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Dications of Fluorenylidenes: Conformational and Electronic Effects on the Paratropicity/Antiaromaticity of Fluorenyl Cations with Cyclic Substituents

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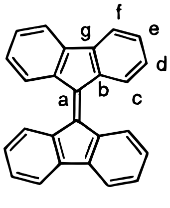
Oxidation of tetrabenzofulvalene derivatives **1**−**5** containing fluorenylidene and 5−7-membered rings resulted in the formation of dications which are effectively fluorenyl cations with perpendicular cyclic substituents. The observed paratropicity of the fluorenyl cation in these systems is attributed to an antiaromatic ring current, after evaluation of the effects of geometry, charge density, and polarity of the medium, and is dependent on the geometry and electronic character of the cyclic substituent. A linear relationship between the ^{1}H shifts of appropriate protons of the fluorenyl system and ^{13}C shift of *carbon a* suggests that the effect of the substituent is transmitted through *cross-hyperconjugation*.

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 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 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] fluorenyl cations containing cationic substituents (**A**) are indeed antiaromatic as indicated by a paratropic shift in the ^{1}H NMR spectrum.[5−8] Dications $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ exist in a geometry in which the ring systems are perpendicular to each other.[3] Evidence for this geometry comes from the resonance of H-c which is shifted upfield in $\mathbf{2}^{2+}$, because H-c is in the center of the aromatic cycloheptatrienyl cationic system.[6] Analogously, H-c in $\mathbf{1}^{2+}$ is shifted downfield.



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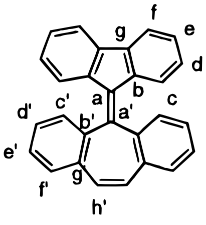

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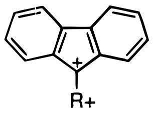
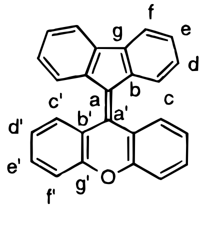


A

These antiaromatic dications and their derivatives lend themselves to the study of antiaromaticity because they are readily accessible and relatively stable, observable species. 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.

We report herein our investigations of **A**, in which R is a cyclic substituent ($\mathbf{1}^{2+}$−$\mathbf{5}^{2+}$). Through variation in ring size and in the electronic character of R, we were able to systematically explore conformational and electronic effects on antiaromaticity and the manner by which those effects are transmitted from the substituent to the fluorenyl cation.



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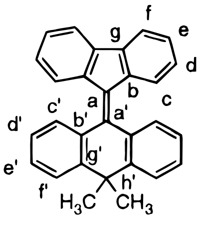

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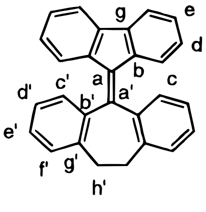

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Table 1. ^{1}H NMR Chemical Shifts (δ) for Dications[a]

	$\mathbf{1}^{2+}$	$\mathbf{3}^{2+}$	$\mathbf{4}^{2+}$	$\mathbf{5}^{2+}$	$\mathbf{2}^{2+}$
c	5.33 ± 0.02[b]	4.86 ± 0.06	5.13 ± 0.06	5.16 ± 0.09	5.01 ± 0.08
d	5.16 ± 0.01	5.06 ± 0.06	5.18 ± 0.06	5.25 ± 0.09	5.24 ± 0.08
e	5.77 ± 0.02	5.86 ± 0.07	5.94 ± 0.06	5.99 ± 0.10	6.10 ± 0.08
f	4.97 ± 0.02	5.21 ± 0.07	5.31 ± 0.06	5.38 ± 0.09	5.57 ± 0.08
c′		7.58 ± 0.07	7.73 ± 0.06	7.87 ± 0.09	8.58 ± 0.08
d′		7.09 ± 0.07	7.02 ± 0.07	6.79 ± 0.09	7.58 ± 0.07
e′		7.59 ± 0.05	7.29 ± 0.06	7.21 ± 0.09	7.69 ± 0.08
f′		7.27 ± 0.07	7.06 ± 0.12	6.63 ± 0.10	7.77 ± 0.07
h′				2.11 ± 0.09	8.28 ± 0.08
				2.25 ± 0.08	
CH_3			0.70 ± 0.07		

