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Dications of Benzyldienefluorene and Diphenylmethylidene Fluorene: The Relationship between Magnetic and Energetic Measures of Antiaromaticity

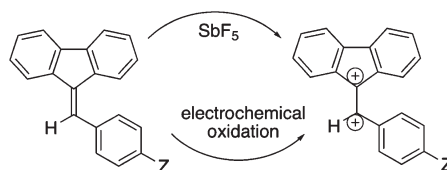
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Oxidation of *m*- and *p*-substituted benzyldiene fluorenes to antiaromatic dications was attempted by electrochemical and chemical means. Electrochemical oxidation to dications was successful for benzyldiene fluorenes with *p*-methoxy, *p*-methyl, *p*-fluoro, and unsubstituted phenyl rings in the 3-position; attempts to oxidize the *m*-substituted derivatives via electrochemistry were unsuccessful. Chemical oxidation with $\text{SbF}_5/\text{SO}_2\text{ClF}$ gave the dication of 9-[(4-methoxyphenyl)methylene]-9*H*-fluorene cleanly; oxidation of all other substituted benzyldiene fluorenes resulted in mixtures of products. The excellent linear relationship between the chemical shifts calculated by the GIAO method and the experimental shifts for the *p*-methoxy-substituted benzyldiene fluorene dication suggests that the calculations satisfactorily reflect the magnetic properties of this dication and potentially those of the other dications studied. The redox potentials from electrochemical oxidation, a measure of the stability of the dications, showed a good linear relationship with another measure of stability, the calculated difference in energy between each dication and its neutral precursor. The dications of benzyldiene fluorenes were less stable than the dications of diphenylmethylidene fluorenes; within each type of compound, dications with *p*-substituted phenyl rings were more stable than dications with *m*-substituted phenyl rings and dications with phenyl rings substituted with electron-donating groups were more stable than dications with phenyl rings substituted with electron-withdrawing groups. The antiaromaticity of the fluorenyl system was assessed through the nucleus-independent chemical shift (NICS) that was also calculated by the GIAO method. The plot of the NICS values per square area versus the calculated energy difference for the dications showed a moderate degree of linearity; the plot of NICS values per square area versus the oxidation potentials was less linear. Thus, a suggestive, but not conclusive, relationship between magnetic and energetic measures of antiaromaticity was observed.

Introduction

Aromaticity is a key tenet of organic chemistry, which has been used to guide the design of synthetic projects and to explain the behavior of cyclic conjugated molecules for nearly two centuries. From the discovery of benzene in 1825,^{1,2}

chemists have appreciated the unusual stability of the “aromatic sextet” and have sought to understand its origin and to increase the number of compounds demonstrating the properties of benzene beyond the direct derivatives of benzene. Because benzene is the quintessential aromatic molecule, its properties have served as the model for evaluation of the aromaticity of non-benzenoid aromatic species. The properties fall into three categories, those related to the existence of

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a ring current, which are considered magnetic properties, those that reflect the stability of an aromatic species, denoted energetic, and those that reflect the effect of delocalization on the degree of alternation of bond lengths, described as a structural property. Because aromaticity is not a phenomenon that can be directly observed, it is difficult to determine which properties are the direct result of aromaticity. The need to invoke a fictitious reference structure³ for evaluation of properties such as aromatic stabilization energy and magnetic susceptibility exaltation further removes the evaluation of aromaticity from experimental data. Depending on the type of measurement, aromaticity has been assumed to be a one-dimensional⁴ or multidimensional^{5,6} phenomenon.

We have been interested in the phenomenon of antiaromaticity, with a particular emphasis on preparing antiaromatic species that can be characterized experimentally.^{7–18} Traditionally, the characterization of antiaromatic species has been through theoretical calculation,^{4,19,20} which opens the conclusions to concerns about the calculation method used, including issues of basis set choice. When theoretical data can be shown to have a good linear relationship with experimental data, the theoretical data are viewed as more reliable, particularly by experimental chemists. We have been able to successfully use this approach to “validate” measures of aromaticity like nucleus-independent chemical shifts (NICS), which have no direct experimental analogue. NICS are the chemical shifts calculated for a ghost atom placed 1 Å above the planar ring system.²¹ The chemical shift is a tensor, and the component of the chemical shift parallel to the π -system has been shown to most reliably correlate with other measures of aromaticity; therefore, we will draw our conclusions from these NICS values, designated as NICS(1)_{zz}.²² If a good linear relationship exists between the experimental shifts and the NMR chemical shifts calculated by the same method as the NICS values, the method for calculation of those NMR shifts, and by extension the NICS values, are considered to be more reliable.

