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Dications of Fluorenylidenes. Electronic Effects on the Paratropicity/Antiaromaticity of Diphenylmethyl-Substituted Fluorenyl Cations

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Oxidation of para-substituted diphenylmethylidenefluorenes results in the formation of antiaromatic fluorenyl cations, as evidenced by the paratropic shift in the ^{1}H NMR spectrum. The magnitude of the shift is affected by the nature of the remote para substituent. Correlations between the paratropic shift and substitutent parameters for field, inductive, and resonance effects were explored. The greatest correlation between substituent parameters and the paratropic shift is found with parameters based on electronegativity, which reflect inductive effects, rather than field effects, although the sample size is small enough for this conclusion to be viewed with some reservations. If inductive effects were the primary mode of transmission of the effect of the substituent, this would reflect the longest σ induction reported to date.

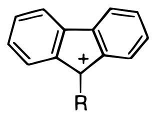
Introduction

The concept of antiaromaticity has been used for over three decades[1,2] to account for the unusual instability and peculiar reactivity associated with planar cyclic conjugated hydrocarbons containing 4*n* 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. We have recently discovered that oxidation of fluorenylidenes such as **1** to dications results in the formation of an antiaromatic fluorenyl cation.[3−5] The experimental evidence for this antiaromaticity lies in the paratropic shift of protons on the fluorenyl ring system observed upon oxidation to the dication.

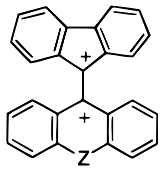
1a, Y=H
b, Y=F
c, Y=Cl
d, Y=CH$_3$

1^{2+}

The paratropic shifts of the protons of **1a**$^{2+}$ are significantly larger than those of the fluorenyl monocation. The antiaromaticity of a fluorenyl cation can be assessed by comparison of its proton chemical shift with that of a reference cation which does not possess the cyclopentadienyl ring system. The average proton chemical shift of the 9-methyl fluorenyl cation (**2**$^+$, R = CH$_3$) is only 0.49 ppm upfield of the corresponding 1,1-diphenylethyl cation[6] while the average shift of **1a**$^{2+}$, a bis-fluorenyl dication, is 3.34 ppm upfield of the corresponding tetraphenylethylene dication.[7]



2^{2+}



3a^{2+}, Z=O
b^{2+}, Z=C(CH$_3$)$_2$
d^{2+}, Z=CH$_2$CH$_2$

We have shown that the greatly increased antiaromaticity of the fluorenyl cation in systems such as **1a**$^{2+}$and **3a**$^{2+}$−**c**$^{2+}$ results from the presence of a cationic substituent at position 9 of the fluorenyl cation.[4] More importantly, we have shown that the degree of antiaromatic character can be modified by changing the electronic and geometric character of that cationic substituent. Interaction of the cationic substituent with the fluorenyl system occurs through donation of electron density from σ bonds of the substituent into the electron deficient π-system of the fluorenyl cation.

Most recently[5] we have examined the effects of substituents on antiaromaticity, through the oxidation of 2,7-disubstituted tetrabenzo[5.5]fulvalenes, **1b**−**d**. We have observed a correlation with $\sigma_P{}^+$ and σ_I values that revealed that electron donation, either through resonance or through induction, increased the antiaromatic character of the *substituted* ring system of **1**$^{2+}$. However, there was no correlation between antiaromatic character and $\sigma_I/\sigma_P{}^+$ for the *unsubstituted* ring system of **1**$^{2+}$.

We have chosen to examine the effect of substituents on the dications of diphenylmethylidenefluorenes (**4a**$^{2+}$−

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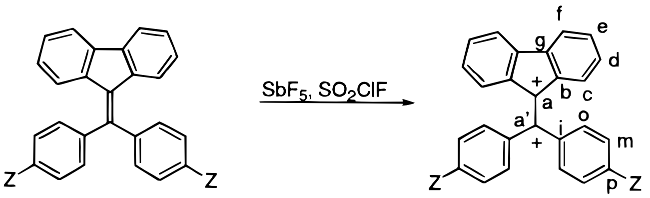
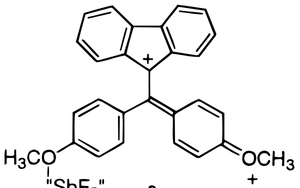
e^{2+}) to better understand the ability of a substituent to affect the degree of antiaromaticity of fluorenyl cations.



4a, Y=H
b Y=OCH$_3$
c, Y=CH$_3$
d, Y=Cl
e, Y=F

4^{2+}



5^{2+}

An additional benefit of studying **4a**$^{2+}$−**e**$^{2+}$ is that all protons on the fluorenyl ring system can be used in the assessment of antiaromaticity. Because the fluorenyl ring systems of **1**$^{2+}$ are perpendicular to each other, the protons on positions c and d of **1**$^{2+}$ are affected by the antiaromatic ring current of the perpendicular substituent.[4] Thus only protons e and f can be used as probe protons to assess the degree of paratropicity and therefore the antiaromaticity of the fluorenyl cation of **1**$^{2+}$.

