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Dications of Fluorenylidenes. Electronic Effects on the Paratropicity/Antiaromaticity of 2,7-Disubstituted Fluorenyl Cations

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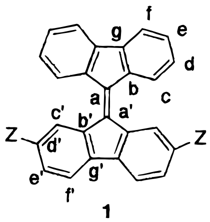
Oxidation of 2,7-disubstituted tetrabenzo[5.5]fulvalene derivatives **1a**−**d** resulted in the formation of dications which are fluorenyl cations linked by a single bond. These fluorenyl cations exhibit significant paratropicity in the ^{1}H NMR spectrum, which is attributed to an antiaromatic ring current. Interaction of the perpendicular ring systems is evident in the upfield shift of carbons a and a′, presumably due to σ−p donation. The lack of variation in the upfield shift of carbons a and a′, compared to previously reported systems, is attributed to the similarities of the geometries of **1a**−**d**$^{2+}$. Substitution at a remote site affects the antiaromaticity of the unsubstituted fluorenyl cation, but the nature of the effect of the substituent is not understood. Direct substitution on the fluorenyl cation by substituents which increase electron density, either through inductive π polarization or through resonance, cause a paratropic shift in the probe proton.

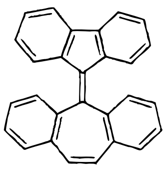
Introduction

Since 1965,[1,2] chemists have used the concept of antiaromaticity to account for the unusual instability and peculiar reactivity associated with planar cyclic conjugated hydrocarbons containing 4n π electrons. Unfortunately, direct investigations into the nature of the electronic, steric, and/or geometric factors which contribute to antiaromaticity in organic compounds have been limited by the inherent instability of the antiaromatic systems. However, recent work in our laboratories on dications of tetrabenzo[5.5]fulvalene (**1**) and tetrabenzo[5.7]fulvalene (**2**)[3] indicates that, although the fluorenyl cation is not antiaromatic,[4,5] fluorenyl cations containing cationic substituents (**A**) are indeed antiaromatic as indicated by a paratropic shift in the ^{1}H NMR spectrum.[3,6−10] These antiaromatic dications and their derivatives lend themselves to the study of antiaromaticity because, as a species, they are readily accessible and relatively stable and observable. Furthermore, as the cationic substituent appears to be crucial to the antiaromaticity of the fluorenyl subunit, a systematic study of fluorenyl dications containing modified cationic substituents may further our understanding of the factors contributing to antiaromaticity in these systems.



1

a, Z=H
b, Z=CH_3
c, Z=Cl
d, Z=F
e, Z=Br
f, Z=OCH_3



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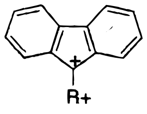

A

We report herein our investigations of dications of **1**$^{2+}$ in which one fluorenyl ring is disubstituted at the 2,7-position (**1b**−**f**$^{2+}$). These systems provide two probes for understanding antiaromaticity. First, we can examine how varying the substitution on the fluorenyl cation affects the antiaromaticity of that ring. Second, since our previous studies indicated that the nature of the cationic substituent affects the antiaromaticity of the fluorenyl cation, we can investigate the effects of changing the electronic nature of R+ (structure **A**) by varying the substituents at the 2,7-positions of one ring system and examining the effect on the antiaromaticity of the unsubstituted ring.

