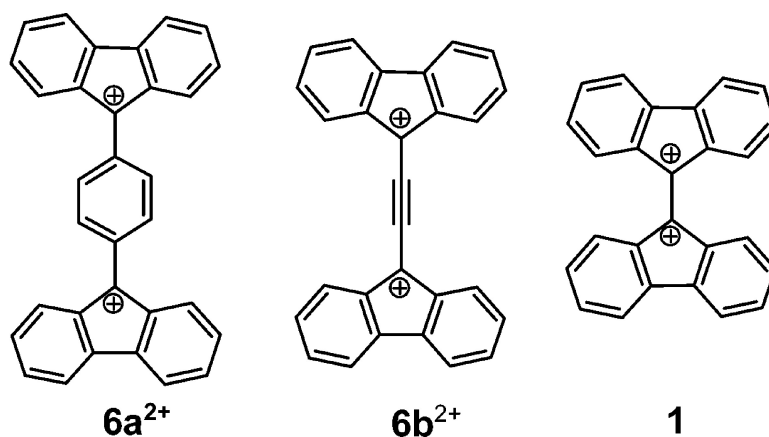


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Antiaromatic Spacer-Bridged Bisfluorenyl Dications Generated by Superacid Induced Ionization

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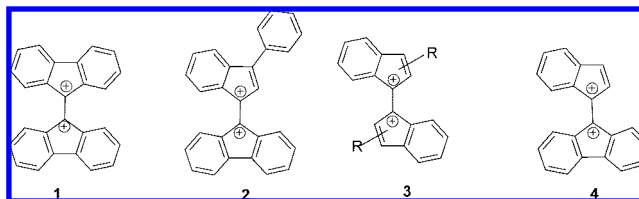
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Abstract: Derivatives of the dication of tetrabenzo[5.5]fulvalene were prepared with phenyl and ethynyl spacers through ionization of the appropriate bis-methylethers. The antiaromaticity shown by the parent dication was demonstrated for these dications with spacers, although it was attenuated by the presence of the spacer. It was substantially greater than that of fluorenyl monocations with similar substituents. Antiaromaticity was evaluated through comparison of ^1H NMR shifts with those of acyclic analogues, through nucleus independent chemical shifts, and through magnetic susceptibility exaltation. Although the fluorenyl systems are separated by spacers, the antiaromaticity of one system is affected by the other remote fluorenyl system. An explanation for this interaction may lie in the ability of a remote cationic substituent to attenuate delocalization in the spacer. The use of spacers is designed to prevent side reactions in less stable antiaromatic dications, allowing exploration of a number of species that have previously been inaccessible.

Introduction

While often subjects of great theoretical interest, the inherent instability of compounds of an antiaromatic nature such as 1,3-cyclobutadiene has severely limited the collection of experimental data on these often fleeting molecules.^{1–4} However, numerous antiaromatic bisfluorenyl (**1**),^{5–7} 3-phenylindenyl-fluorenyl 1,2-carbocationic systems (**2**),⁸ and other similar compounds,^{9–12} in which the two cations are located on directly adjacent carbon atoms, have been prepared and studied experimentally due to their surprising kinetic stability. The method for generating carbocations in each of these systems is low-temperature oxidation of the corresponding neutral olefin precursors with the highly reactive $\text{SbF}_5/\text{SO}_2\text{ClF}$. While this route has been very successful in producing dications that further our understanding of antiaromaticity, its overall scope has been currently limited to the aforementioned systems. Potentially interesting less stabilized antiaromatic systems, including bis-indenyl (**3**) and unsubstituted indenyl-fluorenyl carbocations

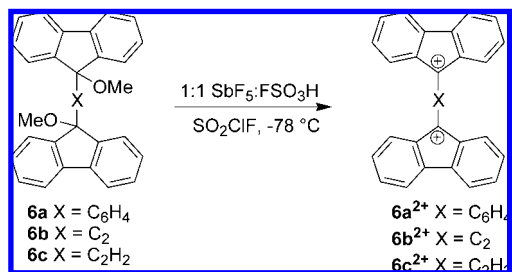
(**4**), have not been successfully observed using these methods because of their tendencies to cyclize under the reaction conditions. Cyclization of unstable dications has been commonly observed in similar systems.^{13–15} Additionally, synthetic methods to achieving the appropriate neutral precursors are dependent on the ability to form sometimes highly strained^{16,17} or electronically unstable^{18–22} double bond species.



Superacids such as fluorosulfonic acid and Magic acid have been staple reagents for Olah et al.^{23,24} in their groundbreaking and ongoing experimental studies of carbocationic molecules

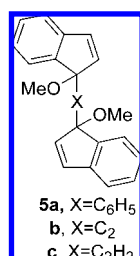
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Scheme 1



by way of ionization reactions. These superacids could be useful in generating antiaromatic dications of neutral precursors containing readily ionizable lone pair containing functionalities such as alcohols and ethers, thus expanding the library of compounds capable of being studied. In theory, this approach to 1,2-dications is thermodynamically more favorable than alkene oxidation because the bond breaking is partially compensated by the creation of the new protonated bonds. However, although the presence of such intermediates is often indirectly supported, *experimentally observed* 1,2-carbocationic species from 1,2-diols or diethers is unknown in the literature, presumably due to the propensity for fast cyclization, rearrangement, or elimination reactions of those intermediates in the superacidic media.²⁵ In unpublished studies by our group, attempted preparation of dications such as **3**, R = 3-CH₃, resulted in rapid cyclization when the dications were formed by oxidation with SbF₅/SO₂ClF, and would also be predicted to be inaccessible by superacid ionization of its 1,2-diol analogue. Therefore, in order to employ superacidic ionization routes for the production of *experimentally observable* antiaromatic dications, neutral precursors with ionizable moieties on nonadjacent carbon atoms must be utilized.