TABLE 1. Oxidation Potentials^a in Volts for Formation of 3²⁺ and 4²⁺, and 1²⁺ and 2²⁺

	3 ²⁺	4 ²⁺	1 ²⁺	2 ²⁺
a	NA ^b	NA ^b	1.54 ± 0.01	1.53 ± 0.01
b	1.50 ± 0.01	NA ^b	1.27 ± 0.01	1.27 ± 0.01
c	1.48 ± 0.01	NA ^b	1.26 ± 0.01	1.41 ± 0.01
d	1.41 ± 0.01	NA ^b	1.06 ± 0.01	1.26 ± 0.01
e	1.17 ± 0.01	NA ^b	1.03 ± 0.01	NA ^b

^aPotentials for a scan rate of 50 V/s in CH₂Cl₂ with (*n*-Bu)₄NBF₄ (0.10 M) as the supporting electrolyte and reported vs the Ag/AgNO₃ (0.1 M) reference electrode. ^bNot available.

We have demonstrated a good linear relationship between two measures of aromaticity, the nucleus-independent chemical shift and magnetic susceptibility exaltation, the response of an aromatic system to a magnetic field that is due to the presence of a ring current.²³ The good linearity also allowed us to demonstrate that the sum of the NICS values for each individual ring in a polycyclic system is an effective measure of the aromaticity of the system as a whole. This study also showed the value of using a combination of aromatic and antiaromatic species because the greater range of values obtained with the inclusion of antiaromatic species gave a more convincing demonstration of linearity.

One would expect that methods that evaluate the response of an aromatic system to a magnetic field would be internally consistent. We have been interested in examining the relationship between aromaticity and antiaromaticity in the different classes of properties assumed to measure aromaticity. A linear relationship between measures of stability, for example, and properties like NMR chemical shifts or NICS, which originate in a response to a magnetic field, would suggest that these different properties are measuring the same phenomenon. In the past, we demonstrated a rough linear relationship between energetic and magnetic properties through the relationship between the oxidation potential for formation of the antiaromatic dications of substituted diphenyl methylidenefluorenes (**1** and **2**) and the NICS values for the corresponding dications.^{12,15} We were interested in seeing whether the linear relationship existed within a related set of dications, the dications from oxidation of substituted benzylidene dications (**3** and **4**). Because we are attempting the preparation of antiaromatic species, we have no assurance that all dications shown for **3** and **4** will be available through chemical or electrochemical oxidation. Our plan, therefore, is to use the experimental properties of those species that can be prepared and characterized to examine their relationship to related properties obtained through calculation. We can then with greater assurance calculate the measures of antiaromaticity for species that we cannot prepare and provide a more complete set of data to sort out relationships between different measures of aromaticity and antiaromaticity. In the case of this study, a good linear relationship between calculated and experimental NMR chemical shifts will support the conclusions drawn from NICS values. A linear relationship between the experimentally determined redox potentials, a measure of stability, and the energy difference between the dication and its neutral precursor, will allow the use of that energy difference for dications that cannot be prepared experimentally.