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Results

Tetrabenzo[5.5]fulvalene (**1**, 9-(9H-fluoren-9-ylidene)-9H-fluorene) was synthesized via literature preparation from 9-bromofluorene.[11] The 2,7-disubstituted tetrabenzo[5.5]fulvalenes were synthesized via Peterson olefination[12] of the appropriately substituted fluorenone[13−16] with fluorene or through reaction of the appropriately substituted fluorenone[17] with fluorenyllithium, followed by dehydration of the resulting alcohol. Dications were formed via oxidation with a 30-fold excess of SbF_5 in SO_2ClF. Both **1e** and **1f** were oxidized only to the cation radical under these conditions, as evidenced by broad signals in the ^1H NMR spectrum of the reaction mixture. We assume that complexation between SbF_5 and the substituent occurred, which would make the substituent electron-poor and further oxidation to the dication impossible. Such complexation has been reported for a *m*-methoxy substituent.[18] ^1H and ^{13}C NMR data for the remaining dications and their neutral precursors are reported in Tables 1−4. Complete assignments were made through two-dimensional correlation spectroscopy (COSY) and heteronuclear correlation spectroscopy (HETCOR) for all neutral compounds and for **1a,b**$^{2+}$. Long-range HETCOR spectroscopy focusing on three-bond couplings allowed the assignment of chemical shifts for carbons a, b, g, a′, b′, and g′ of **1a**−**d** and **1a,b**$^{2+}$. ^1H spectra of **1c,d**$^{2+}$ were assigned through COSY spectra which allowed the determination of connectivity and by analogy with other dications containing fluorenyl substituents, which have been completely assigned.[3,10] ^{13}C shifts for carbons b−g and b′−g′ were assigned by applying the substituent additivity rule.[19] Confirmation of the accuracy of the method was made by application to the assignments of carbons b−g and b′−g′ of **1b**$^{2+}$. The average standard deviation between the calculated and the experimental ^{13}C shift for carbons b−g and b′−g′ of **1b**$^{2+}$ was 0.5 ppm, with the difference ranging from 0.1 to 1.7 ppm.

Table 1. ^1H NMR Chemical Shifts for Dications[a]

	1a^{2+}	**1b**$^{2+}$	**1c**$^{2+}$	**1d**$^{2+}$
c	5.33 ± 0.02[b]	5.65 ± 0.13	5.57 ± 0.15	5.16 ± 0.09
d	5.16 ± 0.01	5.38 ± 0.16	5.33 ± 0.12	4.94 ± 0.09
e	5.77 ± 0.02	5.94 ± 0.12	5.91 ± 0.11	5.52 ± 0.09
f	4.97 ± 0.02	5.14 ± 0.14	5.08 ± 0.13	4.76 ± 0.09
c′		4.79 ± 0.12	5.24 ± 0.04	4.67 ± 0.08
d′				
e′		5.32 ± 0.15	4.64 ± 0.13	4.29 ± 0.09
f′		4.44 ± 0.12	5.59 ± 0.12	4.01 ± 0.08
CH_3		0.68 ± 0.12		

[a] Solvent, 0.75 g of SbF_5, 1.5 mL of SO_2ClF; temperature, −50 °C, reference, TMS in acetone-d_6 in an external capillary. [b] Standard deviation in a minimum of three separate preparations of dication, see text.

Table 2. ^1H NMR Chemical Shifts for Neutral Precursors[a]

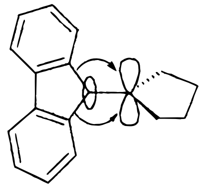
	1a	**1b**	**1c**	**1d**
c	8.38	8.40	8.22	8.29
d	7.20	7.21	7.19	7.21
e	7.32	7.33	7.32	7.34
f	7.69	7.71	7.63	7.66
c′		8.17	8.27	7.00
d′		–	–	–
e′		7.12	7.24	7.01
f′		7.53	7.52	7.54
CH_3		2.34		

[a] Solvent, $CDCl_3$ reference, TMS.

Discussion

A comparison of the ^1H NMR chemical shifts in Tables 1 and 2 reveals that, upon oxidation to a dication, the protons of both the substituted and the unsubstituted fluorenyl systems undergo a substantial upfield (paratropic) shift. The analogous paratropic shift in a set of dications of polycyclic aromatic hydrocarbons has been attributed to the antiaromaticity of the dication.[6] However, chemical shifts in ^1H NMR spectra may be due to a variety of effects, which must be examined prior to the postulation of an antiaromatic ring current. These effects include changes in the geometry of the molecule and the hybridization of the carbons to which the proton is attached, the polarity of the medium, and the charge density of the carbon to which the proton is attached, in addition to the existence of ring currents.[20] We have previously reported studies of the polarity of the medium, and these studies demonstrate that variation in chemical shift is not due to variation in SbF_5 concentration.[10]