Possible precursors that would be suitable to afford antiaromatic carbocations via superacid ionization are neutral dimethyl ethers with conjugating phenyl, ethynyl, or ethenyl “spacer” units connecting the ionizable moieties, such as **5a–c**. Conjugated spacer separated dications and dianions of an aromatic nature have been reported in the literature,^{26–31} but similar antiaromatic species are thus far unknown. The diether functionality has been chosen due to the relative ease of purification for the neutral precursors and the potential for fewer side reactions upon superacid ionization when compared to the corresponding diol species. The spacer unit would serve three purposes: (1) it hinders cyclization of less stable antiaromatic dications by rendering the products more sterically demanding in comparison to the cyclized products of dications with no spacer unit, (2) it avoids the aforementioned rapid decomposition of 1,2-dications generated with superacids, and (3) it provides extra stabilization to the cationic species through delocalization.



In order to establish proof of concept for this novel and potentially scope-expanding route to antiaromatic carbocations,

several bisfluorenyl spacer-separated diether systems **6a–c** were synthesized (Scheme 1). The corresponding nonadjacent dications **6a²⁺** and **6b²⁺** were generated by Magic acid ionization and characterized at low temperatures with ¹H NMR spectroscopy. Dication **6c²⁺** could not be reliably generated. The experimental ¹H NMR shifts along with calculated ¹H NMR shifts of **6a²⁺** and **6b²⁺**, nucleus independent chemical shift (NICS) values, and magnetic susceptibility exaltation (Δ) calculations for **6a²⁺–c²⁺** were analyzed to evaluate the relative antiaromaticity of the dications and compared to that of the well studied tetrabenz[5,5]fulvalene dication system.^{5,9,32–34} The quality of the calculated NICS values was evaluated by comparison of ¹H NMR shifts, which could be compared to experimental values to determine their accuracy, calculated by the same method.

Results and Discussion

Synthesis of Precursors to Dications. Phenyl bridged dimethyl ether **6a** was synthesized by double lithium–halogen exchange on *p*-dibromobenzene and subsequent addition to 9-fluorenone to achieve diol **7** (Scheme 2). The diol was then methylated with NaH and MeI resulting in **6a**. Ethynyl and ethenyl bridged dimethyl ethers **6b** and **6c** were synthesized by the addition of ethynylmagnesium bromide to 9-fluorenone. Alkyne deprotonation of **8** and a second addition of 9-fluorenone gave diol **9**. The diol **9** was methylated with NaH and MeI, resulting in **6b**. Lithium aluminum hydride reduction of **9** resulted in olefin diol **10** which was methylated to produce **6c**.

In order to make a direct comparison between olefin oxidation and methyl ether ionization as routes toward antiaromatic dications, the syntheses of the corresponding bridged olefins were examined. Cyclohexadiene-bridged bisfluorene **14**, the neutral olefin precursor that should produce **6a²⁺** upon oxidation, proved to be elusive following two independent synthetic routes. The first route was a stepwise double Peterson olefination of monoketal protected 1,4-cyclohexadione with fluorene to ultimately achieve **13**. Unfortunately, oxidation of **13** with DDQ under several different conditions produced no desired product (Scheme 3). SnCl₂ reduction of phenyl bridged diol **7** was also unsuccessful, although the product was observed transiently as evidenced by the bright purple color that was observed immediately after the Sn(II) addition. To our disappointment, the product decomposed immediately upon reaction workup. In other reports synthetic attempts to achieve **14**³⁵ and similar species^{21,22} were also unsuccessful via Zn or Hg reduction of the dibromo analogue of **7**. These reports suggest that **14** is very difficult to isolate due to the formation of a cyclic tetramer