We here report the preparation of dications of bis(4-substituted phenyl)methylidenefluorenes (**4**) and the effect of the substituent on the antiaromaticity of the corresponding fluorenyl cation.

Results

Diphenylmethylidenefluorene, **4a**,[8] and its appropriately substituted derivatives, **4b**−**e**,[9] were oxidized with SbF$_5$ in SO$_2$ClF at −78 °C. The progress of the oxidation was followed by ^{1}H and ^{13}C NMR spectroscopy at temperatures from −78 to −30 °C. For **4a**, Y = H, the oxidation was so rapid that the ^{1}H NMR spectrum showed only a cyclized product, with no evidence of **4a**$^{2+}$.[10] Oxidation of **4b**−**e** with SbF$_5$/SO$_2$ClF resulted in formation of dications (**4b**$^{2+}$−**e**$^{2+}$) whose ^{1}H NMR shifts at −50 °C are shown in Table 1 along with the spectra of the neutral precursors.[11] Assignments for the spectra of **4c**$^{2+}$ and **4d**$^{2+}$ were made on the basis of COSY and HETCOR 2D spectra. The assignments for **4e**$^{2+}$ were made on the basis of COSY spectra and by analogy to **4c**$^{2+}$/**4d**$^{2+}$ and **3a**$^{2+}$−**c**$^{2+}$.[4] The instability of **4b**$^{2+}$ (vide infra) prevented analysis by 2D NMR techniques, so assignments were made on the basis of analogy to the fluorenyl systems of **4c**$^{2+}$−**e**$^{2+}$ and **3a**$^{2+}$−**c**$^{2+}$**.** Assignments for the ^{1}H NMR spectra of the neutral compounds were made via COSY, HETCOR, and long-range (three-bond) HETCOR spectra.

Table 1. ^{1}H NMR Chemical Shifts for Dications[a,b]

	4b^{2+}	**4c**$^{2+}$	**4d**$^{2+}$	**4e**$^{2+}$
c	5.0 ± 0.1	4.80 ± 0.01	4.58 ± 0.03	4.44 ± 0.06
d	5.2 ± 0.1	5.06 ± 0.03	4.89± 0.03	4.75 ± 0.06
e	5.8 ± 0.1	5.86 ± 0.01	5.69± 0.03	5.54 ± 0.06
f	5.2 ± 0.1	5.12 ± 0.03	4.98± 0.03	4.83 ± 0.06
c′[c]	6.3 ± 0.1 (1H), 6.5 ± 0.1 (1H), 6.9 ± 0.1 (1H), 7.4 ± 0.1 (1H)	7.1	7.2	7.2
d′	6.8 ± 0.1	6.78 ± 0.03[d]	6.84 ± 0.03[e]	6.43 ± 0.06[f]
OCH$_3$	3.5/3.9 ± 0.1			
CH$_3$		1.66 ± 0.01		

[a] Solvent, 0.75 g of SbF$_5$, 1.5 mL of SO$_2$ClF; reference,TMS in acetone-d_6 in an external capillary; temperature, −50 °C. [b] Standard deviation in a minimum of three separate preparations of dication, see text. [c] Broad peak due to partial coalescence for **4c**$^{2+}$−**e**$^{2+}$, see text. [d] Doublet, J = 8 Hz. [e] Doublet, J = 7.8 Hz. [f] Triplet, J = 7.8 Hz.

Table 2. ^{1}H NMR Chemical Shifts for Neutral Precursor[a]

	4b	**4c**	**4d**	**4e**
c	6.79	6.72	6.70	6.73
d	6.96	6.94	6.97	7.03
e	7.24	7.24	7.27	7.32
f	7.73	7.72	7.71	7.77
c′	7.27	7.25	7.43	7.38/7.41
d′	6.95	7.25	7.31	7.18
OCH$_3$	3.87			
CH$_3$		1.53		

Dication **4b**$^{2+}$ is short-lived and its ^{1}H NMR spectrum broadened. We believe the broadening is due to the presence of a small amount of radical cation. It also shows two sets of methoxy protons, presumably due to complexation of one methoxy group with the Lewis acid, SbF$_5$.[12] If complexation of one methoxy substituent occurred prior to oxidation, it would not be surprising that subsequent oxidation of this more electron deficient olefin would be more difficult, perhaps resulting in incomplete oxidation to dication.