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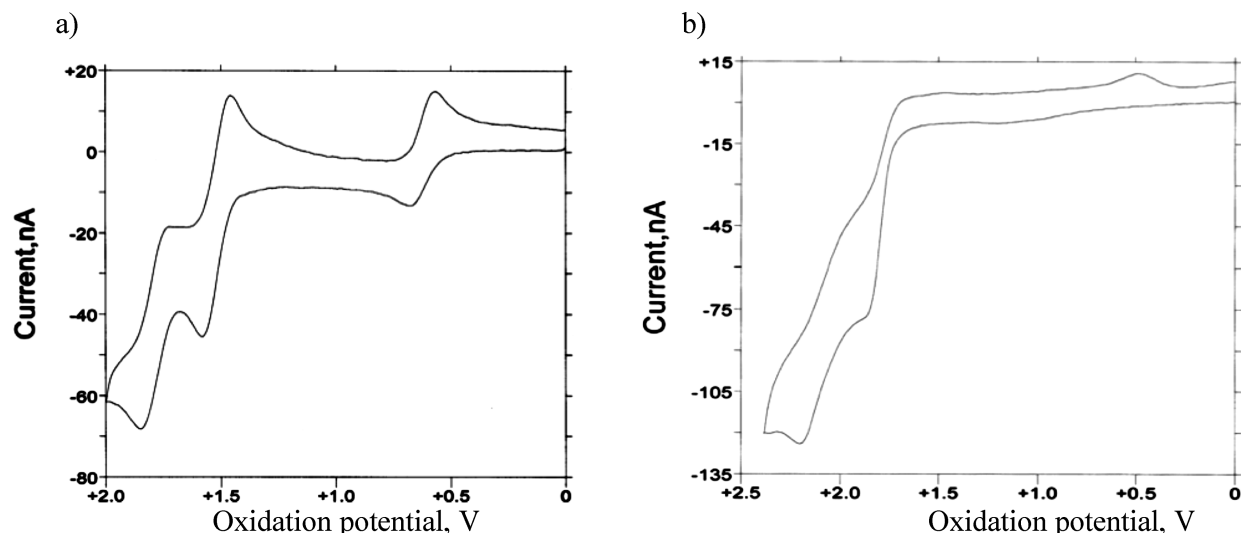
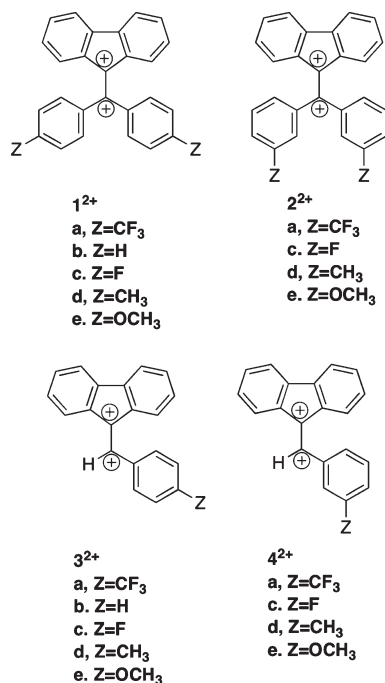


FIGURE 1. Cyclic voltammograms for oxidation of 3e (a) and 3c (b). Note that ferrocene is included in the solution as an internal reference at ~0.5 V.



Results and Discussion

Electrochemical Preparation of 3²⁺. As was true for 1²⁺ and 2²⁺,¹² oxidation in CH₂Cl₂ of the neutral unsaturated precursor to the dication could be observed via cyclic voltammetry for 3 for all species except for 3a. None of the precursors to 4 possessing meta-substituted phenyl rings could be oxidized to dications electrochemically. The redox potentials for formation of 3²⁺, 1²⁺, and 2²⁺ are given in Table 1, with the cyclic voltammograms shown in Figure 1 for 3e²⁺ and 3c²⁺. These cyclic voltammograms were chosen to demonstrate the differences as the substituent became less stabilizing. The cyclic voltammograms for 3c²⁺ and 3d²⁺ can

TABLE 2. Calculated Electronic Energy Differences^a ($\Delta_{\text{dication-neutral}}$) in Electronvolts for 1–4

	1	2	3	4
a	6.09	6.06	6.34	6.30
b	5.84	5.84	6.16	6.16
c	5.83	5.98	6.12	6.25
d	5.70	5.79	6.03	6.11
e	5.52	5.82	5.81	6.15

^aAt the B3LYP/6-31G(d) level with ZPVE energies calculated by the PCM method with CH₂Cl₂ as the solvent. Because the conversion from hartrees per particle or kilocalories per mole assumes a one-electron transfer, the values were divided by two for the two-electron oxidation.

be found in the Supporting Information along with complete electrochemical data for 3²⁺.

Evaluation of Relative Stability through Calculated Energy Differences between Dications and Their Neutral Precursors. Table 1 also repeats the data previously reported for 1²⁺ and 2²⁺. The oxidation potentials for formation of the dications are more positive for the formation of 3²⁺, for a comparison of each substituent, which suggests the greater instability of 3²⁺ versus 1²⁺ and 2²⁺. Support for this comes from a consideration of the calculated difference in energy for the dication versus the neutral species. We have calculated the energy of the neutral precursors and their dications for 1–4 for structures optimized using the polarization continuum method (PCM) with dichloromethane as the solvent. The energies and their differences with zero-point energy corrections are listed in Table 2 for the species calculated with solvent. The relationship between the experimental redox potentials and the calculated energy differences for 3a–d²⁺, 1a–e²⁺, and 2b–e²⁺ is shown in Figure 2 and is roughly linear. Redox potential here is used as a proxy for the stability of each dication, while the calculated energy difference is a direct measure. The linearity of the relationship is probably about as good as we might expect to find for these diverse conditions. If the optimized geometries were vastly divergent from those of the actual dications, we would expect a greater deviation from linearity.