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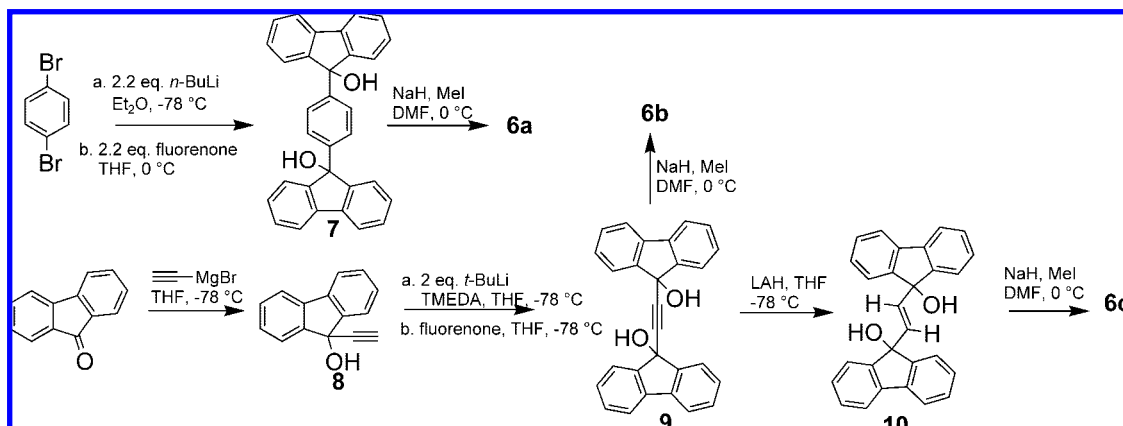
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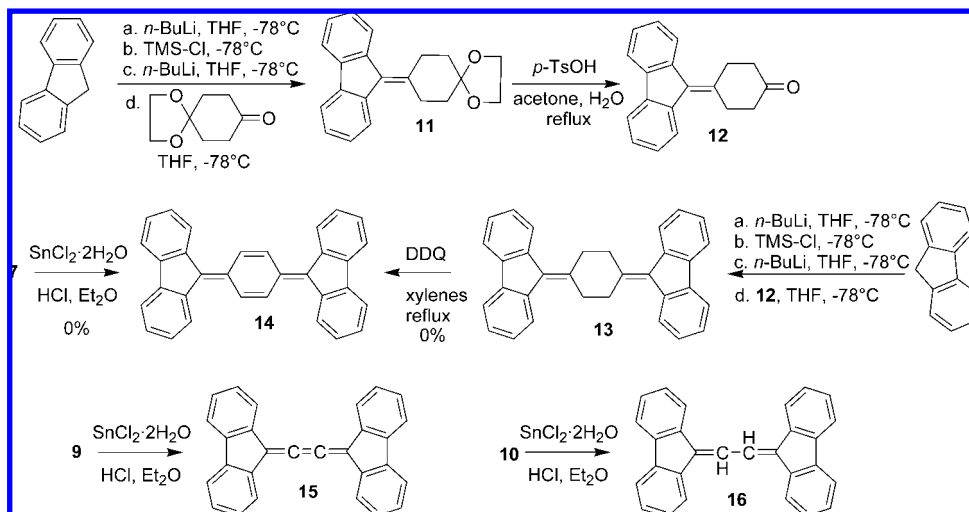
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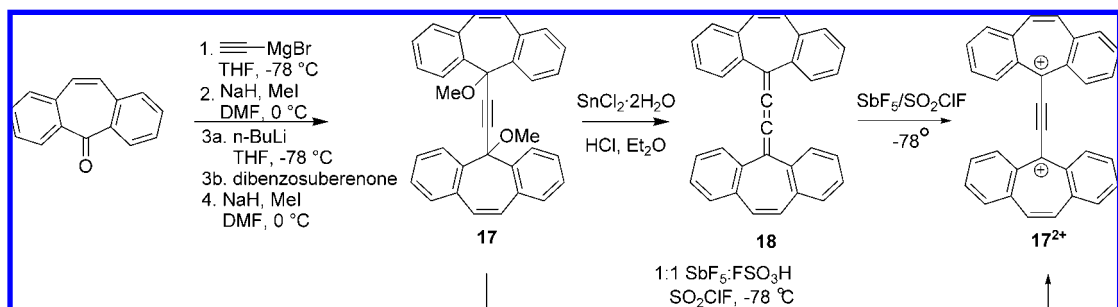
Scheme 2



Scheme 3



Scheme 4

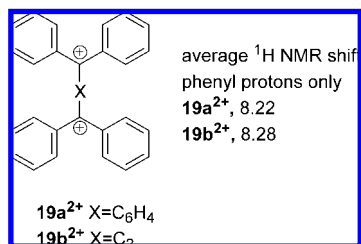


from a diradical intermediate in the reduction process. SnCl_2 reduction was successful, however, in producing butatriene **15** and diene **16** from their corresponding diols (**9** and **10**), which should produce $\mathbf{6b}^{2+}$ and $\mathbf{6c}^{2+}$, respectively, upon oxidation.

Additionally, ethynyl bridged bisdibenzocycloheptatriene dimethyl ether **17** and its corresponding butatriene **18** (Scheme 4) were synthesized in order to determine whether formation of aromatic ethynyl spacer-separated dication $\mathbf{17}^{2+}$ using either superacid ionization or oxidation methods was also feasible.

^1H NMR Shifts for Dications Formed by Ionization. The dimethoxy (**6a–c**) precursors to $\mathbf{6a}^{2+}$ – $\mathbf{6c}^{2+}$ were reacted with Magic acid (1:1 $\text{FSO}_3\text{H}/\text{SbF}_5$) at -78°C in an NMR tube. The

samples were immediately analyzed by ^1H NMR at -50°C . The experimental ^1H NMR shifts for $\mathbf{6a}^{2+}$ and $\mathbf{6b}^{2+}$ as well as the calculated chemical shifts are given in Table 1. Dication $\mathbf{6c}^{2+}$ could not be reliably observed in a reproducible manner due to its probable instability. The average experimental ^1H NMR shift for the fluorenyl protons of $\mathbf{6a}^{2+}$, 5.865 ppm, shows a substantial paratropic shift compared to the average shift for the phenyl protons of $\mathbf{19a}^{2+}$, 8.22 ppm. Dication $\mathbf{6b}^{2+}$ with an average shift for the fluorenyl system of 5.520 shows an even larger paratropic shift in comparison with the phenyl protons of $\mathbf{19b}^{2+}$, 8.28 ppm, as has been seen for related species previously.³²



The relationship between the experimental shifts and those calculated for 6a^{2+} – 6b^{2+} and **1** are shown in Figure 1. It is apparent that the agreement between the experimental and calculated shifts is reasonable, based on the quality of the correlation coefficient.