The ^{1}H NMR spectrum at −50 °C of the diphenylmethylidene portion of **4b**$^{2+}$ shows nonequivalence of the 4 ortho protons. Olah[7] has observed a similar nonequivalence in the ortho protons of the dication of para-substituted tetraphenylethylenes. The presence of 4 distinct signals for the ortho protons could be explained by the existence of a resonance form such as **5**$^{2+}$, perhaps as a result of increased electron deficiency caused by the complexed methoxy group. A similar nonequivalence was seen in the spectrum of **4c**$^{2+}$−**e**$^{2+}$ at −78 °C, with the observation of two sets of ortho protons.[13] We believe that this reflects reduced rotation of the phenyl rings at the lower temperature. Upon warming to −50 °C, the ortho protons begin to coalesce into a single peak. The coalescence is complete by −30 °C.

^{13}C spectra of **4c**$^{2+}$−**d**$^{2+}$ are given in Table 3. The presence of radical cations in the solution of **4b**$^{2+}$ and its short lifetime prevented the acquisition of a good ^{13}C NMR spectrum. Assignments for the proton-bearing carbons of the fluorenyl ring of **4c**$^{2+}$ and **4d**$^{2+}$ were made via COSY and short range (one bond) HETCOR spectra.

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(13) Although **4a**−**e** are known compounds with reported ^{1}H spectra, no assignments were made for the shifts.

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

	4c^{2+}	**4d**$^{2+}$	**4e**$^{2+}$
a	201.2[b]	198.4[c]	198.5[d]
b	148.8	149.8	149.8
c	146.2	146.6	147.1
d	134.2	136.1	136.6
e	158.4	159.4	160.0
f	130.1	130.9	131.4
g	151.8	152.2	152.6
a′	180.3[b]	182.4[c]	176.0[d]
i	134.2	135.1	133.8
o	141.4	133.6	147.1
m	133.0	133.6	122.2
p	169.1	163.4	181.3, $J = 147$ Hz
misc	23.3		

[a] Solvent, 0.75 g of SbF$_5$, 1.5 mL of SO$_2$ClF; 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. [d] These assignments could be interchanged.

Assignments for the quaternary carbons of **4c**$^{2+}$−**d**$^{2+}$ and for all carbons of the fluorenyl ring of **4e**$^{2+}$ were made by analogy to **1a**$^{2+}$−**d**$^{2+}$, **3a**$^{2+}$−**c**$^{2+}$, and, for **4e**$^{2+}$, to **4c**$^{2+}$−**d**$^{2+}$. Assignments for the carbon-bearing protons of the diphenylmethylidene portion of **4c**$^{2+}$−**d**$^{2+}$ were made via COSY and HETCOR spectra. Assignments for the carbon-bearing fluorine and its adjacent carbon of **4e**$^{2+}$ were made on the basis of the magnitude of the coupling constant to fluorine. Assignments of all remaining carbons in **4e**$^{2+}$ and the quaternary carbons of **4c**$^{2+}$−**d**$^{2+}$ were made by analogy to known phenyl-substituted cations.[12,14−18] The nonequivalence of the ortho carbons at −78 °C of **4c**$^{2+}$ is shown by the presence of two broad peaks at 139.2 and 144.7 ppm. By analogy to **3b**$^{2+}$−**c**$^{2+}$, the shifts for carbon a of **4c**$^{2+}$−**e**$^{2+}$ are 201.2, 198.4, and 198.5 ppm, respectively, and for carbon a′ are 180.3, 182.4, and 176.0 ppm, although the respective shifts could be interchanged.

Discussion

Our primary interest is in factors that affect the antiaromaticity of the fluorenyl cationic system, but it is appropriate to determine whether the diphenylmethyl cationic substituent is behaving normally. The ring carbons show very similar shifts to those of other para-substituted benzyl cations. The difference between the ^{13}C NMR shifts for each carbon of the benzene ring and those of the average shift of a set of 12 benzyl cations[12,14−18] is generally less than 3 ppm. However, the shifts at −50 °C for carbon a′ of the diphenylmethyl cation of **4b**−**d**$^{2+}$ are substantially upfield (at ∼180 ppm) of the 228−260 ppm range of most substituted phenyl cations. We believe that the increase of electron density which gives rise to the upfield shift is due to σ−p donation,[19−21] from the fluorenyl cation into the empty p-orbital primarily localized on carbon a′. The relative invariance of the shifts for carbon a′ suggest that the dominant effect is donation of electron density via this method rather than from the para substituent. This is consistent with a situation in which rotation of the phenyl rings at −50 °C prevents substantial resonance interaction with carbon a′. For **4b**$^{2+}$ whose ^{1}H spectrum suggests hindered rotation at −50 °C, we were unable to obtain ^{13}C spectra. We were not able to obtain good ^{13}C spectra at −78 °C for **4d**$^{2+}$−**e**$^{2+}$ and are unable to assess the effect of hindered rotation at that temperature.

