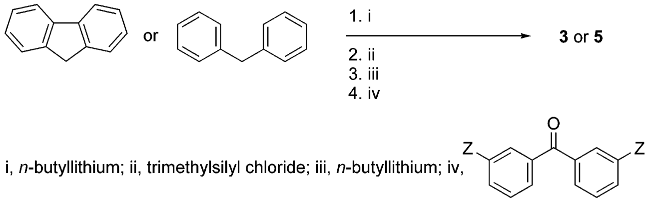
In this paper, we report the electrochemical oxidation of dications of meta-substituted diphenylmethylidenefluorenes, their antiaromaticity, as evaluated through calculation of nucleus-independent chemical shift (NICS), the relationship between stability (redox potential) and antiaromaticity, and the relationship between antiaromaticity and the electron-withdrawing ability of the substituent. We also compare the antiaromaticity of para-substituted diphenylmethylidenefluorene dications with the meta-substituted series and propose a mechanism by which the substituent moderates the antiaromaticity of these fluorenylidene dications.

TABLE 1. Redox Potentials for Cation Radical and Dication of 2a−g, 3a−g, 5a−g, and 6a−g

	$E_{1/2}$, cation radical	$E_{1/2}$, dication		$E_{1/2}$, cation radical	$E_{1/2}$, dication	$\Delta E_{1/2\ \mathrm{dication}}$, **2/3−5/6**
3a	1.24	1.53	**5a**	1.16	1.44	0.09
3b	1.17	1.44	**5b**	1.08	1.32	0.13
3c	1.17	1.44	**5c**	1.09	1.32	0.12
3d	1.15	1.41	**5d**	1.09	1.33	0.08
3e	0.98	1.27	**5e**	0.91	1.20	0.07
3f	0.94	1.26	**5f**	0.86	1.14	0.12
2a	1.25	1.54	**6a**	1.18	1.45	0.09
2b	1.07	1.33	**6b**	1.00	1.26	0.08
2c	1.05	1.31	**6c**	0.98	1.24	0.07
2d	1.00	1.26	**6d**	0.93	1.19	0.07
2f	0.70	1.06	**6f**	0.78	1.08	−0.02
2g	0.66	1.03	**6g**	0.61	0.88	0.14

Results

Synthesis of 3, 5, and 6. The precursors to the fluorenylidene dications, $\mathbf{3}^{2+}$, and the corresponding tetraphenyl ethylene dications, $\mathbf{5}^{2+}$ and $\mathbf{6}^{2+}$, were in general synthesized by Peterson olefination of fluorene or diphenylmethane, respectively, by the corresponding substituted benzophenones as shown in the synthetic scheme below for **3** or **5**.

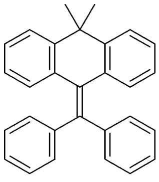


i, *n*-butyllithium; ii, trimethylsilyl chloride; iii, *n*-butyllithium; iv,

Electrochemical Oxidation of Diphenylmethylidenefluorenes. The oxidation of the olefin precursors to **3a**−**g** was examined by cyclic voltammetry in deaerated CH_2Cl_2. The solvent with supporting electrolyte was dried by passing it through a column of dried alumina just prior to use. Oxidation with a 1.6 mm diameter electrode gave irreversible oxidation to the dication at all scan rates accessible, presumably due to its reaction with the traces of residual water in the solution. When the electrode was changed to a 10 μm diameter microelectrode, allowing an increase in scan rates to 25−102 V/s, the cyclic voltammograms showed reversible behavior, as indicated by the invariance of E_{pa} and E_{pc} with scan rates from 25 to 102 V/s; see the Supporting Information. The redox potentials for formation of the cation radical $(\mathbf{3a}-\mathbf{f})^{\bullet+}$ and for formation of the dications $(\mathbf{3a}-\mathbf{f})^{2+}$ are shown in Table 1, along with the same data for **2a**−**g**. The cyclic voltammograms were more poorly resolved than those of the para-substituted diphenylmethylidenefluorenes.[27] The cyclic voltammogram of **3g** was so poorly resolved that determination of the redox potential for formation of the cation radical and dication was unreliable.