[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. ^{1}H NMR Chemical Shifts (δ) for Neutral Precursors[a]

	1	**3**	**4**	**5**	**2**
c	8.38	7.89	7.74	6.86	6.45
d	7.20	7.06	7.00	6.95	6.90
e	7.32	7.28	7.26	7.24	7.22
f	7.69	7.71	7.69	7.70	7.65
c′		8.12	7.86	7.41	7.59
d′		7.12	7.18	7.20	7.47
e′		7.48	7.28	7.29	7.43
f′		7.35	7.54	7.26	7.53
h′				3.45	7.03
				2.81	
CH_3			1.74		

[b] Solvent, $CDCl_3$; reference, TMS.

Results

Olefin precursors **1**−**3** were prepared according to literature methods.[9−11] Olefin **4** was synthesized via Peterson olefination[12] of 10,10-dimethylanthrone[13] with fluorene. Olefin **5** was prepared from reaction of 2,3,6,7-dibenzocycloheptane-1-thione[14] with diazofluorene, after the method of Schönberg et al.[11] Dications were formed via oxidation with a 30-fold excess of SbF_5 in SO_2ClF at −78 or −90 °C.[15]

^{1}H and ^{13}C NMR data for the dications and their neutral precursors are reported in Tables 1−4. Dication spectra (Tables 1 and 3) were normally obtained at three temperatures, −78, −50, and −30 °C, and showed a dependence of the ^{1}H NMR shift as a function of temperature. Although the best resolution was seen at higher temperatures, all spectra are reported at −50 °C to avoid the decomposition which began for some dications at −30 °C. Complete assignments for dications were made through 2-dimensional correlation spectroscopy (COSY) and heteronuclear correlation spectroscopy (HETCOR). Long-range HETCOR spectroscopy focusing on three-bond couplings allowed the assignment of chemical shifts for carbons not bearing hydrogens. Assignment of the NMR spectra for neutral compounds (Tables 2 and 4) was done in an analogous manner and compared with literature assignments where available.[16]

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

	$\mathbf{1}^{2+}$	$\mathbf{4}^{2+}$	$\mathbf{5}^{2+}$	$\mathbf{6}^{2+}$	$\mathbf{2}^{2+}$
a	189	197	202	207	211
b	146	147	148	148	147
c	145	146	146	146	145
d	136	136	136	136	135
e	159	159	158	157	157
f	130	130	129	129	129
g	152	152	151	151	151
a′		158	174	182	159
b′		120	135	134	133
c′		127	138	143	134
d′		131	132	131	135
e′		147	150	154	143
f′		120	131	133	137
g′		156	158	159	146
h′			38	31	146
CH_3			46		

[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.

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

	1	**4**	**5**	**6**	**2**
a	141	130.9	129.6	132.5	132.4
b	145.8	139.3	138.8	138.2	137.9
c	144.8	124.2	125.5	125.2	125.1
d	136.0	125.8	125.9	126.4	126.4
e	158.8	127.4	127.9	127.7	127.8
f	130.4	119.4	119.3	119.2	119.2
g	152.5	140.2	140.8	140.5	140.6
a′		131.2	140.2	145.2	141.2
b′		124.8	139.1	141.6	138.0
c′		130.0	128.4	127.6	127.0
d′		122.8	124.7	126.1	128.6
e′		129.9	127.5	128.1	127.4
f′		117.6	123.7	130.1	128.4
g′		154.0	147.7	136.7	133.5
h′			27.3	31.8	130.8
CH_3			41.1		

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

Discussion

Evidence for Antiaromaticity in the Fluorenyl Systems of $\mathbf{1}^{2+}$−$\mathbf{5}^{2+}$. A comparison of the ^{1}H NMR chemical shifts in Tables 1 and 2 reveals that upon oxidation to a dication, the protons of the fluorenyl system undergo a substantial upfield (paratropic) shift.[17] The analogous paratropic shift in a set of dications of polycyclic aromatic hydrocarbons has been attributed to