The rotation of the phenyl substituents apparent in the spectra at different temperatures reflects a more complicated situation for the ^{1}H spectra for **4b**$^{2+}$−**e**$^{2+}$· The meta protons appear as sharp multiplets for **4c**$^{2+}$−**e**$^{2+}$ with doublets for **4c**$^{2+}$ and **4d**$^{2+}$ and triplets for **4e**$^{2+}$ because of coupling with both adjacent protons and fluorine. Evaluation of the "normalcy" for these shifts is more problematic, in part because the literature contains far fewer examples of ^{1}H spectra of benzyl cations than ^{13}C spectra, giving a smaller data set with which to compare. Olah[17] reports proton shifts for methyl and fluoro-substituted benzyl cations in which the ortho proton appears at lower field than the meta, as expected from consideration of charge density. This pattern is consistent with our observations; however, our chemical shifts approximately 1 ppm higher than Olah's. Lomas[18] reports shifts for 2-(methylphenyl)diadamantyl cations with para methyl, chloro, and fluoro substituents which are virtually identical to the shifts of **4c**$^{2+}$−**e**$^{2+}$ but the assignments are reversed, with the ortho protons appearing at higher fields. His reported ^{13}C shifts also differ fairly substantially, ∼20 ppm for the shifts of the para carbons. We offer no explanation at this time for the unexpected shifts of the protons of the diphenylmethylidene cationic portion of **4b**$^{2+}$−**4e**$^{2+}$.

As was true for carbon a′ of the diphenylmethyl system, the chemical shift of carbon a of the fluorenyl systems of **4b**$^{2+}$−**d**$^{2+}$ is also unusually far upfield (∼200 ppm), in comparison with fluorenyl monocations (∼220 ppm).[6] Again, σ−p donation would allow the increase in electron density which would result in an upfield shift.

The potential antiaromatic character of the cationic fluorenyl ring system remains of greatest interest to us. As we have done in the past,[4,5] we must evaluate other factors which may affect the ^{1}H NMR shift, prior to attributing the paratropic shift to the presence of an antiaromatic ring current. We have examined medium effects by varying the concentration of SbF$_5$ in the solution[4] and have found no relationship between the amount of SbF$_5$ and the shift of the protons of these dications. We have used AM1 calculations to obtain bond lengths and angles for **4a**−**e** as well as for their dications. Dication **4b**$^{2+}$ was modeled without complexation with antimony salts. The calculated values are reported in Table 5, along with some values from the crystal structure determination of **4a**.[22] Both the experimental structure and the calculated structure of **4a** show that the fluorenyl ring system, including carbons a and a′ and the ipso carbons of the phenyl rings, is basically planar, with the phenyl rings twisted substantially out of planarity. The twist angle for each phenyl ring in the experimental structure is reported as 70° and 83°, respectively, while

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

	4b	4c	4d	4e
a	135.9	133.9	135.4	134.8
b	139.5	139.3	138.6	138.7
c	124.9	125.2	125.2	124.6
d	126.6	126.6	127.0	126.5
e	127.5	127.8	128.5	127.8
f	119.5	119.5	119.8	119.4
g	140.4	140.5	141.0	140.6
a′	146.1	146.5	141.4	138.7
i	135.9	140.6	142.6	142.9
o	132.0	129.8	129.5	131.8
m	114.4	129.9	131.7	116.0
p	160.4	138.7	134.8	162.8
misc	55.7	31.8		

[a] Solvent, $CDCl_3$.

the calculated structure gives angles much closer to 90°. Calculations beginning with the experimental geometry always optimized to bond angles near 90°. The most obvious change upon oxidation to a dication is the change of the dihedral angle of the bond between carbons a and a′ (dihedral angle ia′ab) from effectively 0° to approximately 80°. Thus the diphenylmethylidene system becomes almost perpendicular to the fluorenyl system, consistent with the geometry required for σ−p donation. Because the dihedral angles are very similar in both the series of the neutral precursors and the series of the dications, these relatively low-level calculations also suggest that differences in chemical shifts for either the neutral precursors or the dications are not due to conformational differences. Bond a−a′ of each dication is longer than bond a−a′ of the neutral compound, which would be expected from oxidation of the double bond. As we have observed before,[4,5] there is very little variance in bond lengths and bond angles between the calculated values for the neutral compounds **4a**−**e** and the calculated values for the dications **4a**$^{2+}$−**e**$^{2+}$. These calculations confirm that variations in hybridization between carbons of these systems are unlikely, and therefore not important contributors to the differences in chemical shift seen for protons of the different fluorenyl systems or diphenylmethylidene systems.[23]

Finally, changes in the electron density of carbons bearing protons will affect the shift of those protons. The similarity between the carbon shifts for carbons bearing protons in the fluorenyl system of **4c**$^{2+}$−**e**$^{2+}$ suggests that there is very little variation between electron density for analogous carbons of these systems. For example, the shift of carbon c in **4c**$^{2+}$−**e**$^{2+}$ varies less than 0.7 ppm in these systems. The carbon shifts in the fluorenyl system for carbons b−g reflect the expected variation in charge density predicted by resonance, when the effects of 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. Thus variation in chemical shift for fluorenyl protons in these systems is not due to variations in charge density.