To determine if the substituent was playing an unusual role in the formation of the dication, a plot was made of the redox potential ($E_{1/2}$) for formation of both cation radical and dication of **3a**−**g** vs a variety of substituent coefficients, σ. The best correlation was with σ_m,[30] which gave a correlation coefficient (r^2) of 0.980 for formation of the cation radical and 0.926 for formation of the dication; see the Supporting Information. The slightly better correlation with σ_m for formation of the cation radical suggests that the positive charge is localized on the diphenylmethylidene portion of the system which would be more responsive to substituent effects, with the radical localized on the fluorenyl portion. This behavior has been seen previously in studies of the cation radical for **3d** and **3f**.[31] The effect of substituent constants on the redox potential shows that the more electronegatively substituted diphenylmethylidenefluorene was oxidized at a more positive potential, as would be predicted. The relationship of this potential to measures of antiaromaticity will be discussed in a later section.

Choice of the Reference System, Preparation, and Electrochemical Oxidation. To evaluate antiaromaticity, it is necessary to determine whether the stability of the system is less than that of an appropriate reference system. In this context, this would ask whether the redox potential observed in the system is more positive than that for a reference system. The ideal reference system would be one like **7** in which the phenyl rings that were to serve as a model for the incompletely delocalized fluorenyl system were planar, rather than **5/6** in which the phenyl rings would be expected to be oriented in a propellared geometry.[32] Compound **7** was not well-behaved in an electrochemical sense; see the Supporting Information. However, the potentials for formation of the cation radical and dication were roughly similar to those of **5e/6e**, so we were comfortable with the use of **5/6** as model systems. A further advantage of **5/6** as reference systems is that electrochemical oxidations of several derivatives of tetraphenylethylene had been reported in the literature,[32−35] so we had some context for assuming that the oxidations of **5/6** would not have unexpected outcomes. The unsymmetrical **5/6** were synthesized primarily by Peterson olefination of diphenylmethane with the appropriately substituted benzophenones. Electrochemical oxidation was performed in an analogous fashion to that of **3**, and the redox potentials for formation of their cation radicals and dications are reported in Table 1, along with the difference between the redox potential for formation of the dications of the appropriately substituted diphenylmethylidenefluorene and the corresponding tetraphenylethylene. The redox potentials show that, in all cases except for *p*-methyl-substituted diphenylmethylidenefluorene, the dications of diphenylmethylidenefluorenes were formed at more positive potentials than the dications of tetraphenylethylenes, suggesting their decreased stability and greater antiaromaticity. While the redox potential for formation of the dication of *p*-methyl-substituted diphenylmethylidenefluorene is less positive than that of the corresponding tetraphenylethylene, the difference is very small.



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Nucleus-Independent Chemical Shift Calculations. Nucleus-independent shift calculations (NICS) calculations are made by GIAO calculation of the chemical shift of a ghost atom placed 1 Å above the center of a ring.[7,36] A positive value for NICS is associated with antiaromaticity. Its magnitude is dependent on the basis set and on the method used.[26] To determine the appropriate method for calculation of NICS, we compared the experimental carbon and proton shifts for **2c**$^{2+}$, **d**$^{2+}$, and **f**$^{2+}$ and those calculated using several calculational methods.[37] As we have seen in the past, the most effective correlation, r equals 0.998 for the carbon shifts and 0.952 for the proton shifts of the fluorenyl system,[28] is found when the calculations are done using the density functional theory method B3LYP with basis set 6-31G(d) on geometries optimized using B3LYP with basis set 6-31G(d) using the Gaussian 94,[38] Gaussian 98,[39] or Gaussian 03[40] suite of programs. The good correlation between experimental and calculated shifts suggests that other magnetic properties, such as NICS, will also be calculated effectively by this method.

The values for the nucleus independent chemical shift calculated using density functional theory for the 5-(NICS-5−1) and six-membered rings (NICS-6-1) of (**3a**−**g**)$^{2+}$ are given in Table 2, along with the values for (**2a**−**g**)$^{2+}$. Although the NICS values for (**2a**−**g**)$^{2+}$ were reported previously,[27] they were calculated in the plane

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[37] We compared experimental NMR shifts with those calculated with the GIAO method at RHF/6-31G(d)//RHF/6-31G(d) and B3LYP/6-31G(d)//B3LYP/6-31G(d) levels and with the IGLO method (Kutzelnigg, W.; Schindler, M.; Fleischer, U. *NMR, Basic Principles and Progress:* Springer-Verlag: Berlin, Germany, 1990), basis sets DZ and II, on geometries optimized at B3LYP/6-31G(d).

