JOC Article

Dications of Fluorenylidenes. The Effect of Substituent Electronegativity and Position on the Antiaromaticity of Substituted Tetrabenzo[5.5]fulvalene Dications

Amalia Levy, Amber Rakowitz, and Nancy S. Mills*

Department of Chemistry, Trinity University, San Antonio, Texas 78212-7200

nmills@trinity.edu

Received December 31, 2002

Oxidation of 3,6-disubstituted tetrabenzo[5.5]fulvalenes by SbF_5 results in the formation of dications that behave like two antiaromatic fluorenyl cations connected by a single bond. Both fluorenyl systems exhibit the paratropic shifts and nucleus independent chemical shifts (NICS) characteristic of antiaromatic species. Comparison with analogous 2,7-disubstituted tetrabenzo[5.5]fulvalenes reveals that the antiaromaticity of the substituted ring system can be altered substantially by changes in the placement of the substituents, possibly due to changes in the delocalization of charge in the system. Substituents in the 3,6-position decrease the antiaromaticity because of the increase in the benzylic resonance compared to 2,7-substituents.

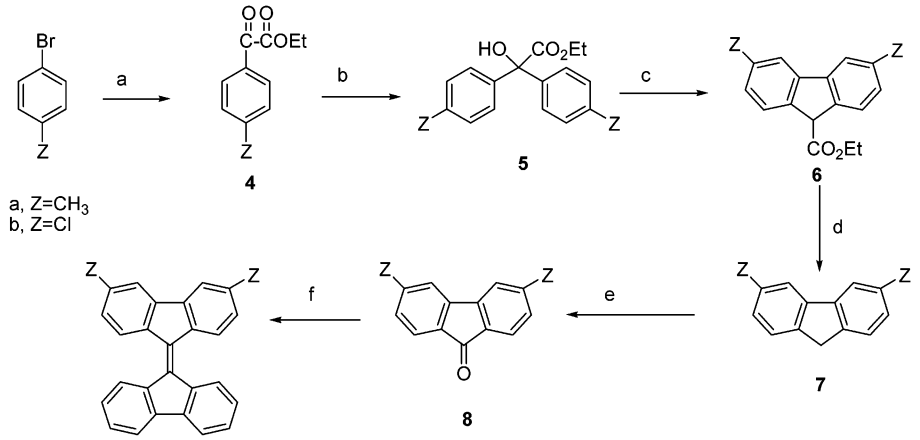
During the 20th century, the interest of organic chemists was captured by the definition of aromaticity based on theoretical principles and on the power of those principles to guide the synthesis of novel nonbenzenoid aromatic compounds. Unfortunately, the chemical community has yet to come to agreement on what experimental observations are de facto evidence of aromatic behavior. In general, the criteria used fall into three categories, energetic, structural, and magnetic.[1,2] The *energetic criterion* is based on the observation that benzene is thermodynamically more stable than its open-chain analogues, which requires that appropriate open-chain analogues be defined. Assessment of aromaticity based on *structural* properties returns to the structure of benzene for the definition of those properties. Thus, planarity and lack of bond length alternation are the primary descriptors of this property. The harmonic oscillator model of aromaticity (HOMA)[3−5] allows evaluation of the deviation of bond lengths in a species from the optimal bond length of benzene, considering both the increase in bond length alternation (a geometric contribution to dearomatization) and the deviation from the mean bond length (the energetic contribution, EN).[6] *Magnetic criteria* are based on the existence of a ring current which, while experimentally unobservable, can be measured indirectly through the chemical shift of the protons,[7] the magnetic susceptibility exaltation (Λ),[8] and anisotropy,[9−12] as well as evaluated through the calculated nucleus independent chemical shift (NICS, vide supra).[13−15] The question of whether these criteria can be quantititatively related, whether conclusions drawn about relative aromaticity agree under all the criteria, is under vigorous debate.[16−18] Even a very recent article, which was intended to "present an authoritative assessment of all of this work"[17] ends with the authors divided in their conclusions. Authors Cyrañski, Krygowski, and Katritzky stress that for a system to be considered fully aromatic, it must follow all the main criteria, while Schleyer suggests that the special behavior associated with induced ring currents is most closely related to the cyclic electron delocalization that characterizes aromatic species.