Since any variation between analogous protons in these systems is not due to changes in hybridization, charge density, or medium effects, we attribute them to differences in the magnitude of the ring current and therefore to differences in antiaromaticity. An examination of the proton shifts for protons c−f of **4c**$^{2+}$−**e**$^{2+}$ in Table 1 shows a steady decrease in the paratropicity of the protons of **4c**−**e**$^{2+}$ in the order F > Cl > CH_3. With the exception of proton e, the protons of **4b**$^{2+}$ are all further downfield than the corresponding protons of **4c**$^{2+}$. Thus remote substitution by F causes the greatest increase in the antiaromaticity of the cationic fluorenyl system and substitution by (partially complexed) OCH_3 shows the least.

A second way to evaluate the antiaromaticity of systems of this type is to examine the change in the proton chemical shift upon oxidation to the dication. Using the degree of paratropic shift as a probe of antiaromaticity, **4e**$^{2+}$ with an averaged upfield shift upon oxidation of 2.32 ppm is the most antiaromatic of the dications reported here. Comparison of the degree of paratropic shift for the remaining dications shows the following order of antiaromaticity, with the upfield shift difference in parentheses: **4e**$^{2+}$ (2.32 ppm, Y = F) > **4d**$^{2+}$ (2.12 ppm, Y = Cl) > **4c**$^{2+}$ (1.95 ppm, Y = CH_3) > **4b**$^{2+}$ (1.9 ppm, Y = OCH_3, partially complexed). The order parallels the order of decreasing antiaromaticity seen when the shift of the protons of the fluorenyl system are considered.

For the explanation of these trends we turn to a consideration of linear free energy relationships or, more accurately, correlation analysis.[24] NMR chemical shifts have shown a linear correlation with substituent constants (σ), and this relationship has been used to give insight into the electronic effect of the substituent.[25] Ideally, the systems examined should include a range of substituents, including at least two strong donors (e.g., NH_2 or OCH_3), two halogens (not both Cl and Br), CH_3, H, one acceptor (NO_2, CF_3, or CN), and one carbonyl acceptor ($COCH_3$ or CO_2R).[26,27] Our data set is of necessity much smaller. Dication **4b**$^{2+}$ demonstrates that a donor substituent will undergo complexation with the Lewis acid, SbF_5, giving a substituent for which no substituent constants have been determined. Our experience with acceptor substituents such as NO_2[28] suggests that oxidation of highly electron-deficient compounds to dications is very difficult and we have not explored the oxidation of **4** where Z = NO_2. Thus, our data set is necessarily smaller than ideal and the conclusions from the set are correspondingly less valid than those from a larger data set.

The electronic effects of substituents fall into four general categories, the field effect *F*, with substituent constant σ_F, where the substituent dipole induces electronic perturbations by through-space interactions; the inductive effect *X* (σ_X), where the electronegativity of the substituent results in through-σ bond charge transfer; the resonance/hyperconjugative effect *R* (σ_R), where charge transfer occurs between orbitals of suitable symmetry involving either p or s electrons; and the polarizability effect *P* (σ_P), where a charge or a dipole results

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[23] It must be noted that the calculated values for **4b**$^{2+}$ are for the uncomplexed dication and a resonance form such as **5**$^{2+}$ would affect proton and carbon shifts.