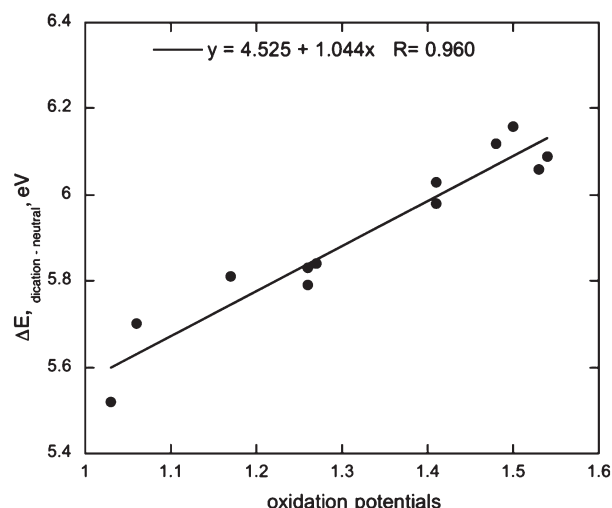


FIGURE 2. Comparison of oxidation potentials for **3a**–**d**²⁺, **1a**–**e**²⁺, and **2b**–**e**²⁺ with the corresponding differences in energy between the dication and its neutral precursor. See Table 2 for details of the calculations.

Evaluation of Antiaromaticity through Magnetic Measures.

The primary experimental measures of aromaticity and antiaromaticity that probe a ring current and are considered magnetic measures are the diatropic shifts in the ¹H NMR spectra of aromatic species and paratropic shifts in the NMR spectra of antiaromatic species. The use of NMR chemical shifts for evaluation of aromaticity has been called into question because the out-of-plane component of the magnetic tensor is necessary for evaluation of the ring current. The chemical shift, which is an average of all the magnetic tensors, can mask the contribution of the out-of-plane component.²⁴ We will use the nucleus-independent chemical shift as the primary tool for the evaluation of antiaromaticity through magnetic measures because we can include only the out-of-plane component of the magnetic tensor. However, as mentioned previously, the comparison of experimental chemical shifts to the chemical shift obtained in the same calculation as the NICS values helps to validate the NICS calculations.

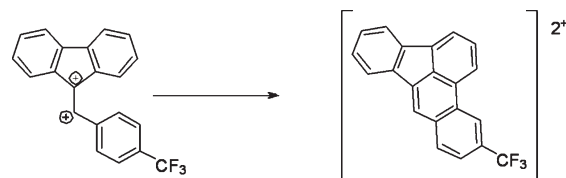
¹H NMR Chemical Shifts. The formation of dications **3**²⁺ and **4**²⁺ by oxidation of the corresponding substituted benzylidene fluorenes with SbF₅/SO₂ClF resulted in complex changes in the ¹H NMR spectra for the majority of the precursors. Spectra for reaction mixtures that could contain **3**²⁺ were cleaner than the reaction mixtures for oxidation to give **4**²⁺, but only the oxidation to give **3e**²⁺ gave a spectrum that was primarily due to a benzylidene fluorene dication (Figure 3). Assignments of chemical shifts were made on the basis of COSY spectra and by comparison with calculated spectra (see the Supporting Information). Note that while the upfield chemical shifts of the fluorenyl system appear symmetrical, the phenyl ring must possess restricted rotation on the NMR time scale, giving rise to four individual proton signals. While there is more splitting for those signals than we might anticipate, the COSY spectrum supports this assignment. In addition, the assignment from calculated shifts is in good agreement with the experimental shifts (see Figure 4).

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The correlation was best when solvent was included in the calculation. The chemical shifts for the fluorenyl systems are found in the region between 4.7 and 5.5 ppm and support the antiaromaticity of **3e**²⁺.

The most stable dication from para-substituted 3-phenyl benzylidene fluorenes would have been the methoxy-substituted one, **3e**²⁺, which was the only one to form cleanly. It is not surprising that dication **4**²⁺ could not be cleanly formed by chemical oxidation because we were unable to record good data for its electrochemical formation. It was of course disappointing to fail to form other dications cleanly, but as the instability of the species increases, we are going to have more difficulty with their preparation.