If the evaluation of aromaticity is under dispute, the situation with antiaromaticity is even less well resolved. We have discovered a class of fluorenylidene dications

(1) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*; John Wiley and Sons: New York, 1994.
(2) Glukhovtsev, M. *J. Chem. Educ.* **1997**, *74*, 132−136.
(3) Krygowski, T. M.; Cyranski, M. K. *Chem. Rev.* **2001**, *101*, 1385−1419.
(4) Kruszewski, J.; Krygowski, T. M. *Tetrahedron Lett.* **1972**, 3839−3842.
(5) Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70−78.
(6) Krygowski, T. M.; Cyranski, M. *Tetrahedron* **1996**, *52*, 1713−1722.
(7) Elvidge, J. A.; Jackman, L. M. *J. Chem. Soc.* **1961**, 859−866.
(8) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209−218.
(9) Pascal, P. *Ann. Chim. Phys.* **1910**, *19*, 5−70.
(10) Dauben, H. J. J.; Wilson, D. J.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811−813.
(11) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1971; Vol. II, pp 167−206.
(12) Haberditzl, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 288−298.
(13) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.
(14) Williams, R. V.; Armantrout, J. R.; Twamley, B.; Mitchell, R. H.; Ward, T. R.; Bandyopadhyay, S. *J. Am. Chem. Soc.* **2002**, *124*, 13495−13505.
(15) Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075−7083.
(16) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 7−340.
(17) Cyranski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1333−1338.
(18) Katritzky, A. R.; Karelson, M.; Sild, S.; Krygowski, T. M.; Jug, K. *J. Org. Chem.* **1998**, *63*, 5228−5231.

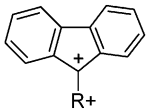
10.1021/jo026924h CCC: $25.00 © 2003 American Chemical Society
Published on Web 04/23/2003

SCHEME 1[a]



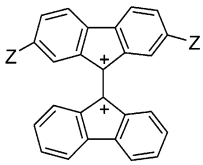
[a] Reagents and conditions: (a) Mg, ether; EtO_2CCO_2Et, Et_2O, −78 °C; (b) ZC_6H_4MgBr, Et_2O, −78 °C; H_3O^+; (c) polyphosphoric acid/ H_3PO_4 (**a**), H_2SO_4, CH_3CO_2H (**b**); (d) KOH, H_2O.

$\mathbf{1}^{2+}$ [19−25] in which the cationic fluorenyl system shows an

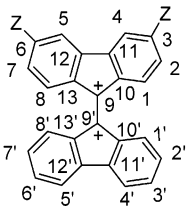


$\mathbf{1}^{2+}$

appreciable paratropic shift and calculated NICS and Λ that are characteristic of antiaromatic compounds. For one system,[24] the redox potentials for formation of the dications have been measured and show potential differences with respect to a reference system that appear to indicate substantial destabilization with respect to the reference system.[26] The paratropicity of the cationic fluorenyl system can be altered by changes in the substituent R^+. We have explored the effect of changing the electronegativity of the substituent[22] and on changing the geometry of the substituent.[19,25] We here report the effect on the magnetic properties related to antiaromaticity of varying both the electronegativity and the position of a substituent on a series of 2,7- and 3,6-disubstituted dications of tetrabenzo[5.5]fulvalenes, $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$, and suggest the manner in which the substituent acts to moderate the antiaromaticity of the cationic fluorenyl system.