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Table 5

	4b	**4c**	**4d**	**4e**	**4a**	**4a**, exp[a]	std dev	**4b**$^{2+}$	**4c**$^{2+}$	**4d**$^{2+}$	**4e**$^{2+}$	**4a**$^{2+}$	std dev
					Calculated Bond Lengths, AM1 Calculation								
ab	1.4809	1.4808	1.4810	1.4810	1.4808	1.493 1.488	0.000	1.4319	1.4319	1.4302	1.4301	1.4300	0.0010
bc	1.3838	1.3838	1.3836	1.3836	1.3838		0.000	1.3981	1.3981	1.3998	1.4001	1.4000	0.0010
cd	1.4037	1.4037	1.4039	1.4039	1.4037		0.000	1.4020	1.4020	1.4008	1.4006	1.4006	0.0007
de	1.3898	1.3898	1.3896	1.3896	1.3897		0.000	1.3903	1.3903	1.3912	1.3914	1.3913	0.0006
ef	1.4028	1.4028	1.4031	1.4031	1.4028		0.000	1.4212	1.4212	1.4217	1.4218	1.4218	0.0003
fg	1.3824	1.3824	1.3822	1.3822	1.3824		0.000	1.3682	1.3682	1.3679	1.3679	1.3678	0.0002
gb	1.4350	1.4350	1.4349	1.4350	1.4350		0.000	1.4561	1.4561	1.4571	1.4572	1.4572	0.0006
gg	1.4604	1.4604	1.4606	1.4606	1.4605		0.000	1.4725	1.4725	1.4724	1.4724	1.4724	0.0001
aa′	1.3483	1.3481	1.3479	1.3481	1.3480	1.349 1.491	0.000	1.4702	1.4702	1.4703	1.4707	1.4702	0.0002
a′i	1.4712	1.4716	1.4716	1.4715	1.4718	1.495	0.000	1.4101	1.4101	1.4143	1.4138	1.4158	0.0026
io	1.4011	1.4009	1.4011	1.4012	1.4012		0.000	1.4300	1.4300	1.4263	1.4275	1.4258	0.0020
om	1.3963	1.3925	1.3930	1.3908	1.3939		0.002	1.3722	1.3722	1.3797	1.3767	1.3838	0.0050
mp	1.3987	1.3998	1.3984	1.4072	1.3947		0.005	1.4235	1.4235	1.4121	1.4112	1.4025	0.0090
p−Z	1.3815	1.4807	1.6998	1.3544	1.0997		0.217	1.3435	1.3435	1.6675	1.3335	1.1064	0.2001
					Calculated Bond Angles, AM1 Calculation								
abc	131.38	131.37	131.38	131.39	131.31		0.032	131.78	131.78	131.96	131.99	131.98	0.1083
bcd	119.14	119.12	119.13	119.14	119.31		0.080	118.66	118.66	118.71	118.73	118.71	0.0321
cde	121.08	121.09	121.06	121.06	121.08		0.013	121.07	121.07	121.10	121.10	121.10	0.0164
def	120.61	120.61	120.63	120.62	120.62		0.008	121.28	121.28	121.10	121.25	121.26	0.0760
efg	118.66	118.65	118.65	118.65	118.65		0.004	118.37	118.37	118.38	118.34	118.39	0.0187
fgb	121.04	121.03	121.03	121.04	121.03		0.005	120.86	120.86	120.90	120.91	120.90	0.0241
fgg	130.79	130.80	130.79	130.78	130.79		0.007	132.03	132.03	132.00	131.99	132.00	0.0187
gba	109.14	109.14	109.12	109.12	109.14		0.011	108.47	107.11	108.38	108.38	108.36	0.5774
bab	105.37	105.37	105.40	105.39	105.38	104.8	0.013	108.84	108.84	109.04	109.05	109.07	0.1173
baa′	127.32	127.31	127.30	127.30	127.31		0.008	125.58	125.58	125.48	125.48	125.47	0.0578
aa′i	123.48	123.51	123.57	123.55	123.53	124	0.035	117.40	117.40	117.55	117.53	117.61	0.0942
a′io	120.26	120.32	120.24	120.22	120.23	122.7	0.040	121.28	121.28	121.03	121.14	121.03	0.1258
iom	120.68	120.25	120.42	120.63	120.17		0.225	121.62	121.62	120.54	121.49	120.71	0.5285
omp	119.29	120.54	119.59	119.50	120.20		0.524	119.80	119.80	120.23	119.83	120.36	0.2699
mpm	120.63	119.11	120.50	120.22	119.88		0.608	119.65	119.65	119.45	119.72	119.91	0.1652
					Calculated Dihedral Angles, AM1 Calculation								
ia′ab	−0.1	0.0	0.2	0.3	0.2		0.1	81.8	81.8	82.5	82.7	82.5	0.4
a′abc	−0.1	0.0	0.1	0.1	0.0		0.0	−0.5	−0.5	−0.5	−0.5	−0.5	0.0
abcd	180.0	180.0	180.0	180.0	180.0		0.0	−179.5	−179.5	−179.4	−179.4	−179.4	0.0
bcde	0.0	0.0	−0.0	−0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0
cdef	0.0	−0.0	−0.0	−0.0	0.0		0.0	0.1	0.1	0.1	0.1	0.1	0.0
defg	0.0	0.0	0.0	−0.0	0.0		0.0	−0.1	−0.1	−0.1	−0.1	−0.1	0.0
efgb	0.0	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0
fggf	0.0	−0.0	0.5	−0.1	−0.1		0.2	0.7	0.7	0.8	0.8	0.9	0.1
aa′io	90.4	91.0	90.3	90.2	90.4	70,83	0.3	21.7	21.7	22.0	21.7	22.3	0.2
a′omp	178.0	178.1	178.1	178.1	178.1		0.0	178.4	178.4	179.0	179.0	179.2	0.4
iomp	0.2	0.1	0.2	0.2	0.2		0.0	0.1	0.1	0.4	1.5	0.6	0.6
ompm	0.0	0.1	0.0	0.0	0.0		0.0	1.3	1.3	0.8	0.9	0.6	0.3

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in polarization of the substituent.[26] The effects can be dominated by one type of effect or two or more effects can act in concert, requiring the use of a multisubstituent parameter equation[29] such as (1), in which the substituent chemical shift, SCS, is defined by both resonance and "inductive" effects.[25,28]