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(17) The dication of tetraphenylethylene can be used as the model for a dication which is similar in substitution but not antiaromatic. The ^{1}H NMR spectrum has peaks at 8.55 ppm (4H) and 9.07 ppm (1H). Olah, G. A.; Grant, J. L.; Spear, R. J.; Bollinger, J. M.; Serianz, A.; Sipos, G. *J. Am. Chem. Soc.* **1975**, *98*, 2501−2507.

the antiaromatic ring current of the dication.[5] However, chemical shifts in ^{1}H NMR spectra are 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, as well as to the existence of ring currents.[18]

The geometry of dications $\mathbf{1}^{2+}-\mathbf{5}^{2+}$ cannot be examined directly because of the difficulty in obtaining a crystal of X-ray quality; thus both semiempirical (AM1)[19] molecular orbital calculations and molecular mechanics calculations[20] of $\mathbf{1}^{2+}-\mathbf{5}^{2+}$ were used to obtain bond lengths, bond angles, and dihedral angles. If one considers *only* the fluorenyl system and the variation between analogous bonds, like the b−c bond in $\mathbf{1}^{2+}-\mathbf{5}^{2+}$, the percent standard deviations in bond lengths are less than 0.3%. Bond angles and dihedral angles are equally invariant.[21] Since changes in hybridization are normally reflected in changes in geometrical parameters, such as bond length, this invariance between systems reflects a lack of variation in hybridization. Thus, variation in ^{1}H NMR shifts of the fluorenyl system for these dications is not due to changes in geometry or hybridization.

Medium effects were explored because a minor variation in the amount of SbF_5 in the solution used to generate the dication could affect the polarity of the medium and therefore the ^{1}H chemical shift. The chemical shifts of the protons of the dications varied slightly from run to run and are reported with the standard deviation for at least three different preparations of dication.[22] To evaluate the effect of differing amounts of SbF_5, $\mathbf{1}^{2+}$ was prepared with 20−50-fold excesses of SbF_5, with the amount of SO_2ClF and **1** constant. There was no relationship between the mass of SbF_5 used and the chemical shift of the protons. The lack of variation of the ^{1}H chemical shift with the amount of SbF_5 demonstrates that changes in the medium of this type are not responsible for variation in the chemical shift.

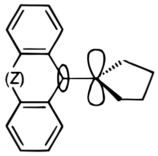
One of the most important effects on the ^{1}H NMR shift is the charge density of the carbon to which the proton is attached. Charge density is also an important factor in ^{13}C NMR shifts and contributes far more to the carbon shift than do anisotropic effects such as ring current.[23] ^{13}C NMR shifts can be used, therefore, to evaluate charge density. To have a valid correlation between charge density and ^{13}C NMR shifts, there must be minimal variation in the bonding of the systems considered,[24] as has already been demonstrated through our molecular orbital calculations. An examination of the ^{13}C chemical shifts in Table 3 shows that the chemical shifts of carbons b−g for each dication 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.

However, when the chemical shift for individual carbons are considered for $\mathbf{1}^{2+}-\mathbf{5}^{2+}$, there is very little variation in the chemical shifts of carbons of the fluorenyl system, with the exception of carbon a. That is, the shift of carbon b, for example, is effectively the same in $\mathbf{1}^{2+}-\mathbf{5}^{2+}$. Thus the change in the charge density for the carbons bearing protons, and those adjacent to these carbons, does 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 do not reflect changes in charge density.

The paratropicity of the fluorenyl systems of $\mathbf{1}^{2+}-\mathbf{5}^{2+}$ is not the result of changes in geometry, in the medium, or in variations of the charge density of carbons b−g of these systems. We therefore attribute the paratropicity to an antiaromatic ring current.

Effect of Substituents on the Magnitude of Antiaromaticity. The previous discussion dealt with arguments for the existence of an antiaromatic ring current as the cause of the paratropicity of these fluorenyl-substituted dications. It remains to be shown whether variation in the conformation and/or electronic character of the substituent R in **A** affects the magnitude of the antiaromatic ring current and to determine the manner by which those effects are transmitted from the substituent to the fluorenyl cation.