Our previous research[3,10] suggests that the two fluorenyl ring systems are perpendicular to each other. Primary evidence for this geometry comes from the ^{13}C shift of carbon a which, at 189 ppm for **1a**$^{2+}$, is substantially upfield from the analogous carbon in the fluorenyl monocation[21] which resonates at ~228 ppm, depending on the substituent. This upfield shift indicates increased electron density at carbon a, relative to the fluorenyl monocation. In these dication systems, an orthogonal orientation of the two fluorenyl ring systems allows for the donation of electron density from one ring to another via σ to p donation, in which the σ system of one ring overlaps with the "empty" p orbital of the other, as shown.[22−24] Further evidence for the orthogonal geometry of **1a**$^{2+}$ and related systems comes from the ^1H NMR shift of the protons on carbons c and d[10] which are



phenyl rings not shown on second fluorenyl system for clarity

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Table 3. ^{13}C NMR Chemical Shifts for Dications[a]

	$1a^{2+}$	$1b^{2+}$	$1c^{2+}$	$1d^{2+}$
a	188.6	188.6	186.8 [b]	186.0[c]
b	145.8	148.1	145.3	146.1
c	144.8	149.2	143.5	145.0
d	136.0	135.7	132.7	137.0
e	158.9	158.5	159.0	160.1
f	130.4	129.9	131.2	131.2
g	152.5	152.1	153.2	153.1
a′		189.6	193.0[b]	193.1[c]
b′		148.3	146.6	146.3
c′		145.2	144.6	132.0
d′		145.1	137.0	167.6
e′		159.5	162.2	145.5
f′		131.0	131.9	132.4
g′		152.4	149.0	150.2
CH_3		17.4		

[a] Solvent, 0.75 g of SbF_5, 1.5 mL of SO_2ClF; temperature, −50 °C, reference, TMS in acetone-d_6 in an external capillary. [b] These assignments could be interchanged. [c] These assignments could be interchanged.

Table 4. ^{13}C NMR Chemical Shifts for Neutral Precursors[a]

	1a	1b	1c	1d
a	141.0	140.4	143.6	143.2
b	138.7	138.3	137.6	137.2
c	127.1	126.5	126.7	126.6
d	127.3	126.7	127.3	127.2
e	129.6	128.9	130.1	130.0
f	120.3	119.8	120.1	120.1
g	141.7	141.2	141.8	141.7
a′		141.7	138.1	136.5
b′		136.1	139.4	139.9
c′		127.2	126.2	113.2
d′		138.5	132.7	162.0
e′		130.1	128.9	116.1
f′		119.0	120.7	120.3
g′		139.0	138.4	136.5
CH_3		21.7		

[a] Solvent, $CDCl_3$.

affected by the opposing ring. Those protons are shifted downfield because they are pointing toward the center of an antiaromatic ring system.[3]

^{13}C NMR shifts of carbons a and a′ (Table 3) are analogous to those which were observed previously and which were shifted substantially upfield from those for the fluorenyl monocation. These data suggest σ to p donation and, thereby, an orthogonal geometry for these compounds. The orthogonal geometry of dications **1a**−**d**$^{2+}$ is supported by semiempirical (AM1)[25] molecular orbital calculations and molecular mechanics calculations,[26] which also allow comparison of variation in bond length, bond angles, and the remaining dihedral angles. The calculated bond lengths for the substituted and unsubstituted fluorenyl rings of **1a**−**d**$^{2+}$ [27] show bond lengths with relatively small variation between analogous bonds. For example, the bond lengths of b−c for **1a**−**d**$^{2+}$ show an average standard deviation of 0.03%. The lack of variation in the structures is also seen in the calculated bond angles and dihedral angles. The calculations do not reveal important variations in the geometry and hybridization between the fluorenyl ring systems of **1a**−**d**$^{2+}$. Thus, variation in the ^1H shifts of these cations is not due to changes in geometry or hybridization.