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

For the dications of **1a**$^{2+}$−**d**$^{2+}$, we observed that the antiaromatic character of the ring system in which the substituent was *directly* attached to the fluorenyl ring decreased in the following order: F > CH_3 > H > Cl. The magnitude of the effect could be correlated with σ_R^+ constants using a dual substituent parameter equation. The values for ρ_I and ρ_R revealed that electron donation through resonance or induction increased the paratropic shift and therefore the antiaromaticity of the substituted fluorenyl ring. For the fluorenyl ring system of **1a**$^{2+}$−**d**$^{2+}$ which lacked substituents on the 2,7-positions, the order of antiaromaticity was F > H > Cl > CH_3. There was no correlation with any value of σ_R or σ_R^+ and σ_m.[29]

Linear free energy relationships of the proton chemical shifts of the fluorenyl system of the dications **4b**$^{2+}$−**d**$^{2+}$ were also examined. There was no correlation between any type of σ_R for the para position (σ^+ or σ)[30] and the average proton shift of the fluorenyl system or the chemical shift difference for the fluorenyl system between the dication and the corresponding neutral compound ($\Delta\delta$). There was a slightly better correlation with σ_F[29,31,32] with the *r* ranging from 0.92 to 0.95 for correlation with the average proton chemical shift and a range of *r* from 0.86 to 0.90 for correlation with $\Delta\delta$. By far the best correlations were with parameters related to electronegativity. As shown in Table 6, correlations with $\Delta\delta$ range from 0.970 to 0.999.

We are interested in evaluating the relative importance of the various electronic effects in order to understand how the effect of a remote substituent is transmitted to the fluorenyl cation and how it is able to affect the

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Table 6. Correlation (*r*) between Substituent Parameters Based on Electronegativity and Average Chemical Shift of Fluorenyl Protons (δ) or $\Delta\delta$

	i^a	$\chi_G{}^b$	$\sigma_\xi{}^c$	σ^d
δ_{ave}	0.934	0.959	0.960	0.990
$\Delta\delta$	0.970	0.986	0.986	0.9998

[a] Inamoto, N.; Masuda, S. *Tetrahedron Lett.* **1977**, 3287−3290. Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1007−1010. [b] Mullay, J. *J. Am. Chem. Soc.* **1984**, *106*, 5842−5847. Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271−7275. [c] Marriott, S.; Reynolds, W. F.; Taft, R. W.; Topsom, R. D. *J. Org. Chem.* **1984**, *49*, 595−565. [d] Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111−145.

antiaromaticity of that system. Of the four types of electronic effects described previously, the lack of correlation with σ_R suggests that resonance effects are unimportant. The distance of the substituent from the fluorenyl cation argues against the importance of polarizability of the substituent. This leaves field and inductive effects as the primary means through which the substituent Z moderates the antiaromaticity of the fluorenyl cation.

It is tempting to conclude that the inductive effects of the substituents are more important than field effects because of the better correlation between the average chemical shift of the fluorenyl protons or $\Delta\delta$ with substituent constants associated with electronegativity (I, χ_G, or σ_X). Normally, field effects are considered of greater importance than inductive effects, which fall off rapidly with distance.[33] The better correlation with the inductive substituent constants would indicate σ induction over at least 8 bonds, the longest reported to date.[34]

Although the correlation with σ_X in particular is excellent, the small size of the data set suggests that any conclusions about the relationship between field and inductive effects should be viewed with some reservation. In addition, Cook et al.[26] suggest that electronegativity, field, and resonance parameters are substantially interdependent for most of the commonly used substituents, although this interdependence is considered most problematic at positions close to the substituent.

The effect of the remote substituent appears to be a general one. The effect of remote substituents on the antiaromaticity of **4b**$^{2+}$−**e**$^{2+}$ roughly parallels that of **1a**$^{2+}$−**d**$^{2+}$. Protons on carbons e and f were used as "probe" protons in the evaluation of the antiaromaticity of **1a**$^{2+}$−**d**$^{2+}$. A plot of the proton shifts for protons on carbon e in **1b**$^{2+}$−**d**$^{2+}$ vs the shifts for analogous protons in **4b**$^{2+}$−**d**$^{2+}$ showed a roughly linear relationship (R = 0.85), as did a similar plot for protons on carbon f (R = 0.94). The deviation from linearity is not unexpected because the substituent on **1a**$^{2+}$−**d**$^{2+}$ is separated from carbon a of the fluorenyl ring system by 4 bonds, while the substituent in **4b**$^{2+}$−**d**$^{2+}$ is separated by 5 bonds, allowing for differences in both field and inductive effects. In addition, the benzene rings in **1a**−**d**$^{2+}$ are held planar while those in **4b**−**d**$^{2+}$ are free to rotate. We believe however that the similarity of the effects of remote substituents suggests that the same effect is operating in both, and we continue to examine the effects of remote substituents in other systems to understand this phenomena.