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TABLE 2. NICS[a] for $(\mathbf{3a-g})^{2+}$ and $(\mathbf{2a-g})^{2+}$

	NICS-5-1	NICS-6-1
$\mathbf{3a}^{2+}$	24.4	10.4
$\mathbf{3b}^{2+}$	23.7	9.8
$\mathbf{3c}^{2+}$	23.9	10.1
$\mathbf{3d}^{2+}$	24.1	10.3
$\mathbf{3e}^{2+}$	23.2	8.9
$\mathbf{3f}^{2+}$	22.8	8.6
$\mathbf{3g}^{2+}$	22.6	8.4
$\mathbf{2a}^{2+}$	24.0	10.0
$\mathbf{2b}^{2+}$	22.6	8.6
$\mathbf{2c}^{2+}$	22.9	8.9
$\mathbf{2d}^{2+}$	22.9	9.1
$\mathbf{2f}^{2+}$	22.2	7.5
$\mathbf{2g}^{2+}$	22.2	7.5

of the ring rather than 1 Å above. The strongly positive values for the calculated values of NICS substantiate the claim of antiaromaticity for these fluorenylidene dications.

Discussion

Assessment of Redox Potential as a Measure of Antiaromaticity. The redox behavior of substituted tetraphenylethylenes was examined so that the redox potentials for formation of their dications could be compared with that of substituted diphenylmethylidenefluorenes. As was reported previously, in the majority of cases the redox potential for formation of the dications of **2/3** was greater than the potential for formation of dications of **5/6**. If the difference in redox potential is truly measuring antiaromaticity, it should show a linear correlation with other measures of antiaromaticity, such as NICS. The plot of redox potential differences vs NICS-5-1 and NICS-6-1 showed effectively no correlation. This is not surprising, however, when one looks at the magnitude of the differences in redox potential. For almost all of the compounds examined, the measurement itself is no more than 1 order of magnitude greater than the error in the measurement. The primary value of the electrochemical study of the model systems is to demonstrate that the dications of **2/3** are indeed less stable than the dications of **5/6**.

However, when the redox potentials for formation of the dications of **2/3** are plotted against the NICS values, a strong linear correlation is shown, as seen in Figure 1. The correlation between redox potential for formation of the dication and NICS suggests that in these closely related systems, redox potential, a measure of thermodynamic stability, correlates well with antiaromaticity, with the greatest antiaromaticity shown by the dications with the largest positive redox potential, those that are most difficult to oxidize.

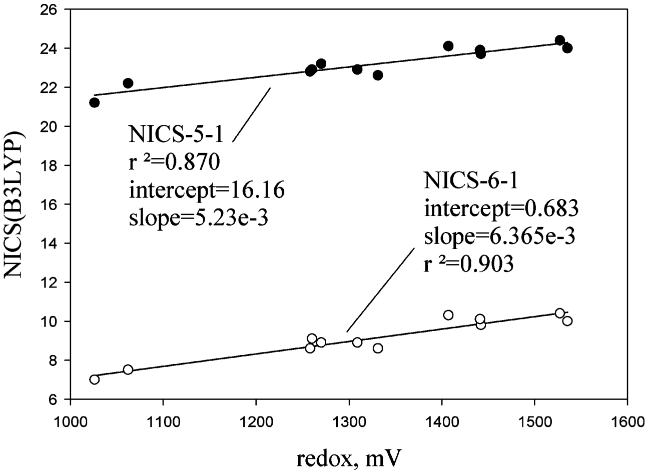
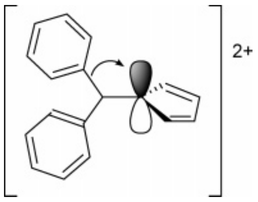


FIGURE 1. Redox potential for formation of the dications of **2/3** vs NICS-5-1 and NICS-6-1 values for those dications.