Differences in charge density for the carbons of **1a**−**d**$^{2+}$ can be assessed through the examination of their ^{13}C chemical shifts. Comparison of the shifts for the dications with those of their neutral precursors shows that, as anticipated,[20] the shifts for the dications are downfield, reflecting the decrease in electron density of a positively charged system. This is in marked contrast to the upfield shift of the protons. The ^{13}C chemical shifts for carbons b−g of the unsubstituted system (Table 3) show the expected variance due to resonance, when differences in environment are considered. That is, carbons d and e are in similar environments, and e, which would possess a greater partial positive charge than d, is more deshielded. Analogous arguments exist for the pairs c/f and b/g. However, comparison *between* systems reveals very little variation in chemical shift for analogous carbons. That is, the shift of carbon b, for example, is effectively the same in **1a**−**d**$^{2+}$. Thus the changes in the charge densities for the carbons bearing protons and for those adjacent to these carbons do not vary appreciably between the systems under study. Because there is little variation in the carbon NMR shift for analogous carbons of the fluorenyl systems and, therefore, little variation of charge density, any differences in the proton shifts for the unsubstituted system do not reflect changes in charge density.

As we expected, the charge densities for the carbons of the substituted rings showed significant variation due to the substituents. The presence of a substituent on the ring affects the charge density of the carbon to which it is attached (d′) as well as that of the neighboring carbons (c′ and e′). Those carbons which are removed from substituents by two or more bonds (b′, f′, g′) do not show large deviations (less than 2 ppm) in charge density across dications **1a**−**d**$^{2+}$. While shifts for H-c′, -e′, and -f′ vary significantly between these dications, the relative invariance of the shift of carbon f′ allows the shift of H-f′ to be used as a probe of antiaromaticity.

Since the observed paratropicity of the substituted and unsubstituted rings in dications **1a**−**d**$^{2+}$ geometry does not reflect differences in hybridization, in the polarity of the medium, or in the charge density, we attribute the changes in the proton shifts to the presence of antiaromatic ring currents. Since the observed paratropicity differs in the substituted and unsubstituted fluorenyl systems of **1a**−**d**$^{2+}$, the factors contributing to these antiaromaticities must be different and, therefore, must be explored separately.

Antiaromaticity in the Unsubstituted Ring Systems of 1a−d^{2+}. Protons c−f show the anticipated paratropic shift for an antiaromatic system, but the shifts of protons on carbons c and d are also affected by their proximity to the center of the opposing ring system. Any assessment of antiaromaticity must therefore be based on the shifts of protons e and f.[10] Averaging the chemical shifts of H-e and H-f for each of the dications **1a**−**d**$^{2+}$ shows that the system with the greatest upfield shift is **1d**$^{2+}$ (5.14 ± 0.09 ppm) followed by **1a**$^{2+}$ (5.37 ± 0.02 ppm), and **1c**$^{2+}$ (5.50 ± 0.11 ppm) and **1b**$^{2+}$ (5.54 ± 0.13 ppm) which are identical within experimental error. One can also evaluate the effect by determining the change in chemical shift of the neutral compound upon oxidation. The difference between the averaged shifts of the H-e and H-f of the dications and that of the neutral precursor gives the same order, in terms of decreasing antiaromaticity, **1d**$^{2+}$ (2.36 ± 0.9 ppm), **1a**$^{2+}$ (2.14 ± 0.02 ppm), and

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[27] See Supporting Information.

1b^{2+} (1.98 ± 0.13 ppm)/**1c**$^{2+}$ (1.98 ± 0.11 ppm). A remote fluorine substituent increases the antiaromaticity of the unsubstituted ring relative to **1a**$^{2+}$, whereas remote substitution by CH_3 or Cl decreases the antiaromaticity.

We have previously observed[10] a linear relationship between the ^{13}C NMR shift of carbon a and the ^{1}H shift of either H-e or H-f in dications of **A** in which R+ is a substituent containing 5−7-membered rings. This linear relationship suggests that the σ−p interactions which affect the shift of carbon a are related to the antiaromaticity of the fluorenyl cation. In those systems the ^{13}C shifts varied from 189 to 211 ppm, while the shift of H-f, for example, varied from 4.97 ± 0.02 ppm to 5.57 ± 0.06 ppm. Thus a range in ^{1}H NMR shift of ~0.60 ppm was associated with a range of ~22 ppm in the ^{13}C NMR shift of carbon a. The correlation between the paratropic shift of H-f (antiaromaticity) and the shift of carbon a suggested that the ^{13}C shift of carbon a could be used as a second probe of antiaromaticity.