$\mathbf{2}^{2+}$
a, Z=CH_3
b, Z=Cl
c, Z=F
d, Z=H



$\mathbf{3}^{2+}$
a, Z=CH_3
b, Z=Cl
c, Z=F

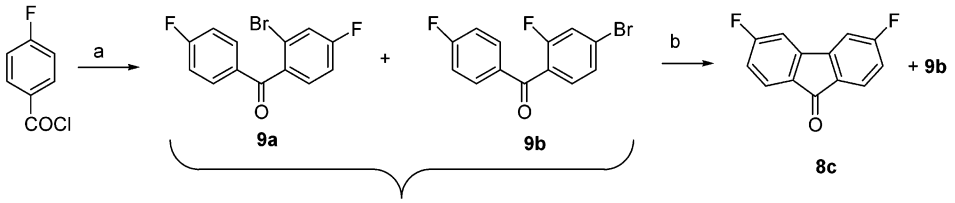
Synthesis of the Neutral Precursor to 3 and Oxidation to Dications. The syntheses of **2b**, the olefinic precursors to $\mathbf{2}^{2+}$, have already been reported.[22] The synthesis of **3a** and **b** is shown in Scheme 1. The key steps in the synthesis are the acid-catalyzed cyclization of **5** to **6** (Scheme 1). Synthesis of **3** followed decarboxylation of the carboxylic acid to give **7**. The cyclization is based on the superacid cyclizations of Ohwada et al.[27,28] The cyclization is very sensitive to the nature of the *Z*-substituent. A mixture of polyphosphoric acid in phosphoric acid gave high yields of **6a**, while formation of **6b** required a mixture of concentrated sulfuric acid in acetic acid. The unusual decarboxylation of the benzylic acid of **6** is effective because of the stability of the resulting fluorenyl anion.[29] After oxidation of **7** to the corresponding fluorenone, Peterson olefination resulted in formation of **3**.

The superacid-catalyzed cyclization of **5c** resulted in unacceptably low yields of **6c**, as was also found by Ohwada.[28] The alternative approach to **8c** is shown in Scheme 2. Friedel−Crafts acylation of 1-bromo-3-fluorobenzene with *p*-fluorobenzoyl chloride gave a mixture of isomeric **9**. The palladium-catalyzed coupling[30] resulted in formation of **8c** and unreacted **9b**, which were easily separated. Peterson olefination then gave **3c**.

Dications were prepared by oxidation of the neutral precursors at −78 °C with a 5-fold excess of SbF_5 in SO_2ClF and then characterized by 1D and 2D NMR spectroscopy at temperatures between −78 and −30 °C.

(19) Mills, N. S.; Malandra, J. L.; Burns, E. E.; Green, A.; Unruh, K. E.; Kadlecek, D. E.; Lowery, J. A. *J. Org. Chem.* **1997**, *62*, 9318−9322.
(20) Malandra, J. L.; Mills, N. S.; Kadlecek, D. E.; Lowery, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 11622−11624.
(21) Mills, N. S.; Burns, E. E.; Hodges, J.; Gibbs, J.; Esparza, E.; Malandra, J. L.; Koch, J. *J. Org. Chem.* **1998**, *63*, 3017−3022.
(22) Mills, N. S.; Malinky, T.; Malandra, J. L.; Burns, E. E.; Crossno, P. *J. Org. Chem.* **1999**, *64*, 511−517.
(23) Mills, N. S. *J. Am. Chem. Soc.* **1999**, *121*, 11690−11696.
(24) Mills, N. S.; Benish, M. M.; Ybarra, C. *J. Org. Chem.* **2002**, *67*, 2003−2012.
(25) Mills, N. S. *J. Org. Chem.* **2002**, *67*, 7029−7036.
(26) Breslow, R.; Murayama, D. R.; Murahashi, S.-I.; Grubbs, R. *J. Am. Chem. Soc.* **1973**, *95*, 6688−6699.
(27) Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1988**, *110*, 1862−1870.
(28) Ohwada, T.; Suzuki, T.; Shudo, K. *J. Am. Chem. Soc.* **1998**, *120*, 4629−4637.
(29) Hopkinson, A. C.; Lee-Ruff, E.; Maleki, M. *Synthesis* **1986**, 367−371.
(30) Ames, D. E.; Opalko, A. *Synthesis* **1983**, 234−235.