We suspected that part of the complexity of the spectra of the other oxidation reaction mixtures was due to the instability of the benzylidene fluorene dication and subsequent cyclization to benz[e]acephenanthrylenes and their probable subsequent oxidation, shown below. To support this conjecture, we quenched the reaction of **3a**²⁺ and were able to identify starting material **3a** as well as downfield peaks that were consistent with the formation of the substituted benz[e]acephenanthrylene²⁵ (see the Supporting Information).



Nucleus-Independent Chemical Shifts (NICS). The linearity of the experimental and calculated chemical shifts for **3e**²⁺ suggests that calculations of NICS using the same basis set should be reliable. The NICS values were calculated with the GIAO method in Gaussian 03²⁶ or Gaussian 09²⁷ with B3LYP/6-311+g(d,p) on ghost atoms 1 Å above and below the center of

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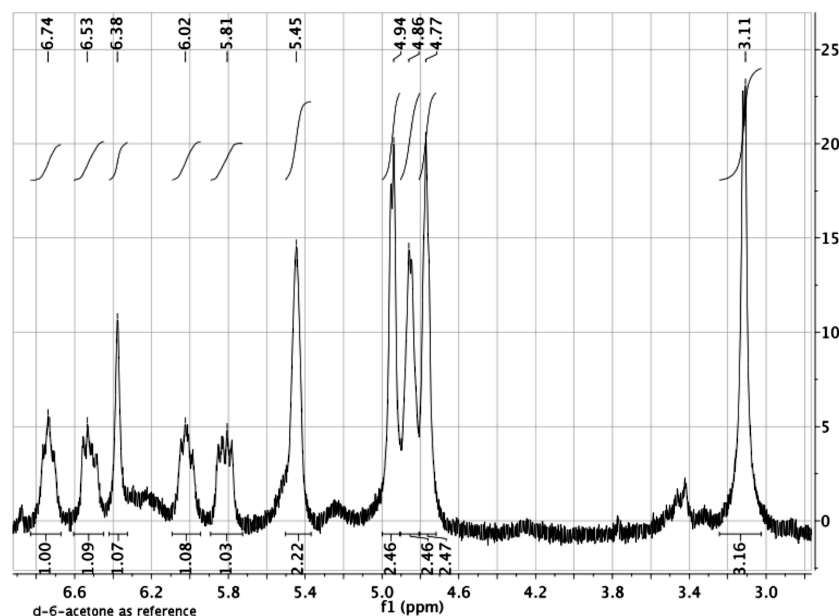


FIGURE 3. ^1H NMR spectrum of 3e^{2+} at $-50\text{ }^\circ\text{C}$, with acetone- d_6 and TMS as external references.

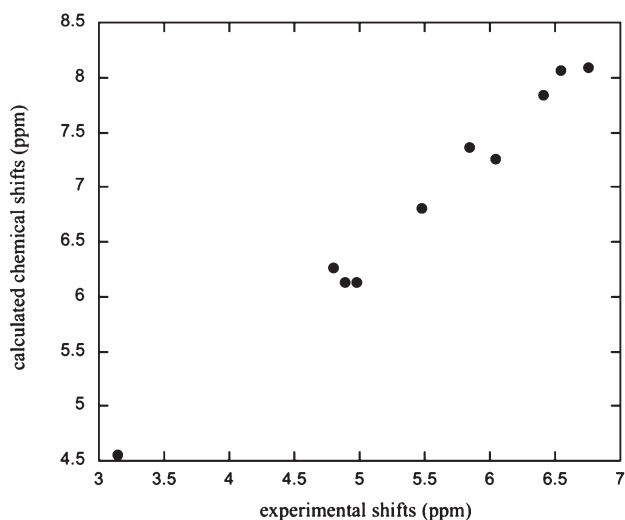


FIGURE 4. Calculated vs experimental ^1H NMR shifts for 3e^{2+} . NMR shifts were calculated with the GIAO method, with basis set B3LYP/6-311+g(d,p), the solvent (DMSO) included via PCM, on geometries optimized at the B3LYP/6-31g(d) level.