Effect of Substituent Position on Redox Potential and on Antiaromaticity. A comparison of the redox potentials for formation of the meta-substituted dications **3a**−**g** with the redox potentials for formation of the para-substituted dications **2a**−**g**, shown in Table 1 shows that **3a**−**g** have more positive redox potentials and are more difficult to form by oxidation than **2a**−**g**. A similar comparison of NICS-5 and -6 for **3a**−**g** shows that they are more antiaromatic than **2a**−**g**. It is apparent from these data that substitution in the meta position of the diphenylmethyl cationic substituent results in greater antiaromaticity than substitution in the para position. But how is this effect manifested? We have considered two modes by which the cationic substituent on a fluorenyl cation can interact with the fluorenyl system to affect its antiaromaticity. Because the fluorenyl system and its cationic substituent are not planar, it is not possible for interaction between the systems to occur through simple resonance. However, if fluorenyl system and diphenylmethyl substituent were basically orthogonal, the geometry would be appropriate for σ- to π-donation, as shown below with the benzene rings of the fluorenyl cation removed for ease of viewing.[41]



There is experimental evidence for the perpendicular geometry of this type of system.[22] The ability of the substituent to donate electron density into the π-system of the fluorenyl cation could explain the upfield shift for carbon 9 in dications such as the dication of tetrabenzo[5.5]fulvalene in comparison with fluorenyl

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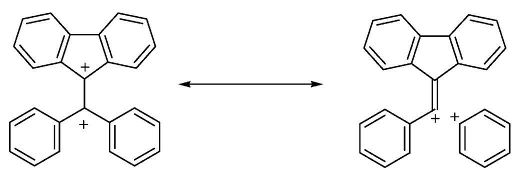
monocations.[23] Alternatively, the presence of a positively charged substituent on the fluorenyl cation might simply function to force greater electron delocalization on the fluorenyl system, resulting in greater antiaromaticity. We had observed such an increased electron delocalization for the dication of tetrabenzo[5.5]fulvalene, in comparison with the analogous fluorenyl monocation.[26] Schleyer et al. had explained the lack of antiaromaticity in the fluorenyl monocation by suggesting that the aromaticity of the two benzene rings of the fluorenyl system negated the antiaromaticity of the central 5-membered ring.[20] In such a situation, one would expect substantial delocalization within each benzene ring, as opposed to throughout the fluorenyl system, with the majority of charge localized on carbon 9 of the fluorenyl system.

If the primary manner for the diphenymethyl substituent to interact with the fluorenyl system was σ to p donation, we would expect that the bond lengths between the *ipso* and benzylic (α) carbons would be lengthened and those between the benzylic carbon of the diphenylmethyl system and between carbon 9 of the fluorenyl system to be shortened, from participation in the hyperconjugative resonance forms shown below. The bond lengths are tabulated in the Supporting Information along with the analogous bond lengths for the tetraphenylethylene dication. The bond lengths show very little variation with substituent, suggesting that if σ to p donation is occurring, it is a very subtle effect. When the bond lengths for the dication of the unsubstituted diphenylmethylidenefluorene (**2e/3e**) is compared with the unsubstituted tetraphenylethylene dication $(\mathbf{5e/6e})^{2+}$, there is no difference in the length of the bond between the ipso and α carbons. There is a substantial elongation of the length of the bond connecting the two cationic systems in the tetraphenylethylene dication compared to the diphenylmethylidenefluorene dication, 1.5063 Å for $\mathbf{5e/6e}^{2+}$ vs 1.4848 Å for $\mathbf{2e/3e}^{2+}$. Although the shorter bond length in $\mathbf{2e/3e}^{2+}$ might support σ to p donation, it might also reflect the consequence of a greater delocalization of positive charge in the fluorenyl system, resulting less charge repulsion in the two systems. Kochi et al. observed a similar elongation of the bond connecting the diphenylmethyl systems of the *p*-methoxy- and *p*-methyltetraphenylethylene dications.[32]



The second mechanism for interaction between the nominally perpendicular ring systems would be through the greater delocalization in the fluorenyl system forced by the magnitude of the positive charge on the α carbon of the diphenylmethyl system. The bond length changes described above are consistent with this. A second piece of evidence that supports this may come from the relationship between the Hammett substituent constants and NICS. The ability of a substituent to stabilize a charged species is demonstrated by a linear free energy relationship. However, the substituents of necessity only stabilize the charge on the diphenylmethyl system, not the charge on the fluorenyl system. There would be no reason to expect a correlation between NICS, which reflects the behavior of the fluorenyl system and a Hammett substituent constant. The plot of NICS vs σ_m/σ_{p+}[30] in Figure 2, however, shows such a correlation. This correlation would be consistent with a modification in the charge on the α carbon of the diphenylmethyl system that is then transmitted to the fluorenyl system, affecting its antiaromaticity.