SCHEME 2. Synthesis of 8c[a]



[a] Reagents and conditions: (a) 3-bromofluorobenzene, $AlCl_3$; (b) $Pd(OAc)_2$, Na_2CO_3, DMA.

TABLE 1. Experimental ^{1}H NMR Shifts for 2^{2+} and 3^{2+} [a,b]

H	$2a^{2+}$	$2b^{2+}$	$2c^{2+}$	$2d^{2+}$	$3a^{2+}$	$3b^{2+}$	$3c^{2+}$
1	4.79 ± 0.12	5.24 ± 0.04	4.67 ± 0.08		5.28 ± 0.02	5.79 ± 0.26	5.54 ± 0.17
2					5.43 ± 0.01	5.66 ± 0.26	5.61 ± 0.27
3	5.32 ± 0.15	4.64 ± 0.13	4.29 ± 0.09				
4	4.44 ± 0.12	5.59 ± 0.12	4.01 ± 0.08		5.23 ± 0.02	5.57 ± 0.26	5.80 ± 0.33
av	4.85 ± 0.12	5.16 ± 0.13	4.32 ± 0.08		5.31 ± 0.01	5.67 ± 0.26	5.65 ± 0.26
CH_3	0.68 ± 0.12				1.13 ± 0.03		
1	5.65 ± 0.13	5.57 ± 0.15	5.16 ± 0.09	5.33 ± 0.02	5.54 ± 0.02	5.39 ± 0.26	5.45 ± 0.08
2	5.38 ± 0.16	5.33 ± 0.12	4.94 ± 0.09	5.16 ± 0.01	5.32 ± 0.02	5.23 ± 0.26	5.29 ± 0.08
3	5.94 ± 0.12	5.91 ± 0.11	5.52 ± 0.09	5.77 ± 0.02	5.94 ± 0.01	5.86 ± 0.26	5.92 ± 0.08
4	5.14 ± 0.14	5.08 ± 0.13	4.76 ± 0.09	4.97 ± 0.02	5.18 ± 0.02	5.08 ± 0.26	5.13 ± 0.07
av	5.53 ± 0.14	5.47 ± 0.12	5.10 ± 0.09	5.31 ± 0.02	5.50 ± 0.02	5.39 ± 0.26	5.45 ± 0.08

[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.

Relationship between Experimental and Calculated Chemical Shift. There are several measures of ring current that are available through calculation, including nucleus independent chemical shift. The nucleus independent chemical shift (NICS)[13] is based on the observation that protons in the center of an aromatic ring system experience a dramatic upfield shift because of the effect of the ring current.[31,32] By computing magnetic shieldings at ring centers, effectively putting a dummy atom in the center of the ring system to "sense" the effect of the ring current, one can evaluate both the aromatic or antiaromatic character through the sign of the shielding, with aromatic species possessing negative NICS, as well as from its relative magnitude through the size of the shielding. Because the local contributions of the σ bonds[33−35] might affect the magnetic shieldings, NICS values are normally calculated at a distance, usually 1 Å, above the plane of the ring. The magnitude of chemical shifts or NICS is dependent upon the basis set used for the calculation[23,36,37] and it seemed prudent to begin with a comparison of the calculated NMR shifts with the experimental NMR shifts for those dications for which measurements exist.

The ^{13}C NMR shifts for $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ were calculated using the GIAO method in Gaussian 98 using the density functional theory method with the B3LYP functionals and the 6-31G(d) basis set, on geometries optimized at the same level (B3LYP/6-31G(d)), and the calculated shifts are given in the Supporting Information along with the experimental ^{13}C chemical shifts for $\mathbf{3b}^{2+}$ and $\mathbf{3c}^{2+}$. We were unable to obtain ^{13}C NMR data for $\mathbf{3a}^{2+}$ and have no explanation for this.[38] The correlation between calculated and experimental shifts is very good, $r^2 = 0.954$. A good correlation between experimental ^{13}C NMR shifts and shifts calculated with density functional theory for aliphatic cations has been reported recently.[39]