The comparison of the calculated ^1H NMR shifts to the experimental ones is important in the validation of the calculated NICS values, *vide infra*, but they also serve to support the geometry calculated for each species. NMR shifts have been shown to be very sensitive to the geometry of the species under examination.^{36,37} For 6a^{2+} , geometry optimization resulted in two geometries, one in which the phenyl spacer had a dihedral angle of 90° and one with a dihedral angle of 135° , the latter having the best agreement with experimental chemical shifts (Figure 1a). This geometry, which frequency calculations showed to be a minimum on the potential energy surface, was also about 8 kcal/mol lower in energy. The plot of the calculated and experimental shifts for the other geometry are given in the Supporting Information. Similarly, optimization of 6b^{2+} gave two geometries, one with the fluorenyl systems perpendicular to each other and another in which the fluorenyl systems had a dihedral angle of 113° . The energy difference between the two geometries was <1 kcal/mol, with the geometry in which the fluorenyl systems was perpendicular of slightly lower energy. The agreement between the calculated and experimental shifts was approximately the same for each species, and the calculated shifts for the slightly lower energy species are shown in Figure 1b. Finally, comparison of experimental shifts of **1** with the ^1H NMR shifts also calculated with solvent are shown in Figure 1c, along with the composite plot for all species in Figure 1d. Plots of experimental vs calculated shifts in the Supporting Information also demonstrate that inclusion of solvent in the calculated chemical shifts is important for good agreement with experimental shifts.

^1H NMR Shifts for Dications Formed by Oxidation. One goal in this study was to evaluate the effect of spacers on the magnitude of the antiaromaticity of dications related to species such as **1**. It is difficult to compare the chemical shift of **1** with the chemical shifts of 6a^{2+} and 6b^{2+} because the media, Magic acid/SO₂ClF for ionization and SbF₅/SO₂ClF for oxidation, are different. We attempted the ionization of 9,9-dihydroxy-tetrazobenz[5.5]fulvalene with Magic acid/SO₂ClF but were unable to obtain **1** by this method. Olah et al. were also unable to form dications from 1,2-diols,³⁸ because of other avenues for reaction in these species. Thus, in order to make a proper comparison, formation of 6a^{2+} – c^{2+} by oxidation was attempted.

As described previously, attempts to make the unsaturated precursor to 6a^{2+} , **14**, were unsuccessful. Oxidation of the

Table 1. Experimental^a and Calculated^b ^1H NMR Shifts (ppm) for 6a^{2+} and 6b^{2+} and **1**, as well as the Estimated Shift of **1** in Magic Acid, *Vide infra*

	6a^{2+}		6b^{2+}		1		
	expt	calcd	expt	calcd	expt ^c	estimated ^d	calcd
1,8	5.980	6.830	5.638	6.714	5.33	5.23	6.523
2,7	5.670	6.780	5.346	6.491	5.16	5.06	6.328
3,6	6.161	7.478	5.903	7.106	5.77	5.67	7.044
4,5	5.650	6.734	5.196	6.371	4.97	4.87	6.228
spacer	6.885	8.035	-	-			
fluorenyl	5.865		5.520			5.21	
proton ave.							

^a Spectra obtained in a mixture of SO₂ClF, FSO₃H, and SbF₅, with an external capillary of *d*₆-acetone, -50°C . ^b NMR shifts calculated using the GIAO method in Gaussian 03 with basis set B3LYP/6-311+g(d,p) on geometries optimized with basis set B3LYP/6-31 g(d). ^c Spectra obtained in SbF₅/SO₂ClF; see refs 5 and 24. ^d Calculated from the experimental shifts for **1**, using the upfield shift seen for 6b^{2+} when formed in Magic acid compared to SbF₅/SO₂ClF, *vide infra*.

unsaturated precursor to 6c^{2+} , **16**, resulted in a very complex spectrum; see Supporting Information, from which no useful information could be obtained but which is consistent with our failure to reliably prepare 6c^{2+} by ionization. Oxidation of **15** also gave a complex mixture, but the predominant species formed immediately upon mixing **15** with the oxidizing solution, SbF₅/SO₂ClF, appeared to be 6b^{2+} . With time, these resonances disappeared, to be replaced by apparent decomposition products. Comparison of the data for 6b^{2+} from ionization with that from oxidation showed that the peaks in the Magic acid/SO₂ClF solution were shifted upfield by ~ 0.10 ppm relative to the peaks in the SbF₅/SO₂ClF solution. To the authors' knowledge, these appear to be the first reported data on a dication formed both by ionization in Magic acid/SO₂ClF and by oxidation with SbF₅/SO₂ClF. Based on the chemical shift difference for 6b^{2+} in the two solvents, we estimated the chemical shift for **1** in Magic acid, which is given in Table 1 and which was used in Figure 1d.

The average chemical shift of the fluorenyl system in 6a^{2+} and 6b^{2+} and in **1** shows the following order of antiaromaticity, $6\text{a}^{2+} < 6\text{b}^{2+} < \mathbf{1}$. The shift for protons 1,8 and, to a lesser extent, protons 2,7 of **1** are further downfield than would be expected based solely on the antiaromaticity of the fluorenyl ring system; the two fluorenyl rings of **1** are almost perpendicular to each other, allowing the ortho protons on one ring system to feel the effect of the center of the opposing antiaromatic fluorenyl system.^{5,32} This results in an additional diatropic shift for those protons.

Because the quality of the spectra for the antiaromatic dication 6b^{2+} formed by oxidation was relatively poor, we examined the feasibility of forming an analogous bis-aromatic dibenzotropylium dication with a spacer by the oxidation of cumulene **18**. While dication formation was successful for this system, the ^1H NMR spectrum (see Supporting Information) for the dication formed by ionization of dimethoxy **17** had much better resolution. Comparison of calculated with experimental ^1H NMR shifts, given in the Supporting Information, shows the same excellent relationship as that for the antiaromatic dications with spacers. Thus, the ionization method appears to be advantageous over oxidative methods in the generation of spacer-separated dications.