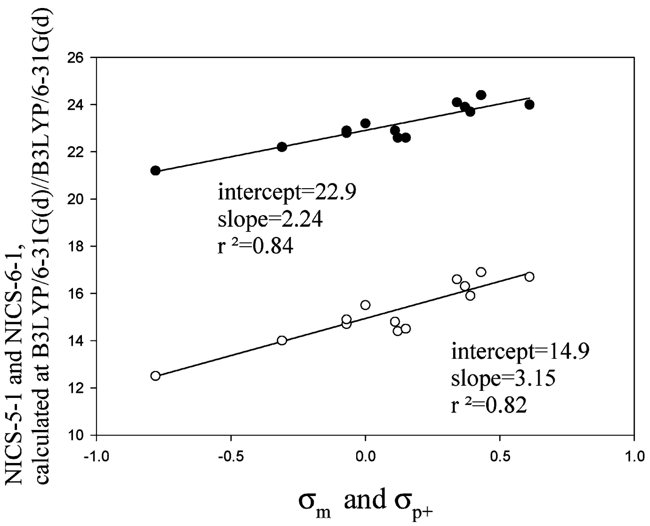


FIGURE 2. NICS-5-1 and NICS-6-1 vs σ_m/σ_{p+} for $(\mathbf{2a-g})^{2+}$ and $(\mathbf{3a-g})^{2+}$.

If greater delocalization of electron density in the fluorenyl system is occurring as a function of the magnitude of the positive charge on the α carbon, then we should see that as a change in the atomic charges of the carbons of the fluorenyl system. It is helpful to consider Schleyer's assessment of the lack of antiaromaticity in the unsubstituted fluorenyl cation[20] in greater depth. On the basis of NICS calculations and calculated magnetic susceptibility exaltation, he concluded that the aromaticity of the two benzene rings counterbalances the antiaromaticity of the five-membered ring system, resulting in very small magnetic susceptibility exaltation. In effect, the positive charge would tend to remain localized on carbon 9, to avoid the decrease in aromaticity of the benzene rings that delocalization throughout the system would require. However, if a positively charged substituent on carbon 9 of the fluorenyl system forced delocalization of charge, the consequence would be to decrease the aromaticity of the benzene rings and to increase the antiaromaticity of the entire fluorenyl ring system.[26] We have calculated the atomic charge for each carbon using natural population analysis[42] and the results for each carbon are tabulated in the Supporting Information. A plot of average atomic charge for all carbons of the fluorenyl system vs NICS-5-1 or NICS-6-1 shows no correlation; see the Supporting Information. However, not all carbons of the fluorenyl system would respond in the same way. That is, Schleyer's analysis would suggest that in the absence of perturbing influences, carbon 9 of the fluorenyl system would bear the majority of the positive charge. As greater delocalization of charge occurs, its

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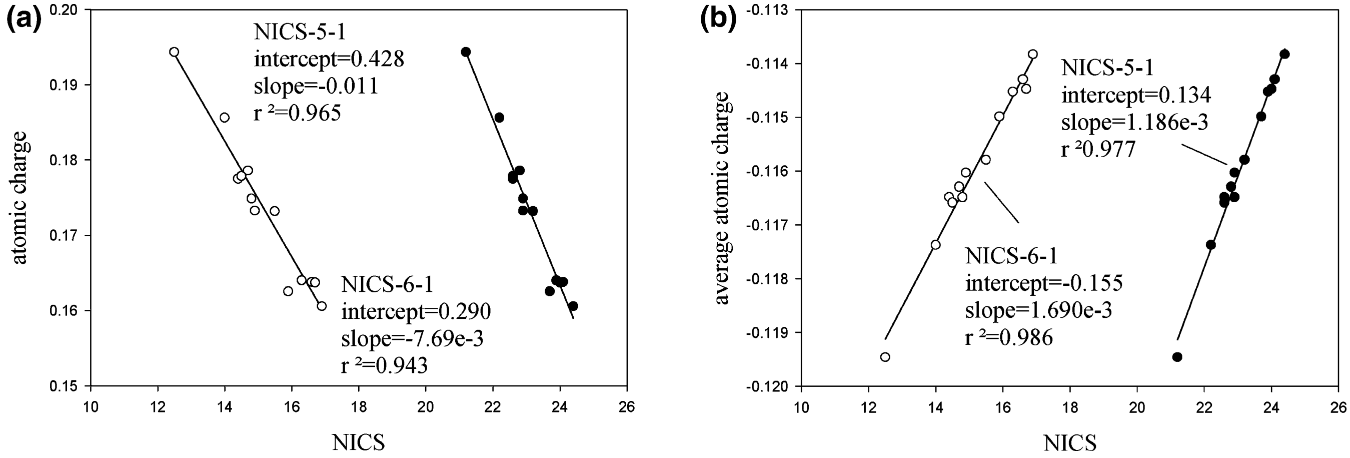