Because ^{1}H NMR shifts are much more sensitive to ring current effects,[31] and because NICS is designed to evaluate ring current effects, the magnitude of this correlation should be of particular importance. The ^{1}H NMR shifts for $\mathbf{2}^{2+}$ have been reported previously[22] but are included in Table 1 along with the previously unreported shifts for $\mathbf{3}^{2+}$. The calculated shifts for both are given in Table 2 along with the correlation coefficients with the experimental values for each individual dication. The square of the correlation coefficient for all dications is 0.857 when all protons are considered, but when only the protons on the unsubstituted fluorenyl systems are included, r^2 drops to 0.540. A comparison of experimental with calculated proton shifts for the unsubstituted fluorenyl systems gives r^2 of 0.825 that drops to 0.442 for the shifts for the substituted fluorenyl systems. An examination of correlations for each system shows that the correlation is particularly poor for the calculated ^{1}H NMR shifts of $\mathbf{2b}^{2+}$. In addition, the ratio of experimental to calculated shift for $\mathbf{2b}^{2+}$ is uncharacteristically high for these systems, 1.05 compared to 0.91−0.96 for the other systems (see the Supporting Information). Thus,

(31) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301−1316.
(32) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349−1384.
(33) Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Mühlenkamp, V. J. *J. Am. Chem. Soc.* **1994**, *116*, 5298−5306.
(34) Schleyer, P. v. R.; Jiao, H.; van Eikema Hommes, N. J. R.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669−12670.
(35) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465−2468.
(36) Helgaker, T.; Jaszunski, M.; Ruud, K. *Chem. Rev.* **1999**, *99*, 293−352.
(37) de Dios, A. C. *Prog. Nucl. Magn. Spectrosc.* **1996**, *29*, 229−278.

(38) Slight broadening of the ^{1}H NMR spectrum suggests the possible presence of some paramagnetic impurities that might have affectd our ability to get an adequate ^{13}C NMR spectrum.
(39) Vrcek, V.; Kronja, O.; Siehl, H.-U. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1317−1321.

TABLE 2. Calculated ^{1}H NMR Shifts for 2^{2+} and 3^{2+} [a]

H	$2a^{2+}$	$2b^{2+}$	$2c^{2+}$	$2d^{2+}$	$3a^{2+}$	$3b^{2+}$	$3c^{2+}$
1	4.52	4.01	3.91		5.71	6.23	6.45
2					5.77	6.23	5.92
3	5.41	4.89	4.79				
4	4.30	3.46	3.58		5.63	6.04	5.89
1′	6.11	5.89	5.87	5.81	5.92	5.70	5.71
2′	5.93	5.81	5.80	5.84	5.89	5.82	5.82
3′	6.61	6.46	6.45	6.56	6.64	6.60	6.61
4′	5.93	5.31	5.30	5.54	5.64	5.60	5.59
CH_3	1.20				2.19		
r^2	0.951 (0.979)[b]	0.080	0.771	0.940	0.918 (0.990)	0.865	0.477[b]

[a] Shifts calculated with the GIAO method, B3LYP/6-31G(d)//B3LYP/6-31G(d). [b] Correlation including methyl substituents is in parentheses.

TABLE 3. Nucleus Independent Chemical Shifts for Each Ring of 2^{2+} and 3^{2+} [a]

		$2a^{2+}$	$2b^{2+}$	$2c^{2+}$	$2d^{2+}$	$3a^{2+}$	$3b^{2+}$	$3c^{2+}$
unsubst	NICS-5−1	20.3	21.5	21.7	21.4	20.4	21.2	21.5
	NICS-6−1	7.4	9.1	9.3	8.4	7.2	7.9	8.2
subst	NICS-5−1	30.9	37.4	37.2		18.9	14.1	15.1
	NICS-6−1	15.4	20.1	18.85		6.48	3.3	3.3