Nucleus Independent Chemical Shifts. A second way of evaluating the antiaromaticity of the 6a^{2+} and 6b^{2+} is through

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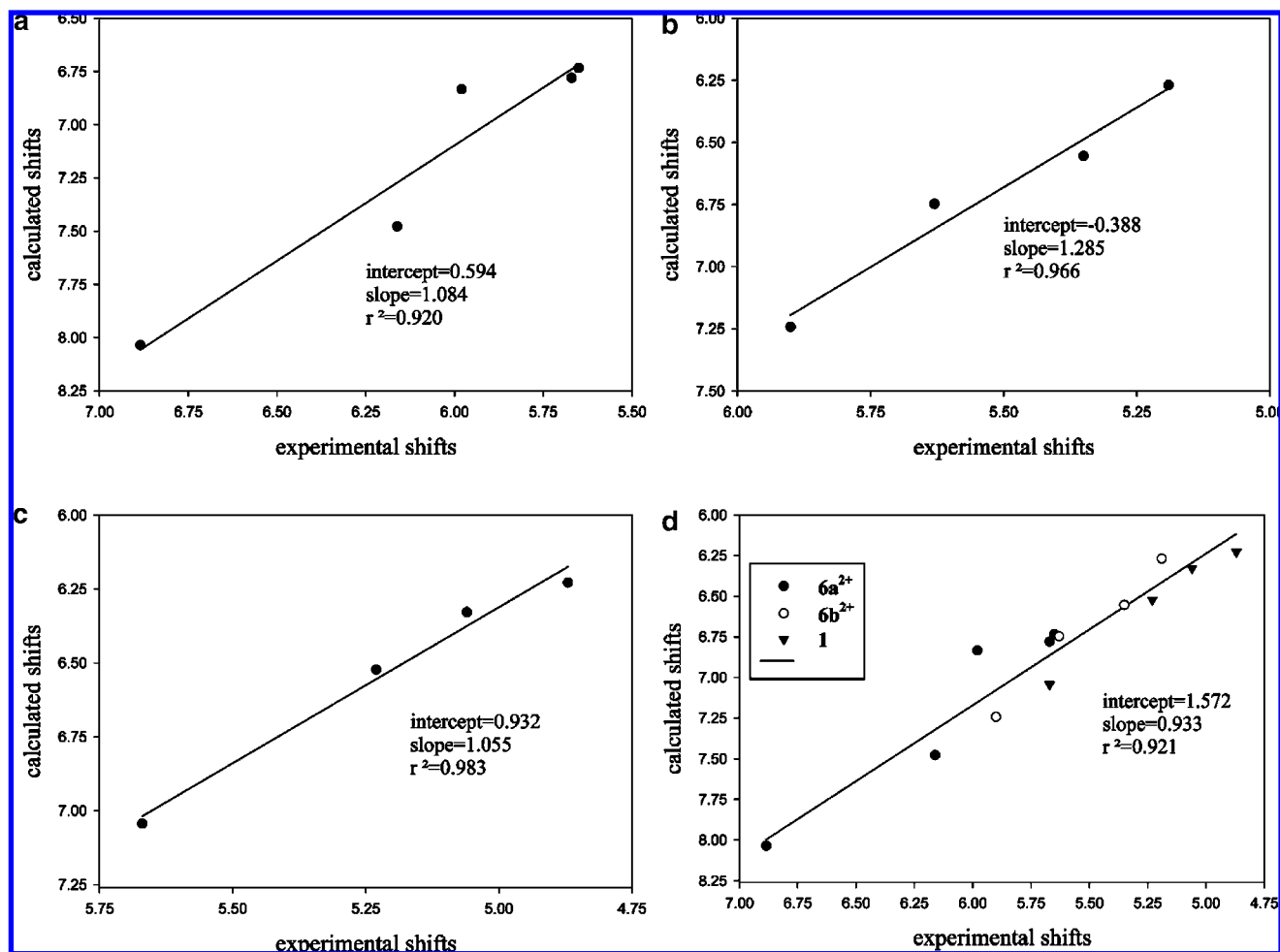


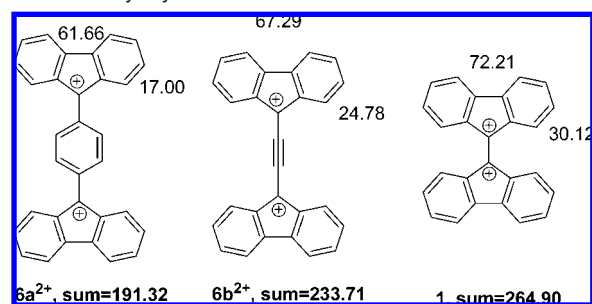
Figure 1. Calculated vs experimental ¹H NMR shifts for 6a²⁺–b²⁺: (a) 6a²⁺; (b) 6b²⁺; (c) 1. (d) Composite for 6a²⁺, 6b²⁺, and 1. Experimental shifts for 1 are those estimated for Magic acid solution, *vide infra*.

the use of nucleus independent chemical shifts³⁹(NICS) which evaluate the chemical shift of a dummy atom placed at the center of the aromatic or antiaromatic ring system. Because the electrons of the σ -system may affect the chemical shift calculated for the dummy atom, it is normally placed 1 Å above the plane of the ring, NICS(1). In addition, because the ring current is due to the electrons in the π -system, the magnetic tensor of the chemical shift perpendicular to the plane of the ring, NICS(1)_{zz}, is used to evaluate aromaticity or antiaromaticity.⁴⁰ In the traditional model of a ring current, protons on the periphery of an aromatic system are shifted downfield and have more positive values for the chemical shift, while a probe in the center of the ring system would be shifted upfield and would have a more negative value for the chemical shift. Thus aromatic compounds have negative NICS while aromatic systems have positive NICS.