each ring of the fluorenyl system. The magnetic tensor perpendicular to the planar fluorenyl ring system was used, giving the $\text{NICS}(1)_{zz}$ value recommended for evaluation of aromaticity and antiaromaticity.²² The $\text{NICS}(1)_{zz}$ values are reported for the individual ring systems as well as for the summation of the three rings in the fluorenyl system (Tables 3 and 4).²³ The dihedral angles of the phenyl rings of 1^{2+} and 2^{2+} are approximately 50° ; those for the phenyl rings of 3^{2+} and 4^{2+} are approximately 60° (see the Supporting Information). Because the top and bottom sides of the fluorenyl systems are not exactly the same, there is a slight difference in the magnitude of the NICS values. We have averaged the NICS values for each ring of the fluorenyl system for Tables 3 and 4, but the unaveraged NICS values are available in the Supporting Information. We have determined that NICS

values are inversely related to the square of the area of the ring,²³ and even though the ring systems examined via NICS are very similar, the correction for ring area has an effect on the comparison of NICS between systems (see the Supporting Information). The values for 1^{2+} and 3^{2+} are given in Table 3 and the values for 2^{2+} and 4^{2+} in Table 4. We have previously reported NICS for 1^{2+} and 2^{2+} , but those values were the isotropic NICS values, from the sum of the three orthogonal magnetic tensors, and were calculated at a different basis set; therefore, we recalculated the values to allow comparison with those of 3^{2+} and 4^{2+} .

Comparison of the data for 3^{2+} with those for 4^{2+} is consistent with the observations of stability from ^1H NMR spectral data and from electrochemical measurements. In addition, the summation of $\text{NICS}(1)_{zz}$ demonstrates that for all systems the greater the electron-withdrawing effect of the substituent, the greater the antiaromaticity of the positively charged fluorenyl system.

Comparison of Energetic and Magnetic Measures of Aromaticity and Antiaromaticity. We now have two energetic measures of antiaromaticity, the experimental redox potential for formation of the fluorenylidene dications and the computed ab initio energy differences, and one magnetic measure, $\text{NICS}(1)_{zz}$. The relationship between NICS per square area and the calculated energy differences is shown in Figure 5a. There is a suggestion of linearity between these computed energetic and magnetic measures of aromaticity, although it is certainly not definitive.

Figure 5b shows the relationship between the summation of the calculated NICS per square area and the experimental redox potentials for those dications of 1^{2+} – 3^{2+} that could be prepared via electrochemical oxidation. The data show a trend with an increasing difficulty of formation by electrochemical oxidation, reflecting instability that is related to increasing antiaromaticity. Further work to increase the range of redox potentials and NICS values by the inclusion of related aromatic dianions is underway. As we demonstrated in the examination

TABLE 3. NICS(1)_{zz} Values for Para-Substituted Fluorenylidene Dications 3²⁺ and 1²⁺^a

	3 ²⁺				1 ²⁺			
	NICS-5 ^b	NICS-6 ^c	ΣNICS ^d	ΣNICS/area ²	NICS-5 ^b	NICS-6 ^c	ΣNICS ^d	ΣNICS/area ²
a	88.79	58.10	204.99	1.255	74.94	35.12	145.18	0.782
b	87.43	51.87	191.17	1.087	68.72	29.10	126.92	0.706
c	80.86	44.86	170.59	0.993	75.05	32.45	139.94	0.733
d	76.49	39.44	155.36	0.907	72.23	28.81	129.85	0.681
e	74.02	35.67	145.37	0.842	55.65	21.50	98.64	0.649

^aNICS values calculated by the GIAO method with B3LYP/6-311+g(d,p) on geometries optimized at the B3LYP/6-31g level. ^bValues obtained in the center of the five-member ring. ^cValues obtained 1 Å above the center of the six-member ring. ^dThe sum of NICS(1)-5 and 2 × NICS(1)-6.

TABLE 4. NICS(1)_{zz} Values for Meta-Substituted Fluorenylidene Dications 4²⁺ and 2²⁺^a

	4 ²⁺				2 ²⁺			
	NICS-5	NICS-6	ΣNICS	ΣNICS/area ²	NICS-5	NICS-6	ΣNICS	ΣNICS/area ²
a	100.82	66.59	234.00	1.226	69.74	33.52	136.79	0.807
c	87.73	54.25	196.23	1.158	77.68	36.28	150.24	0.787
d	88.13	49.07	186.27	0.976	73.55	30.98	135.52	0.710
e	94.52	57.61	209.75	1.102	73.02	30.77	134.57	0.705

^aAs in Table 3.