FIGURE 3. (a) Atomic charge (calculated using natural population analysis in Gaussian O3) vs NICS-5-1 and NICS-6-1 (NICS calculations on dummy atoms 1 Å above the center of each ring using the GIAO method in Gaussian 03 at B3LYP/6-31G(d)// B3LYP/6-31G(d)) for carbon 9 of the fluorenyl system of (**2a**−**g**)$^{2+}$ and (**3a**−**g**)$^{2+}$. (b) Average atomic charge for carbons 1−8 and 10−13 of the fluorenyl system of (**2a**−**g**)$^{2+}$ and (**3a**−**g**)$^{2+}$.

atomic charge would become less positive as that of the remaining atoms of the system becomes more positive. This is shown clearly in Figure 3a, showing a very strong inverse correlation between electron density, as shown by the calculated atomic charges, and antiaromaticity, as evaluated through NICS. That is, the greater the positive charge on carbon 9, the smaller the antiaromaticity, as measured through NICS values. Similarly, when the positive charge is forced to be delocalized throughout the fluorenyl system, the antiaromaticity of the fluorenyl system would increase, as shown by the positive correlation between the average calculated atomic charge and NICS values in Figure 3b. Note that for both plots, the *Y*-axis is showing increasing positive charge (decreasing negative charge).

Summary. Control of antiaromaticity in these and possibly all fluorenylidene dication systems comes from control of the pattern of delocalization of the positive charge of the fluorenyl cation. More importantly, this helps to establish the principle that both aromatic and antiaromatic systems are characterized by extensive delocalization, with the greater degree of aromaticity/ antiaromaticity demonstrated in systems with the greatest delocalization of electron density. Antiaromatic properties have been considered as manifested in an opposite sense to those of aromatic compounds. That is, antiaromatic compounds are anticipated to be unstable, have paratropic ^{1}H NMR shifts and magnetic susceptibility exaltations of opposite sign, and have bond length alternation which is a consequence of limited delocalization.[5,10] This study shows that extensive electron delocalization is demonstrated in both aromatic and antiaromatic species. Furthermore, it suggests that properties related to extensive electron delocalization, such as lack of bond length alternation would be manifested in both aromatic and antiaromatic species.

Experimental Section

The olefin precursors to **3a**−**d**,**f**,**g** were synthesized by Peterson olefination of the appropriate benzophenone with fluorene, as described below for the synthesis of **3a**. Experimental details for the synthesis of the appropriate benzophenones and NMR data for **3a**−**g** can be found in the Supporting Information.

Bis(*m*-trifluoromethylphenyl)methylidenefluorene (3a). To a solution of 9-trimethylsilylfluorene (0.39 g, 1.65 mmol) in 21 mL of THF at −78 °C was added *n*-butyllithium (0.70 mL of a 2.5 M solution in hexanes, 1.7 mmol). The resulting orange suspension was stirred at −78 °C for 10 min and then at 0 °C for 1.5 h. The reaction mixture was recooled to −78 °C, and a solution of 3,3′-bis(trifluoromethyl)benzophenone (0.50 g, 1.6 mmol) in 20.5 mL of THF was added via cannula. The cooling bath was removed, and the orange solution was stirred for 3 h at room temperature. The reaction mixture was quenched with 5 mL of 10% aqueous HCl. After addition of 60 mL of ether, the reaction mixture was extracted with 10% HCl, water, and saturated NaCl. The solvent was evaporated under reduced pressure, giving a bright yellow solid. Recrystallization from ethanol gave 0.41 g of bis(*m*-trifluoromethylphenyl)methylidenefluorene as white plates (61% yield): mp 185−186 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.50 (t, $J = 7.6$ Hz, 2 H), 6.93 (t, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 2 H), 7.54−7.74 (m, 10 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 119.6, 122.6, 124.8, 125.3, 126.8, 128.0, 128.6, 129.7, 131.5, 131.8, 133.3, 137.9, 140.8, 140.9, 143.0. Anal. Calcd for $C_{28}H_{16}F_6$: C, 72.10; H, 3.46; F, 24.44. Found: C, 71.94; H, 3.27; F, 24.63.