The range of ^{1}H shifts for H-f of **1a**−**d**$^{2+}$ is 0.38 ± 0.10 ppm, while the range of ^{13}C shifts for carbons a and a′ is much smaller, with the largest being 6.5 ppm. The relative lack of variation in the shifts of carbons a and a′ and the difficulty of making unambiguous assignments for all dications prevents this shift from being a second measure of antiaromaticity.

The magnitude of the ^{13}C shifts of carbons a/a′ is dependent upon the increase in electron density from σ−p donation from the opposing substituent. At least two factors play a major role in this increase in electron density: the electron density available to the σ system and the geometry of the opposing substituent, which defines the effectiveness of overlap between the opposing substituent and the fluorenyl cation. Calculations of **1a**−**d**$^{2+}$ showed that the geometries of the systems are very similar. However, the fluorenyl cations with cyclic substituents[10] show greater variation in geometry, as would be anticipated for rings which vary from five to seven members. The conformational differences which affect the overlap of the cyclic substituent with the fluorenyl cation and the resulting σ−p donation result in large variances in the shift of carbon a. Thus, a dominant effect on the magnitude of the shift of carbon a is due to the effectiveness of this overlap.

Certainly the two fluorenyl ring systems interact, presumably via σ−p donation, but it is not clear what effect varying the electronic character of the fluorenyl substituent of the unsubstituted ring has on its antiaromaticity. A methyl substituent is normally an electron-donating substituent, and its effect on antiaromaticity would be expected to be different from that of substituents that are normally electron-withdrawing, for example, F and Cl. The observed order of antiaromaticity, from the ^{1}H shifts of carbons e and f, is **1d**$^{2+}$ > **1a**$^{2+}$ > **1c**$^{2+}$, **1b**$^{2+}$ (F > H > Cl, CH_3), which is not in agreement with this prediction.

Linear free energy relationships allow evaluation of the relative electron-donating or -withdrawing ability of a substituent through the sign and magnitude of the σ constant. However, the effects of the substituent can be grouped into two classes: those which act inductively and those which transmit the effect through resonance. The two effects have been combined in the dual substituent parameter method of Taft[18,28] (eq 1, where SCS refers to substituent chemical shift) and have been applied to ^{1}H NMR chemical shifts.[29]

$$\mathrm{SCS} = \rho_I\sigma_I + \rho_R\sigma_R \qquad (1)$$

If the effect of the substituent is transmitted via σ bonds from its fluorenyl system into the unsubstituted ring system (σ−p donation), we would expect the inductive effect of the substituent to dominate. The relative effects of the resonance and inductive contributions can be assessed through multiple regression analysis using eq 1. Because it was not obvious how the resonance effect would be manifested, the σ_R values used in the analysis included those designed for positively charged species, $\sigma_R{}^+$,[30] as well as those for neutral species, σ.[31] The results of the analysis indicated poor correlation between the substituent coefficients and the chemical shifts of either H-e or H-f. There is also poor correlation with only σ_I. The inductive effect, as evaluated through σ_I, is a composite of a number of factors, including field effects (F) and inductive effects on the π-system (π_I) as well as on the σ system.[32] The failure to observe a correlation with σ constants suggests that substituent effects on σ bonds reflect only a subset of those factors considered as part of the inductive effect. Our examination of these systems by ab initio calculations[33] may allow evaluation of the inductive effect on the σ system.

Antiaromaticity in the Substituted Ring Systems of 1a−d^{2+}. As described earlier, the charge density of carbon f′ is effectively invariant. Using the shift of H-f′ as the probe shift for antiaromaticity for each of the dications **1a**−**d**$^{2+}$, the system with the greatest upfield shift is **1d**$^{2+}$ (4.01 ± 0.08 ppm), followed by **1b**$^{2+}$ (4.44 ± 0.12 ppm), **1a**$^{2+}$ (4.97 ± 0.02 ppm), and **1c**$^{2+}$ (5.59 ± 0.12 ppm).

Substitution by either F or CH_3 increases the antiaromaticity of the fluorenyl cation relative to **1a**$^{2+}$, whereas substitution of Cl decreases the antiaromaticity.

Carbon a′ is shifted upfield compared with the shift of the analogous carbon of the fluorenyl monocation. This is evidence for the σ−p donation described previously for carbon a, in which the orthogonal relationship between the ring systems of **1a**−**d**$^{2+}$ allows electron donation from the unsubstituted fluorenyl system into the substituted fluorenyl cation.