The NICS(1)_{zz} values calculated for the optimized geometries with the lowest energies are shown in Schemes 1 and 5. According to this method of evaluation, the order of antiaromaticity is 6a²⁺ < 6b²⁺ < 1.

Magnetic Susceptibility Exaltation, Λ . A third method for the evaluation of aromaticity or antiaromaticity is through the

Scheme 5. NICS(1)_{zz} for 6a²⁺, 6b²⁺, and 1, including Σ NICS(1)_{zz} for the Fluorenyl Systems^a



^a Calculated with the GIAO method, basis set B3LYP/6-311+g(d,p) for a dummy atom 1 Å above the plane of the ring, magnetic tensor perpendicular to the ring system.

enhancement of the magnetic susceptibility of the species due to the existence of the ring current, magnetic susceptibility exaltation, or Λ .^{41–43} Briefly, the magnetic susceptibility of the species in question is calculated with the CSGT method. The magnetic susceptibility, χ , for the species with localized bonds is obtained through a summation of bond increments (see

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Table 2. Magnetic Susceptibility, χ , Magnetic Susceptibility Exaltation, Λ , and $\Sigma\text{NICS}(1)_{zz}$ for the Fluorenyl Systems of $6\mathbf{a}^{2+}$ – \mathbf{c}^{2+} and $\mathbf{1}^a$

	χ , cgs ppm	Λ , cgs ppm	$\Sigma\text{NICS}(1)_{zz}$
$6\mathbf{a}^{2+}$	–136.40	65.57	191.32
$6\mathbf{b}^{2+}$	–83.61	82.76	233.71
$\mathbf{1}$	–62.05	92.19	264.90

^a Magnetic susceptibility calculated with the CSGT method with basis set B3LYP/6-311+g(d,p) on geometries optimized with basis set B3LYP/6-31g(d). NICS calculated in a similar manner with the GIAO method.

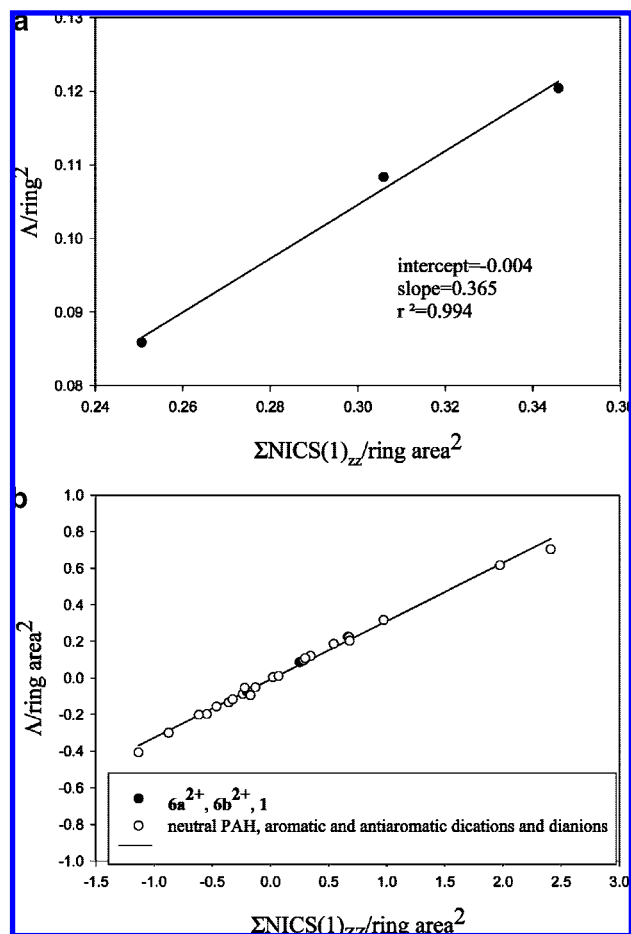


Figure 2. Comparison of $\Lambda/\text{ring area}^2$ with $\Sigma\text{NICS}(1)_{zz}$: (a) $6\mathbf{a}^{2+}$, $6\mathbf{b}^{2+}$, and $\mathbf{1}$; (b) $6\mathbf{a}^{2+}$, $6\mathbf{b}^{2+}$, and $\mathbf{1}$ as well as neutral PAH, aromatic and antiaromatic cations, dications, anions, and dianions; see ref 35.

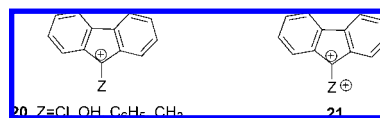
Supporting Information), and the difference between the two gives Λ . Table 2 gives χ and Λ for $6\mathbf{a}^{2+}$, $6\mathbf{b}^{2+}$, and $\mathbf{1}$.

The values of Λ show the order of antiaromaticity to be $6\mathbf{a}^{2+} < 6\mathbf{b}^{2+} < \mathbf{1}$, the same order shown by the NICS(1)_{zz} calculations. We have recently shown⁴⁴ an excellent correlation between the sum of NICS(1)_{zz} and Λ . Magnetic susceptibility exaltation is known to be dependent upon the square of the ring area,⁴² and we demonstrated that the $\Sigma\text{NICS}(1)_{zz}$ is also dependent on ring area squared. That relationship for $6\mathbf{a}^{2+}$, $6\mathbf{b}^{2+}$, and $\mathbf{1}$ is shown in Figure 2a. Inclusion of neutral PAH, aromatic and antiaromatic cations, dications, anions, and dianions gives the plot shown in Figure 2b, confirming that there is nothing unusual about the behavior of $6\mathbf{a}^{2+}$, $6\mathbf{b}^{2+}$, and $\mathbf{1}$.