The tetraphenylethylene **5e** is commercially available. The substituted tetraphenylethylenes **5b**−**d**,**f**,**g** and **6a**−**d**,**f**,**g** were synthesized by Peterson olefination of the appropriate benzophenone with diphenylmethane as described below for the synthesis of **5f**. Yield and NMR data for **5b**−**d**,**g** and **6a**−**d**,**f**,**g** can be found in the Supporting Information.

1,1-Diphenyl-2,2-di-*m*-tolylethylene (5f). To a solution of diphenylmethane (1.68 g, 10 mmol) in 5 mL of THF at −78 °C was added *n*-butyllithium (8 mL, 1.6 M, 12.3 mmol). The solution was allowed to stir at room temperature for 1 h. To the resulting red solution was added chlorotrimethylsilane (1.5 mL, 12,5 mmol), and the resulting solution was stirred at room temperature for 10 min. The reaction was quenched by the addition of 10 mL of a saturated aqueous solution of NH$_4$Cl, and after the addition of 100 mL of CH$_2$Cl$_2$ and 100 mL of water, the two layers were separated and the organic layer was extracted with CH$_2$Cl$_2$. The organic layers were dried over MgSO$_4$ and concentrated in vacuo. The product, trimethylsilyldiphenylmethane, was purified by flash column chromatography on silica gel using hexane as eluant to afford 2.13 g. of a white solid: yield 88.1%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.00 (s, 9 H), 3.48 (s, 1H), 7.06−7.13 (m, 2H), 7.18−7.21 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0, 47.8, 126.7, 129.9, 130.4, 144.6.

To a solution of trimethylsilyldiphenylmethane (480 mg, 2 mmol) in 2 mL of THF at −78 °C was added *n*-butyllithium (1.5 mL, 1.6 M, 2.4 mmol). The solution was allowed to stir at room temperature for 8 h. To the reaction mixture was then added a solution of 3,3′-dimethylbenzophenone (420 mg, 2 mmol) in THF (5 mL), and the resulting solution was stirred at room temperature for other 24 h. The reaction was quenched by the addition of 2 mL of a saturated aqueous solution of NH_4Cl, and after the addition of 50 mL of CH_2Cl_2 and 50 mL of water, the two layers were separated and the organic layer was extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting oil was dissolved in 20 mL of CH_2Cl_2, and to the resulting solution was added 4 mL of a concd solution of H_2SO_4. The reaction mixture was allowed to stir at room temperature overnight. After 16 h, 100 mL of CH_2Cl_2 and 100 mL of saturated aqueous solution $NaHCO_3$ were added to the mixture. The two layers were separated, and the organic layer was extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash column chromatography on silica gel using hexanes as eluant to afford 360 mg of a white solid: yield 50.0%; mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 6H), 6.78 (s, 1H), 6.80−6.81 (m, 3H), 6.84 (d, J = 7.2 Hz, 2H), 6.91 (dd, J = 14.8 Hz, J = 7.6 Hz, 2H), 6.97−6.99 (m, 4H), 7.01−7.03 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0, 127.9, 128.8, 129.1, 129.2, 130.1, 133.0, 133.6, 138.7, 142.3, 142.8, 145.2, 145.6. Anal. Calcd for $C_{28}H_{24}$: C, 93.29; H, 6.71; Found: C, 92.69; H, 6.52.

Analytical data for **5a**, **6f**, **6g,** and trimethylsilyldiphenylmethane agreed with literature values.[43−45] In the case of **5a**, the synthetic pathway involves a Barbier reaction of the appropriate benzophenone with the bromodiphenylmethane followed by a dehydration reaction in acidic conditions, as reported in the Supporting Information.

Model compound **7** was synthesized by Peterson olefination from 9,9-dimethyl-9,10-dihydroanthracene.