Examination of the NMR shifts for $\mathbf{1}^{2+}-\mathbf{5}^{2+}$ shows variation in two types of shifts. The ^{1}H NMR shifts for the fluorenyl systems vary as the cyclic substituent varies, and the differences in those shifts have been shown to be the result of an antiaromatic ring current. More dramatic are the variations in the ^{13}C NMR shifts of carbon a of the fluorenyl systems. While the shifts of carbons b−g are essentially invariant between systems, the shift of carbon a varies from 188 ppm for $\mathbf{1}^{2+}$ to 211 ppm for $\mathbf{2}^{2+}$, a remarkably large variation and particularly striking when compared to the chemical shifts for carbon a of the fluorenyl cation itself,[25] which are between 223 and 228 ppm for alkyl-substituted cations. We have attributed the upfield shift to an increase in electron density at carbon a, through the electrons in the σ-system. As is shown below, the empty p orbital of the fluorenyl system would lie in the plane of the opposing system, allowing the appropriate geometry for σ donation.



This type of $\sigma-\pi$ interaction has been described as *cross-*

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(21) Available in Supporting Information.

(22) The slight variation in chemical shift is probably related to the resolution of the spectra and the difficulty of accurately assigning chemical shift to relatively broad signals. Normally the spectra of these dications, although less well-resolved than the spectra of the neutral precursors, are sufficiently well-resolved to determine splitting (see Supporting Information). However, the presence of trace amounts of paramagnetic material appears to broaden the spectra on occasion.

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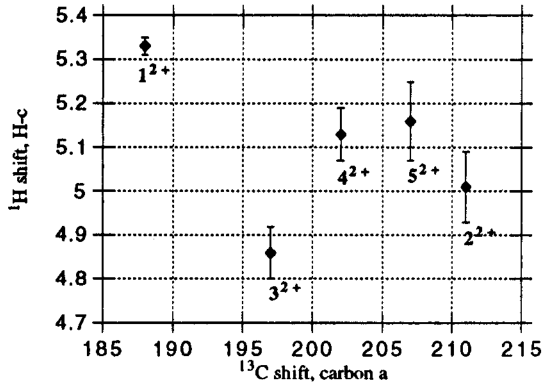

Figure 1. ^{1}H NMR shift for H-c vs ^{13}C NMR shift for carbon a.

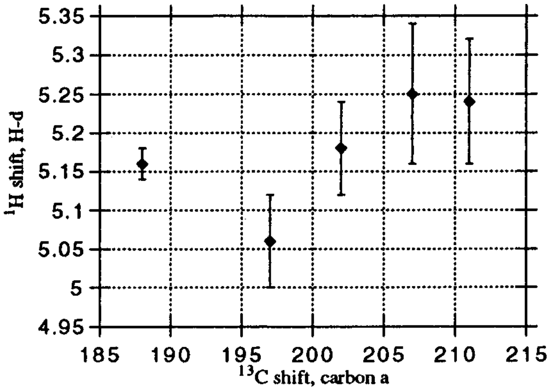

Figure 2. ^{1}H NMR shift for H-d vs ^{13}C NMR shift for carbon a.

hyperconjugation.[26] Calculations of a number of dications suggest that the stabilization offered through an orthogonal geometry is substantial.[27,28]

The ^{1}H NMR chemical shifts are affected by the perpendicular geometry also. As described in the Introduction, H-c in **2**$^{2+}$ is shifted upfield because it is held in the center of the aromatic ring current of the opposing ring.[6] Analogously, H-c in **1**$^{2+}$ is shifted downfield. The ^{1}H chemical shift of H-c for these dications and for **3**$^{2+}$–**5**$^{2+}$ would reflect both its antiaromatic ring current and the effect of the opposing ring. Only protons removed from the effect of the opposing ring, such as H-e and H-f, would demonstrate the effects of antiaromaticity alone.