Because the small sample size is the greatest limitation on conclusions that can be drawn, we have begun to examine these substituent effects using higher level calculational methods. We anticipate that calculations at the density functional theory level will allow us to discern the effects of σ and π donation.[35]

Conclusions

Dications of para-substituted diphenylmethylidene fluorenes possess an antiaromatic fluorenyl cation, as evidenced by a paratropic shift in the ^{1}H NMR spectrum. The para substituent on the cationic diphenylmethyl substituent is able to affect the antiaromaticity of the fluorenyl cation and the effect of the substituent correlates most strongly with substituent parameters related to electronegativity, although there is a fair correlation with parameters measuring field effects. Although the sample size is too small for definite statements about the origin of the effect of the substituent on the antiaromaticity of the fluorenyl cation, the correlation with parameters based on electronegativity suggests that the effect is an inductive one. If true, this would represent the longest σ induction reported to date.

Experimental Section

Antimony pentafluoride was obtained from Ozark-Mahoning (Tulsa) and triply distilled before use. Sulfuryl chloride fluoride was synthesized[36] from sulfuryl chloride which was obtained from Aldrich Chemical Co. The substituted benzophenones were obtained from Aldrich Chemical Co. and were used without further purification. NMR spectra of the dications were obtained with a Varian VXR 300 or Inova 400 spectrometer at temperatures from −78 to −30 °C; see also Supporting Information. The neutral compounds were referenced to internal TMS; dication spectra had an external acetone-d_6 reference.

Synthetic Procedures. Compound **4a**[8] was synthesized according to the literature procedure. Compounds **4b**−**e**[9] were synthesized according to the literature procedures with the adaptations described for **4c**. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) and THF were distilled from the Na/benzophenone ketyl prior to use.

9-(Bis(4-chlorophenyl)methylene)fluorene (4c). TMEDA (6.6 mL, 4.4 mmol) and *n*-butyllithium (5.1 mL, 0.87 M, 4.4 mmol) were combined at 0 °C and added to fluorene (0.73 g, 4.4 mmol) in 40 mL of THF at −50 °C under argon. After 30 min at −50 °C, 4,4′-dichlorobenzophenone (1.00 g, 4.0 mmol) in 22 mL of THF was added dropwise to the fluorenyl anion solution. The reaction was quenched after 4 h with 1 mL of H_2O, followed by 45 mL of saturated aqueous ammonium chloride. The reaction mixture was washed with 2 × 25 mL portions of ether. Removal of ether gave the alcohol, a pale yellow solid which was recrystallized from 2-propanol. Yield: 1.1 g, 62%.

The alcohol (1.189 g, 2.8 mmol) was refluxed in 100 mL of benzene with *p*-toluenesulfonic acid (0.06 g, 0.3 mmol) for 105 min. After removal of the benzene under vacuum, the residue was recrystallized from 2-propanol. Yield: 0.962 g, 84.5%. Mp (uncorrected) 211−215 °C, lit.[37]mp 210 °C.

General Preparation of Dications. SbF_5 (7 mL, 9 mmol) was added to a graduated centrifuge tube in a drybox, the tube was capped with a septum, and the solution was transferred

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to an ice bath. SO_2ClF (1.4 mL) at 0 °C under argon was added by cannula. The reagents were mixed on a vortex-stirrer and rapidly cooled to −78 °C. The alkene (0.25 mmol) was added in small amounts to the SbF_5/SO_2ClF mixture and mixed on a vortex-stirrer. The mixture was allowed to stir for several hours normally. A portion of the dication mixture was transferred by cooled pipet to an argon-filled NMR tube at −78 °C, and a capillary tube with acetone-d_6 was then inserted into the NMR tube to serve as an external standard and deuterium lock. The sample was immediately inserted in the precooled probe of the NMR spectrometer.

Dications were quenched by adding the reaction mixture (or solution after NMR analysis) dropwise to 50 mL of water at 0 °C with stirring. The reaction mixture was extracted with 250 mL of methylene chloride and the organic layer with 50 mL of saturated aqueous ammonium chloride. After filtering with fine filter paper to remove salts which had been insoluble in either layer, the methylene chloride was removed. Recovery was generally 60−80%, based on amount of starting alkene.

Calculations. The AM1[38] calculations were conducted, using the standard methods as implemented in the Spartan package.[39] 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.

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Supporting Information Available: ^{13}C spectra of **4c**$^{2+}$−**e**$^{2+}$ and ^{1}H spectra of **4b**$^{2+}$−**e**$^{2+}$ at −50 °C and the summary of ^{1}H spectra of **4c**$^{2+}$−**e**$^{2+}$ at −78 °C (13 pages). See any current masthead page for ordering and Internet access information.

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