Synthesis of 10,10-Dimethyl-9-diphenylmethylidenanthracene, 7. *n*-Butyllithium (0.75 mL, 1.2 mmol, 1.6 M in hexanes) was added to a solution of 9,9-dimethyl-9,10-dihydroanthracene[46] (0.208 g, 1.00 mmol) in 5 mL of THF at 0 °C under a N_2 atmosphere. After 10 min, trimethylsilane (0.120 mL, 1.2 mmol) was added, and the mixture was allowed to stir at rt for 10 min. The reaction mixture was quenched with satd aqueous NH_4Cl. Ether was added, and the layers were separated. The aqueous layer was extracted with ether, the organic layers were combined and dried over $MgSO_4$, and the solvent was removed in vacuo to afford 280 mg, 99%, of 9,9-dimethyl-10-(trimethylsilyl)-9,10dihydroanthracene as a pale yellow solid.

A mixture of *n*-buthyllithium (0.75 mL, 1.2 mmol, 1.6 M in hexanes) and TMEDA (0.120 mL, 1.2 mmol) in 1 mL of THF was added to a solution of of 9,9-dimethyl-10-(trimethylsilyl)-9,10dihydroanthracene (0.280 g, 1.00 mmol) in 4 mL of THF at −40 °C under a N_2 atmosphere. The reaction mixture was allowed to stir at −40 °C for 1 h. The reaction mixture was then cooled at −78 °C, and a solution of benzophenone (0.180 g, 1.00 mmol) in 10 mL of THF was added. The reaction mixture was allowed to stir at −20 °C for 6 h. The reaction mixture was quenched with satd aq NH_4Cl. Ether was added, and the layers were separated. The aqueous layer was extracted with ether, the organic layers were combined and dried over $MgSO_4$, and the solvent was removed in vacuo. The product was purified by flash chromatography on silica gel using hexanes as eluent to afford 235 mg, 63%, of compound **7** as a pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 6H), 6.62 (t, J = 8.8 Hz, 2H), 6.86 (t, J = 8.6 Hz, 2H 3H), 6.96 (d, J = 9.0 Hz, 2H), 7.03 (d, J = 10.0 Hz, 4H), 7.15 (d, J = 8.4 Hz, 4H), 7.27 (d, J = 9.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.3, 40.4, 122.9, 125.1, 126.6, 126.7, 128.7, 129.4, 129.5, 135.6, 137.3, 137.7, 143.1, 146.5; mp °C. Anal. Calcd for $C_{29}H_{24}$: C, 93.51; H, 6.49; Found: C, 93.00; H, 6.52.

Electrochemistry. Cyclic voltammetric experiments were performed with a 10 μm platinum disk in glass, approximately 7 cm long and 0.3 cm in diameter. The Ag/$AgNO_3$ reference electrode consisted of a silver wire in a saturated aqueous solution of $AgNO_3$. The counter electrode was a 1 cm square platinum gauze. For specific details of the electrochemical procedure, see the Supporting Information.

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[38], 98,[39] and 03[40] program packages. The nucleus-independent chemical shifts (NICS)[7] 1 Å above the ring centers were calculated at B3LYP/6-31G(d) using the GIAO approach with the Gaussian 94, 98, or 03 program packages. Atomic charges were calculated by natural population analysis in the Gaussian 03 package.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **3a−c**,**g**, **5b−d**,**f**,**g**, **6a−d**, and **7**; cyclic voltammograms of **3a−g**, **5a−g**, **6a−g**, and **7**; tables of redox potentials, $\Delta E°$, and current ratios for **3a−g**, **5a−g**, **6a−g**; tables of bond lengths for $(\mathbf{2a{-}g})^{2+}$, $(\mathbf{3a{-}g})^{2+}$, and $\mathbf{5e}^{2+}$; a table of atomic charges for $(\mathbf{2a{-}g})^{2+}$ and $(\mathbf{3a{-}g})^{2+}$; calculated total energies and $[x,y,z]$ coordinates for $(\mathbf{2a{-}g})^{2+}$, $(\mathbf{3a{-}g})^{2+}$, and $\mathbf{5e}^{2+}$; plots of redox potentials vs σ_m, plots of atomic charges vs NICS. This material is available free of charge via the Internet at http://pubs.acs.org.

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