Since variation is seen in both the shift of carbon a and the shifts of the protons on the fluorenyl system, the relationship between those shifts was explored. Figures 1–4 are the plots of the shifts of the individual protons H-c through H-f versus the shift of carbon a for **1**$^{2+}$–**5**$^{2+}$. The effect of the ring current of the opposing ring system in **1**$^{2+}$–**3**$^{2+}$ is apparent in the lack of a linear correlation in Figure 1. Proton c of **1**$^{2+}$ is shifted abnormally far downfield by the effect of the opposing antiaromatic ring system and thus should have a smaller chemical shift in the absence of that effect. Analogously, that proton in **2**$^{2+}$ and **3**$^{2+}$ is abnormally far upfield and should have a larger chemical shift. If one considers that the relationship shown by H-c in **4**$^{2+}$ and **5**$^{2+}$ is devoid of these effects and forms the basis of a linear relationship, the shifts of H-c in for **1**$^{2+}$-**3**$^{2+}$ are consistent with the effects of a ring current in the opposing ring. The effect of the opposing ring is also apparent for H-d but attenuated, presumably because of the greater distance from the opposing ring.

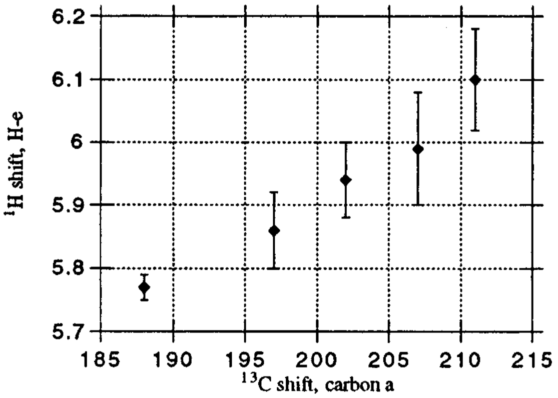

Figure 3. ^{1}H NMR shift for H-e vs ^{13}C NMR shift for carbon a.

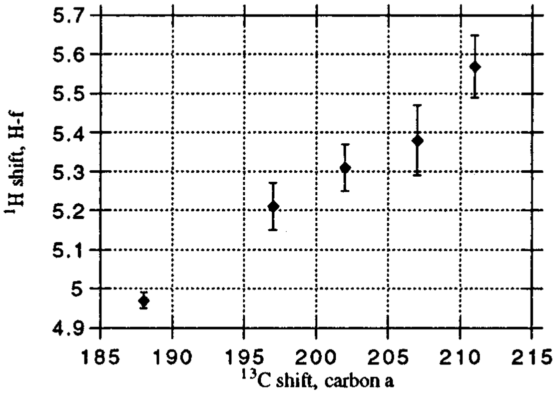

Figure 4. ^{1}H NMR shift for H-f vs ^{13}C NMR shift for carbon a.

For H-e and H-f, which are removed from the opposing ring, the linear relationship between proton shift, due to antiaromaticity, and the shift of carbon a is evident. This relationship reveals the manner in which the cyclic substituent is able to affect the antiaromaticity of the fluorenyl system. It appears that the effect of the substituent is transmitted through electron donation through the σ-system into the π-system of the fluorenyl cation. The fluorenyl cation is affected by electronic effects, such as the aromaticity or antiaromaticity of the opposing ring (**1**$^{2+}$–**3**$^{2+}$), as shown by the variation of H-e and H-f as the electronic nature of the substituent changes.

It is also affected by the conformation of the opposing ring, which presumably affects the effectiveness of the overlap of orbitals involved in σ-donation. Dications **4**$^{2+}$ and **5**$^{2+}$ should possess very similar electronic environments, but the differing ring sizes would result in different conformations of the overall system. This suggestion is given support via the modeling studies previously discussed which show the dihedral angle between the two systems as 97° for **5**$^{2+}$ and 90° for **4**$^{2+}$. The decreased paratropicity of **5**$^{2+}$ compared to **4**$^{2+}$ suggests that the interaction with the substituent is most effective when the ring systems are most perpendicular. Interestingly, all other dications in this series, including **2**$^{2+}$ have dihedral angles of 90°, according to these modeling studies.