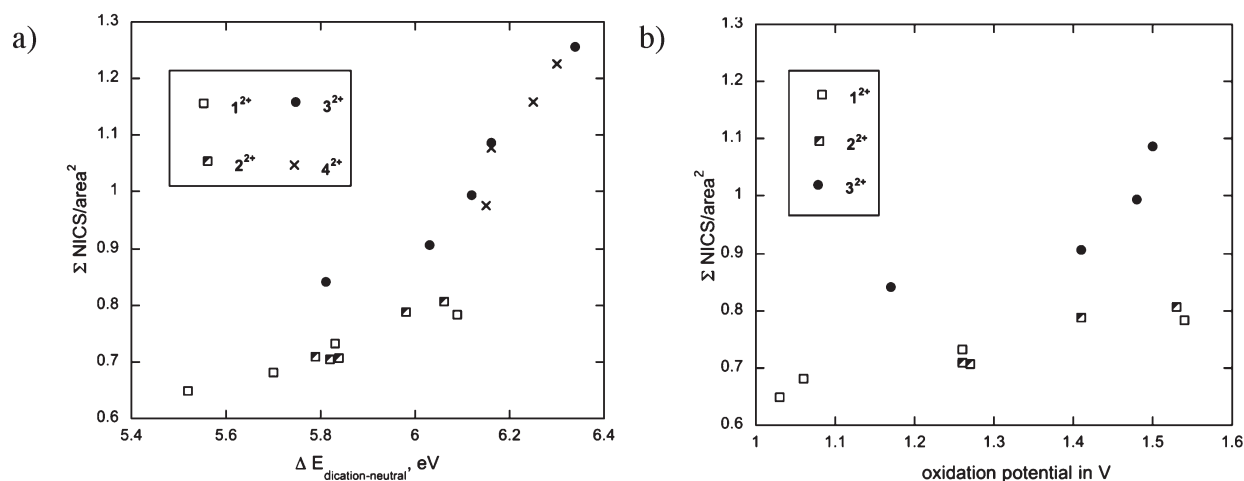


FIGURE 5. Relationship between ΣNICS per square area and measures of stability. (a) Calculated $\Delta E_{\text{dication-neutral}}$ values for 1²⁺–4²⁺. (b) Oxidation potentials for formation of 3b–e²⁺, 1a–e²⁺, and 2a–d²⁺.

of the relationship between ΣNICS and magnetic susceptibility exaltation,²³ the inclusion of data from both aromatic and antiaromatic species expanded the range sufficiently so that the linearity of the relationship was more apparent.

Conclusions

Electrochemical oxidation of 3b–e resulted in the formation of dications whose redox potentials were related to the electronic nature of the para substituent, with more electron-withdrawing substituents giving more positive oxidation potentials. The stability of dications 3²⁺, dications of meta-substituted benzylidene fluorenes, 4²⁺, and the dications from para- and meta-substituted diphenylmethylened fluorenes, 1²⁺ and 2²⁺, respectively, was assessed through the calculated energy difference between the dication and its neutral precursor, $\Delta E_{\text{dication-neutral}}$. For those dications whose oxidation potentials could be observed, there was a moderately good linear relationship between the oxidation potential

and the energy difference when solvent was included in the calculations, which supported the use of the oxidation potential to evaluate stability. Chemical oxidation with SbF₅ in SO₂ClF gave clean formation of only the dication of 3e, presumably because of intramolecular cyclization of the relatively unstable dications. There was a good linear relationship between the experimental ¹H NMR chemical shifts of 3e²⁺ and the chemical shifts calculated with the GIAO method using the B3LYP/6-311+g(d,p) basis set. This method and basis set were also used to calculate the NICS(1)_{zz} values for 1²⁺–4²⁺. The calculated measures of stability, $\Delta E_{\text{dication-neutral}}$, and calculated measures of the ring current, ΣNICS(1)_{zz}, showed a rough linear relationship. The relationship between the experimental measure of stability (oxidation potential for formation of the dication) and ΣNICS(1)_{zz} was much less linear but showed a definite trend, with stability inversely related to antiaromaticity. The relationship suggests that measures of stability and measures of ring current may be related.

Experimental Section

Synthesis of 3a–f and 4a–f. Benzyldiene fluorene and the benzyldiene fluorenes with *p*-fluoro, chloro, methyl, and methoxy substituents and with *m*-trifluoromethyl, chloro, methyl, and methoxy substituents were synthesized as shown for **3b** (see the Supporting Information), and their identities were confirmed by comparison with literature data. The syntheses of previously unknown **3a** and **4c** are also reported in the Supporting Information.