The order of antiaromaticity from ¹H NMR shifts, NICS, or Λ is $6\mathbf{a}^{2+} < 6\mathbf{b}^{2+} < \mathbf{1}$. It is apparent that the ability of the

spacer to delocalize charge results in an attenuation of the antiaromaticity of the fluorenyl system. Of greater importance is the observation that with the inclusion of a spacer, even one that is capable of a great deal of stabilization such as phenyl, the antiaromaticity of the fluorenyl system is maintained. This suggests that derivatives of dications previously unknown, such as $\mathbf{3}$ and $\mathbf{4}$, should be accessible through the use of spacers.

Interaction of the fluorenyl ring systems. We have demonstrated that the antiaromaticity of the fluorenyl system in dication $\mathbf{1}$ is markedly greater than that in the fluorenyl monocation $\mathbf{20}$ and attributed this to the effect of a positively charged substituent in position 9 of the fluorenyl cation, as shown in general terms as $\mathbf{21}$.^{9,32} We have successfully demonstrated that the degree of antiaromaticity in the fluorenyl cation of $\mathbf{21}$ is affected by the nature of Z. In many of the systems we have explored, Z was a ring system, such as an indenyl cation,⁸ or dibenzopyrylium, dibenzotropylium, or dibenzocyclohexadienyl cation,^{5,32} and geometry optimization showed that the ring system of Z was often perpendicular to the fluorenyl ring system. Since these systems appear to be much more antiaromatic than $\mathbf{20}$, the cationic substituent Z in $\mathbf{21}$ must be affecting the electronic nature of the fluorenyl cation. However, since resonance bond delocalization is not possible for these effectively perpendicular and thus orthogonal systems, other possibilities for communication between the ring systems were explored. We had proposed two models for interaction of the systems, σ to p donation,³² also known as cross-hyperconjugation as shown below for $\mathbf{1}$, or electronically enforced delocalization as a consequence of the positive charge of Z.¹² In both cases, this requires that the fluorenyl cation and positively charged substituent be in close proximity. This is obviously not the case for $6\mathbf{a}^{2+}$ and $6\mathbf{b}^{2+}$, in which each cation might be expected to behave independent of each other and more like fluorenyl monocations, $\mathbf{20}$,⁴⁵ due to separation of charge. The fluorenyl monocation with a phenyl substituent is known ($\mathbf{20a}$),⁴⁶ but we also attempted the preparation of $\mathbf{20b}$ with an ethynyl substituent and $\mathbf{20c}$ with an ethenyl group. Ionization of either the alcohol precursor to $\mathbf{20b}$ and $\mathbf{20c}$ or the methoxy precursor resulted only in a polymeric product, presumably through reaction of small amounts of the initially formed monocation with an un-ionized precursor.



The average proton shifts for $\mathbf{20a}$, the sum of the NICS(1)_{zz} values, and the magnetic susceptibility exaltation, Λ , are shown in Table 3 along with the corresponding data for $6\mathbf{a}^{2+}$. Calculated data (NICS(1)_{zz} and Λ) for $6\mathbf{b}^{2+}$ and $\mathbf{20b}$ are included in the table for comparison purposes. To allow proper comparison, the values for the fluorenyl systems of the dications with spacers must be divided by the number of fluorenyl systems. Comparison of the data in Table 3 shows that neither $6\mathbf{a}^{2+}$ nor $6\mathbf{b}^{2+}$ is behaving like a fluorenyl monocation. The fact that the dications with spacers are substantially more antiaromatic than the analogous monocations suggests that there must be some mechanism for the fluorenyl systems to com-

(45) We appreciate the comments of a reviewer who suggested that we consider the behavior of fluorenyl monocations.

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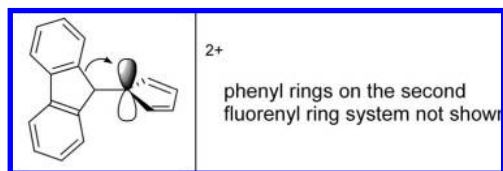
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Table 3. Comparison of the Average ^1H NMR Shift, Where Available, Summation of $\text{NICS}(1)_{zz}$ and Λ for the Fluorenyl Systems of $6\mathbf{a}^{2+}$, $20\mathbf{a}$, $6\mathbf{b}^{2+}$, and $20\mathbf{b}$

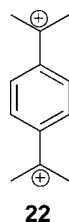
	$6\mathbf{a}^{2+b}$	$20\mathbf{a}^b$	$6\mathbf{b}^{2+}$	$20\mathbf{b}$
$\Sigma\text{NICS}(1)_{zz}$	96.55	56.33	116.86	83.30
Λ	32.78	18.62	41.38	27.13
average proton shift	5.865	7.42	5.520	NA

^a Values of $\Sigma\text{NICS}(1)_{zz}$ and Λ for $6\mathbf{a}^{2+}$ and $6\mathbf{b}^{2+}$ were divided by the number of fluorenyl rings. ^b The optimized geometry for $6\mathbf{a}^{2+}$ and $20\mathbf{a}$ showed that the dihedral angle of the phenyl ring with the fluorenyl system was $\sim 135^\circ$ for both systems.

municate with each other that is of necessity different from the mechanisms proposed previously for 1,2-dications such as **1**.