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Conclusion

Oxidation of **1**−**5** results in the formation of dications whose ^{1}H NMR spectra reveal a paratropic shift for the protons of the fluorenyl systems. Because that shift is not due to variations in geometry in the fluorenyl system, charge density, or the medium, it has been attributed to variations in antiaromaticity of the fluorenyl systems of $\mathbf{1}^{2+}$−$\mathbf{5}^{2+}$. The chemical shift of carbon a varies substantially between $\mathbf{1}^{2+}$−$\mathbf{5}^{2+}$, and the variation correlates linearly with the shift of the protons of the fluorenyl system, most obviously with H-e and H-f. The greatest antiaromaticity is shown in the system ($\mathbf{1}^{2+}$) with the smallest ^{13}C NMR shift for carbon a. We are attributing the change in the shift of carbon a to a change in the electron density at that carbon, which allows the postulation of *cross-hyperconjugation* as the mechanism by which the opposing ring system is able to affect the antiaromaticity of the fluorenyl cation.

We are continuing to explore the phenomenon of antiaromaticity in other derivatives of **A**.

Experimental Section

Starting materials **1**−**3** were synthesized according to literature procedures.[9−11] Antimony pentafluoride was obtained from Ozark Mahonig (Tulsa, OK) and triply distilled prior to use. SO_2ClF was prepared by the method of Olah et al.[29] 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-(9*H*-Fluoren-9-ylidene)-10,10-dimethylanthracene (4). *n*-Butyllithium (0.88 mL, 2.2 mmol, 2.4 M in hexanes) was added to a solution of fluorene (0.332 g, 2.00 mmol) in 20 mL of THF at −78 °C under an Ar atmosphere. After 15 min, trimethylsilane (0.278 mL, 2.20 mmol) was added followed after 15 min by *n*-butyllithium (0.88 mL, 2.2 mmol). 10,10-Dimethylanthrone (0.445 g, 2.00 mmol) in 5 mL of THF was added after 10 min, giving a dark green solution. The reaction mixture was allowed to stir overnight at rt. It was quenched with 10 mL of saturated aqueous NH_4Cl. Ether, 25 mL, was added, and the layers were separated. The aqueous layer was extracted with ether, the organic layers were combined and dried over $MgSO_4$, and the solvent was removed in vacuo. The reaction mixture was separated by flash chromatography on silica gel, using hexanes as eluent. The product was recrystallized from petroleum ether: mp 223−224 °C; yield 0.496 g, 67.1%. Anal. Calcd for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 94.24; H, 6.17.

5-(9*H*-fluoren-9-ylidene)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cycloheptene (5). Diazofluorene[30] (1.8 g, 9.4 mmol) in 20 mL of benzene was added dropwise to 2,3,6,7-dibenzocycloheptane-1-thione[14] (2.2 g, 9.6 mmol) in 30 mL of benzene under argon and refluxed for 3 h. The reaction mixture was cooled, diluted with 35 mL of petroleum ether, and filtered, giving the episulfide, 2.2 g, 59%. Episulfide (0.10 g, 0.26 mmol) was dissolved in 10 mL of toluene and refluxed with copper bronze (0.20 g) for 6 h. The reaction mixture was cooled and filtered and the solvent removed in vacuo: yield, after recrystallization from toluene, 0.061 g, 65%; mp 245−249 °C (lit.[31] mp 251 °C).

General Preparation of Dications. SbF_5 (≈0.7 mL, ≈9 mmol) was added to a graduated centrifuge tube in a drybox and the tube 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.[32] The contents were mixed on a vortex stirrer until homogeneous and 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[19] calculations were conducted using the standard methods as implemented in the Spartan package,[33] on a Silicon Graphics Personal Iris 4DG computer. The starting geometries were created using the PCMODEL program.[20] The molecular mechanics calculations were performed using the MMX software in PCMODEL on a Macintosh Quadra 800 computer with geometry optimization 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.

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Supporting Information Available: ^{13}C and ^{1}H NMR spectra for $\mathbf{1}^{2+}$−$\mathbf{5}^{2+}$ and a listing of calculated bond lengths, bond angles, and dihedral angles (14 pages). This material is contained in libraries on microfiche, 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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