Cyclic Voltammetric Studies on 3 and 4-Substituted Benzyldienefluorenes. Cyclic voltammograms were recorded using a three-electrode assembly involving a platinum microelectrode, Ag/AgNO₃ (0.1 M), (*n*-Bu)₄NBF₄ (0.1 M), and platinum gauze as the working, reference, and counter electrodes, respectively. The solvent, dichloromethane, was dried with P₂O₅ and stored over type 4A molecular sieves.

Solutions of 3- and 4-substituted benzyldienefluorenes for cyclic voltammetry were prepared as 0.5 mM solutions of benzyldienefluorene in dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte in a final volume of 5 mL. Cetyltrimethylammonium bromide (CTAB) was also added to the solution to help with formation of dications of the fluoro-, bromo-, and chloro-substituted benzyldiene fluorenes. The concentrations of CTAB used for each compound were 6.3×10^{-3} , 0.013, and 8.4×10^{-3} , respectively. The methyl- and methoxy-substituted compounds did not need CTAB to facilitate dication formation. 4-Trifluoromethylbenzyldiene fluorene did not form dications in the presence or absence of CTAB. With other surfactants such as sodium dodecyl sulfate and Triton X-100, satisfactory results were not observed.

Approximately 2.5 mL of each solution was added to a 3 mL electrochemistry cell filled at the tip with anhydrous alumina. Cyclic voltammograms were recorded by potential sweep in the positive direction to the desired range depending on the compound and solvent. Scan rates of 10, 20, 50, 102, and 204 V/s were employed for each solution. Ferrocene (5×10^{-3} M) was added to the cell after all scan rates were completed to reference the potentials to the ferrocene–ferrocenium redox couple.²⁸ All potentials in this work are reported with respect to this redox couple (internal standard) because the potential of the reference electrode was not perfectly constant.

Chemical Preparation of Dications. Antimony pentafluoride (6.9×10^{-3} mol) was dissolved in SO₂ClF (1.5 mL). The

oxidant/solvent solution was cooled to -78 °C and mixed repeatedly until the solution was homogeneous. The benzyldiene fluorene ($\sim 2.4 \times 10^{-4}$ mol) was added to the solution, which immediately turned dark brown. The solution was mixed again, and a small volume was transferred to an NMR tube at -78 °C. Proton NMR spectra were recorded at -78 °C and at 10 °C intervals from -60 to -30 °C. COSY spectra were recorded when the reaction mixture appeared relatively clean, at varying temperatures from -60 to -40 °C.

Calculation of ¹H and ¹³C NMR Chemical Shifts, Nucleus-Independent Chemical Shifts, and Energies. ¹H NMR chemical shifts for **3a–e**²⁺, **4a–e**²⁺, **1a–e**²⁺, and **2a–e**²⁺ were calculated using the GIAO method in Gaussian 03²⁶ or Gaussian 09²⁷ with basis set B3LYP/6-311+g(d,p) on structures optimized with basis set B3LYP/6-31 g(d). Geometries for hydrocarbons calculated with density functional theory at this level have been shown to agree well with experimental data.^{29–31} The ¹H NMR shifts were calculated with the inclusion of solvent using the PCM method in Gaussian 03, with DMSO chosen as the solvent. NICS(1)_{zz} was calculated with the GIAO method with basis set B3LYP/6-311+g(d,p) using the component of the magnetic shift tensor in the *z* direction (perpendicular to the plane of the ring) for a dummy atom 1 Å above the center of the ring.²² The energies of **1a–e**²⁺, **2a–e**²⁺, **3a–e**²⁺, and **4a–e**²⁺ and of their neutral precursors were obtained from a frequency calculation using Gaussian 09, with basis set B3LYP/6-31g(p), and include the zero-point energy corrections. Both the geometries and the frequency calculations included solvent (CH₂Cl₂) using the PCM method.

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Supporting Information Available: Complete electrochemical data for oxidation of **3**, experimental and calculated chemical shifts of **3e**²⁺, quench data for **3a**²⁺, cyclic voltammograms for **3b–e**²⁺, experimental procedures for preparation of **3b**, **3a**, and **4c**, Cartesian coordinates, total energies, and numbers of imaginary frequencies for **1a–e**²⁺, **2a–e**²⁺, **3a–e**²⁺, and **4a–e**²⁺. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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