The variation in antiaromaticity shown by the substituted ring of **1a**−**d**$^{2+}$ could be due to the effects of direct substitution on the ring, to the σ−p donation from the unsubstituted ring, or to a combination of these effects. The dual substituent parameter equation can help to assess the participation of the unsubstituted ring in the following way. If the chemical shift for H-f′ shows a very good correlation with σ values, the effect of the substituent is probably due to the normal resonance and inductive effects of the substituent, without additional perturbation by σ−p donation from the unsubstituted fluorenyl system.

There is an excellent correlation between the shift of H-f′ and the resonance substituent parameter $\sigma_m{}^+$.[34] The

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[33] Hyperconjugative effects, for example, may be assessed through variation in bond lengths for structures examined at high calculational levels.

results of the multiple linear regression analysis are given in eq 2. Although the correlation is excellent,

$$\mathrm{SCS} = -16.05\rho_I + 20.07\rho_R \qquad (2)$$

ideally the data set should consist of values from compounds with electron-donating substituents, such as OCH_3, and electron-withdrawing substituents, such as NO_2. As described previously, **1f**$^{2+}$ was not accessible, presumably due to complexation. Oxidation of other electron-deficient compounds was unsuccessful.[35] Thus, the dications represented reflect the greatest possible variation in substitution in these systems.

The signs of the transmission coefficients, ρ_I and ρ_R, show the relative inductive and resonance effects of the substituent. The negative sign for ρ_I classifies it as a "reverse" substituent chemical shift effect[36,37] resulting from a π polarization mechanism[38] in which the substituent acts to polarize the π cloud.[29] Polarization by an electron-withdrawing substituent, for example, would be greatest at the substituent and would act to make that position the most electron-deficient. The π cloud would respond by making positions remote to that position correspondingly more electron-rich. A substituent like F would polarize the π cloud in such a way as to increase the electron density at a site remote to the location of the substituent, whereas an electron-donating substituent like CH_3 would have the opposite effect.

The positive value for the transmission coefficient associated with σ_R means that an electron-donating substituent, with a negative value for σ_R, would contribute to a smaller value for the chemical shift. Since a paratropic shift results in a smaller value for the chemical shift, an electron-donating substituent on the ring would therefore increase the antiaromaticity of the ring system through resonance. Analogously, an electron-withdrawing substituent, with a positive value for σ_R, would increase the magnitude of the shift through resonance and, therefore, decrease the antiaromaticity of the system.

Although the resonance and inductive effects act in opposition, it is possible to evaluate the dominant effect for each substituent by calculating the magnitude of the inductive and resonance effects, using eq 2. For fluorine, with positive values for both σ_I and σ_R, the inductive term is of greater absolute magnitude, giving a negative value for SCS and a decrease in the magnitude of the chemical shift of H-f′ compared **1a**$^{2+}$ (increase in paratropicity/antiaromaticity). For methyl, with negative values for both σ_I and σ_R, the resonance term is of greater absolute magnitude, again giving a negative value for SCS and a decrease in the magnitude of the chemical shift of H-f′ (increase in paratropicity/antiaromaticity). Since the absolute magnitude of the σ coefficients for methyl are smaller than those for fluorine, the decrease in the chemical shift for H-f′ in **1b**$^{2+}$ is smaller than in **1d**$^{2+}$. Finally, for chlorine, with positive values for both σ_I and σ_R, the absolute magnitude of the resonance term is larger than the inductive term, giving a positive value for SCS and an increase in the H-f′ chemical shift (decrease in paratropicity/antiaromaticity). The crucial conclusion to be drawn from this analysis is that an increase in electron density, either via π polarization or through resonance, results in a decrease in the magnitude of the ^1H NMR shift and an increase in antiaromaticity.