Interaction of Fluorenyl Systems Separated by Spacers. A possible explanation for the effect that a distal cationic fluorenyl system has on the antiaromaticity of another could lie in the effect of that substituent on the delocalization of the positive charge of the dication. That is, the presence of a second charge might inhibit the delocalization of charge in the spacer.⁴⁷ Even though the phenyl is not coplanar with the fluorenyl system for either $6\mathbf{a}^{2+}$ or $6\mathbf{b}^{2+}$, others have demonstrated that compounds in which the interacting units have dihedral angles similar to those in $6\mathbf{a}^{2+}$ and $20\mathbf{a}$ show interactions consistent with delocalization between the units.⁴⁸ The extent of delocalization might be examined through a comparison of the ^{13}C NMR shifts of the phenyl substituent of $6\mathbf{a}^{2+}$ and $20\mathbf{a}$. However, the analysis of this (See Supporting Information) was complicated by the comparison of the shift of the para carbon of the phenyl ring which is adjacent to a hydrogen in $20\mathbf{a}$ with the corresponding carbon on $6\mathbf{a}^{2+}$ which is adjacent to a positively charged carbon on the fluorenyl system. A similar comparison of the ^{13}C NMR shifts of the carbons of 22 ³⁸ with those of the dimethylphenylmethyl cation⁴⁹ showed a similar variation in shift, suggesting that the *nature* of the positively charged substituent, antiaromatic vs nonaromatic, is not the key effect here; see Supporting Information.



An alternative measure of relative delocalization would be the comparison of the bond lengths between the positively charged carbon on the fluorenyl system and the adjacent ipso carbon of the phenyl substituent in the monocationic and dicationic systems. The calculated bond length for $6\mathbf{a}^{2+}$ was

1.4596 Å compared to 1.4383 Å for $20\mathbf{a}$. Since the bond in the dicationic system is significantly longer, the presence of a cationic substituent in $6\mathbf{a}^{2+}$ appears to effectively reduce the delocalization of the charge into the phenyl system compared to $20\mathbf{a}$. A similar trend was shown for $6\mathbf{b}^{2+}$ and $20\mathbf{b}$, 1.4030 Å compared to 1.3957 Å. The shorter bond length in the species with ethynyl substituents compared to those with aryl substituents is expected due to the sp -hybridization of the ethynyl carbon compared to the sp^2 -hybridization of the aryl carbon.

Summary

Derivatives of the dication of tetrabenzo[5.5]fulvalene with phenyl, $6\mathbf{a}^{2+}$, and alkynyl spacers, $6\mathbf{b}^{2+}$, have been prepared by ionization of the dimethoxy precursors with Magic acid in SO_2ClF . The dication with an ethynyl spacer, $6\mathbf{b}^{2+}$, could also be prepared by oxidation of the appropriate unsaturated precursor in $\text{SbF}_5/\text{SO}_2\text{ClF}$, allowing evaluation of the effect of the different media on the ^1H NMR shifts of the dication. This allowed the shift of the parent dication **1**, prepared by oxidation to be directly compared to the shifts of $6\mathbf{a}^{2+}$ and $6\mathbf{b}^{2+}$, prepared by ionization of the corresponding diether. The antiaromaticity of the fluorenyl systems of $6\mathbf{a}^{2+}$ and $6\mathbf{b}^{2+}$ was assessed through experimental measurement of their ^1H NMR shifts and through calculation of their nucleus independent chemical shifts and magnetic susceptibility exaltation, Λ . A comparison of NICS and Λ to that of the parent dication of tetrabenzo[5.5]fulvalene reveals that the antiaromaticity of the fluorenyl system is maintained although it is attenuated by the spacers, with an order of increasing antiaromaticity of $6\mathbf{a}^{2+} < 6\mathbf{b}^{2+} < \mathbf{1}$. In addition, the ability of remote fluorenyl cations to interact through spacers appears to be related to the effect of the remote substituent on the delocalization of the positive charge of the fluorenyl substituent. The ability to prepare dications with spacers which maintain their antiaromaticity should allow the preparation of dications which contain antiaromatic systems such as unsubstituted indenyl cations. We are currently examining this type of species in our laboratories.

Experimental Section

Calculation of ^1H NMR Shifts, NICS , and Λ . Calculation of $\text{NICS}(1)_{zz}$ and Λ . ^1H NMR shifts for $6\mathbf{a}^{2+}$, $6\mathbf{b}^{2+}$, and **1** were calculated using the GIAO method in Gaussian 03 with basis set B3LYP/6-311+g(d,p) on structures optimized with basis set B3LYP/6-31g(d). Geometries for hydrocarbons calculated with density functional theory at this level have been shown to agree well with experimental data.^{50–52} The ^1H NMR shifts were calculated with the inclusion of solvent using the PCM method in Gaussian 03, with DMSO chosen as the solvent. $\text{NICS}(1)_{zz}$ was calculated with the GIAO method with basis set B3LYP/6-31 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 plane of the ring.⁴⁰

Magnetic susceptibility exaltation, Λ , is the difference between the calculated magnetic susceptibility, X , for the molecule of interest and that of a reference system. The reference system is formed by the summation of X for increments representing the bonds of the localized species. Details of the calculations can be found in the Supporting Information.

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Supporting Information Available: Experimental procedures for the preparation of all compounds. Spectra of $6a^{2+}$ – c^{2+} from ionization of dimethoxy compounds **6a–c** and **17** and from ionization of **7**, **9**, and **10**; spectra from oxidation of **15**, **16**, and **18**; plots of the calculated and experimental 1H NMR shifts

for alternative geometries of $6a^{2+}$ and $6b^{2+}$; plots of experimental 1H NMR shifts and shifts calculated without solvent for $6a^{2+}$ and $6b^{2+}$; increments for calculation of magnetic susceptibility for localized dications; calculated total energies, and [x,y,z] coordinates for $6a^{2+}$ – c^{2+} . NMR spectra of **6a–c**, **7–13**, and **16–18**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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