Conclusion

The paratropic shifts of protons of the fluorenyl systems of **1a**−**d**$^{2+}$ have been shown to be due to the existence of antiaromatic ring currents. Substantial variation is seen in the ^1H shifts of hydrogens on carbons which do not demonstrate differences in geometry, hybridization, or charge density. The interaction between the two orthogonal ring systems is due to σ−p donation from one fluorenyl system to the other, resulting in an upfield shift of carbons a and a′. The variance of the upfield shift of carbons a and a′ is small, in contrast to other systems studied,[10] presumably due to the lack of conformational differences in **1a**−**d**$^{2+}$. Use of the dual substituent parameter method on the unsubstituted ring system reveals no correlation between the chemical shift of the probe protons H-e and H-f and σ_R/σ_I, presumably because the inductive effect evaluated by σ_I reflects a composite of inductive effects. Use of the dual substituent parameter method on the substituted ring showed excellent correlation with $\sigma_m{}^+$, suggesting that the primary effect of the substituent was a "normal" one, and that the variations in antiaromaticity seen were not due to variation in electron donation from the unsubstituted fluorenyl cationic substituent. In addition, the method revealed a reverse inductive effect, attributed to π polarization by the substituent. Careful examination of the effects of each substituent demonstrated that when the electron density of the substituted ring is increased, either through a dominant resonance term or through π polarization, the ^1H chemical shift is decreased (becomes more paratropic), showing the increased antiaromaticity of the substituted ring system.

Experimental Section

Starting material **1a** was synthesized according to literature procedures.[11] Antimony pentafluoride was obtained from Ozark Mahoning (Tulsa, OK) and triply-distilled prior to use. SO_2ClF was prepared by the method of Olah et al.[39] or was purchased from Aldrich Chemical Co. NMR spectra of the dications were obtained with a Varian VXR-300 or Varian Inova 400 spectrometer at temperatures from −80 up to −30 °C. See also Supporting Information.

9-(9H-Fluoren-9-ylidene)-2,7-dimethyl-9H-fluorene (1b). *n*-Butyllithium (32.0 mL, 2.40 M, 13.2 mmol) was added to fluorene (2.00 g, 12.0 mmol) in 25 mL of THF at −78 °C and allowed to stir for 15 min under 1 atm of Argon. A solution of 2,7-dimethylfluorenone[17] (2.50 g, 12.0 mmol) in 25 mL of THF was added, and the solution was allowed to warm to 0 °C. The solution was added to 50 mL of saturated aqueous NaCl, and the solution was extracted with 2 × 25 mL portions of ether. The ether layer was dried with $MgSO_4$, and the solvent was removed. The alcohol product was isolated by chromatography with hexanes on silica gel. Yield: 3.37 g, 75.0%. The alcohol (3.37 g, 9.01 mmol) was dissolved in 25 mL of acetic anhydride with 2 drops of concentrated H_2SO_4. The solution was gradually warmed to 50 °C, giving a red solution as the fulvalene

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was formed. The solution was neutralized with 1 M NaOH, and the solution was extracted with 2 × 25 mL of CH_2Cl_2. The solvent was removed, and the product was recrystallized from hexanes. Yield: 2.14 g, 67.7%. Anal. Calc for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.29; H, 5.82.

9-(9H-Fluoren-9-ylidene)-2,7-dichloro-9H-fluorene (1c). Fluorene (2.40 mmol, 400 mg) was dissolved in 30 mL of THF under argon and cooled to −78 °C. *n*-Butyllithium (2.40 mmol, 960 μL, 2.4 M in hexanes) was added. After the solution was stirred for 10 min, trimethylsilyl chloride (333 μL, 2.40 mmol) was added, and the solution was stirred for an additional 10 min. A second equivalent of *n*-butyllithium was added, and the solution was allowed to stir for 7 min. 2,7-Dichlorofluorenone[16] (2.40 mmol, 600 mg) in 30 mL of THF was added, and the solution was allowed to warm to room temperature and to stir overnight. Water (75 mL) and saturated NH_4Cl were added, and the reaction mixture was extracted with 115 mL of ether. The organic layer was separated extracted with 3 × 75 mL of water, and dried with $MgSO_4$. After removal of the solvent, the product was recrystallized from hexanes. Yield: 645 mg, 68%; mp 224−227 °C (lit. mp[40] 227−228 °C).

9-(9H-Fluoren-9-ylidene)-2,7-difluoro-9H-fluorene (1d). 2,7-Diaminofluorenone[13] (0.500 g, 2.38 mmol) was added to 22 mL of HF/pyridine complex (70:30, 225 mmol) at 0 °C under argon and was warmed to room temperature. The solution was cooled to 0 °C, $NaNO_2$ (0.345 g, 5 mmol) was added, and the solution was slowly warmed to room temperature, with evolution of gas. The reaction mixture was slowly warmed to 100 °C, at which time N_2 evolution was vigorous. The reaction mixture was heated until the evolution of gas ceased. The mixture was cooled and added to 100 g of ice−water. The reaction mixture was extracted with ethyl acetate, 2 × 50 mL, and the organic layer was extracted with 2 × 50 mL of saturated NaCl. The crude product was isolated by removal of the solvent. Crude yield, 0.32 g, 62%. The Peterson olefination was done as described for **1c**, using the crude 2,7-difluorofluorenone. The crude product was isolated by flash chromatography on silica gel with 90:10 hexanes/methylene chloride. The isolated product was recrystallized from hexanes. Yield, 0.172 g, 24.1%. Anal. Calc for $C_{26}H_{14}F_2$: C, 85.70; H, 3.87; F, 10.43. Found: C, 85.59; H, 4.15; F, 10.15.

General Preparation of Dications. SbF_5 (~0.7 mL, ~9 mmol) was added to a graduated centrifuge tube in a drybox, and the tube was capped with a septum and placed in an ice bath. SO_2ClF (1.3 mL, 17.8 mmol) at −78 °C was transferred by cannula into the centrifuge tube. The contents were mixed on a vortex stirrer until homogeneous, and the solution was cooled to −78 °C. The neutral precursor (~0.3 mmol) was added in small portions, followed by vortex mixing and cooling to −78 °C. Samples for NMR analysis were kept at −78 °C until needed and transferred by chilled pipet into an argon-filled NMR tube. A capillary tube with acetone-d_6 was then inserted into the NMR tube to serve as an external standard and deuterium lock.

Calculations. The AM1[25]calculations were conducted, using the standard methods as implemented in the Spartan package[41] on a Silicon Graphics personal Iris 4DG computer. The starting geometries were created using the PCMODEL program.[26] The molecular mechanics calculations were performed using the MMX software in PCMODEL on a Macintosh Quadra 800 computer, and geometry optimization was begun after an SCF calculation. Geometries were optimized in internal coordinates and were terminated when Herbert's test was satisfied in the BFGS method. All calculations were performed with closed-shell structure, using the restricted Hartree−Fock (RHF) method with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angles) without imposition of symmetry restrictions. The optimization was begun from at least two starting geometries in order to verify global minima.

Linear Free Energy Relationships. The relationships between chemical shifts for H-e, H-f, and H-f′ and for σ_I and σ_R were analyzed via multiple regression using the Axum program.[42] The inductive substituent constant, σ_I, was assumed to be invariant between systems.[28] Several inductive substituent coefficients have been described.[43] We obtained the best correlation with the values of Ehrenson.[28] The resonance substituent constants σ_m^+[30] and σ_m[31] were used. The quality of the fit of the data was evaluated through the statistical parameter *f*,[43] which is defined as SD/RMS, where SD is the root-mean-square of the deviations from linearity and RMS is the root-mean-square of the substituent property, in this case, SCS. A value of *f* of less than 0.1 indicates excellent fit.

For H-f′, using σ_I from Ehrenson's work, the value of *f* was 0.008 for σ_m^+, and 0.23 for σ_m. Values of *f* for H-e were 0.79 for σ_m^+, and 0.85 for σ_m. Values of *f* for H-f were 0.85 for σ_m^+, and 0.91 for σ_m.

At the suggestion of a referee, the shift of H-f′ was plotted vs a single σ value to confirm that multiple regression analysis was necessary. Plots of chemical shift vs σ_m^+, σ_m, and σ_m gave correlation coefficients (*R*) of 0.20 or less.

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Supporting Information Available: ^{13}C and ^1H NMR spectra of **1d** and $\mathbf{1b}^{2+}$; ^1H NMR spectra of $\mathbf{1c}^{2+}$ and $\mathbf{1d}^{2+}$; and a listing of calculated bond lengths, bond angles, and dihedral angles (9 pages). This material is contained in libraries on michrofiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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