[a] NICS values calculated 1 Å above plane of ring, GIAO, B3LYP/6-31G(d)//B3LYP/6-31G(d).

calculations of magnetic properties for this system are suspect. We have observed this for other systems with chloro substituents.[23,40]

Substituent Effects on the Antiaromaticity of the Unsubstituted Ring Systems. These substituted tetrabenzo[5.5]fulvalene dications can be considered as the fusion of two perpendicular fluorenyl cationic systems. As such, the analysis is simplified if the two ring systems are considered separately, with NICS and ^{1}H shifts used to evaluate the antiaromaticity of each system. The NICS, calculated 1 Å above the plane of the ring, for each ring and each system are given in Table 3. An examination of NICS values for the unsubstituted ring systems reveals only small differences between the NICS values as a function of substituent or its placement. Table 1 shows that the variation of the measured chemical shifts for the unsubstituted ring system as a function of substituent is within the errors of the measurements, with the exception of the fluoro-substituted derivatives, in which there is substantially greater paratropicity in **2c**$^{2+}$ compared to **3c**$^{2+}$. Within the 2,7-disubstituted systems, **2**$^{2+}$, fluoro-substituted dication **2c**$^{2+}$ also shows a greater paratropic shift for the unsubstituted ring system than for **2a**$^{2+}$ or **2b**$^{2+}$. Within the error bars, there is no difference in paratropicity for the unsubstituted ring of the 3,6-disubstituted dications as a function of the nature of the substituent, which is consistent with the relatively small difference in NICS. The average ^{1}H NMR shifts for the unsubstituted ring systems of **2**$^{2+}$ and **3**$^{2+}$ are also consistent with the average ^{1}H NMR shifts for the unsubstituted tetrabenzo[5.5]fulvalene dication, **2d**$^{2+}$, as are the NICS values for the five- and six-membered rings. Thus, putting a substituent on the opposing fluorenyl cationic system has little effect on the paratropicity/antiaromaticity of the unsubstituted fluorenyl rings

(40) A referee suggested that the poor correlation for magnetic properties might indicate open-shell singlet contamination of the wave function, but stability calculations for dication **2b**$^{2+}$ as well as the other six dications shows that the singlet wave functions are stable.

TABLE 4. ^{1}H NMR Shifts for 2 and 3

H	2a	2b	2c	2d	3a	3b	3c
1	8.17	8.27	7.00		8.26	8.23	8.31
2					7.01	7.19	6.92
3	7.12	7.24	7.01				
4	7.53	7.52	7.54		7.48	7.63	7.31
1′	8.40	8.22	8.29	8.39	8.37	8.23	8.24
2′	7.21	7.19	7.21	7.20	7.21	7.20	7.19
3′	7.33	7.32	7.34	7.32	7.31	7.34	7.32
4′	7.71	7.63	7.66	7.69	7.71	7.68	7.68
CH_3	2.34				2.42		

TABLE 5. Difference between ^{1}H NMR Shift of Neutral Precursors and Dications for 2 and 3

	$2a^{2+}$	$2b^{2+}$	$2c^{2+}$	$2d^{2+}$	$3a^{2+}$	$3b^{2+}$	$3c^{2+}$
1	3.38	3.03	2.33		2.98	2.44	2.77
2					1.58	1.53	1.31
3	1.80	2.60	2.72				
4	3.09	1.93	3.53		2.25	2.06	1.51
av	2.76	2.52	2.86		2.27	2.01	1.86
1′	2.75	2.65	3.13	3.06	2.83	2.84	2.79
2′	1.83	1.86	2.27	2.04	1.89	1.97	1.90
3′	1.39	1.41	1.82	1.55	1.37	1.48	1.40
4′	2.57	2.55	2.90	2.72	2.53	2.60	2.55
av	2.14	2.12	2.53	2.34	2.16	2.22	2.16
CH_3	1.66				1.29		

Substituent Effects on the Antiaromaticity of the Substituted Ring Systems. An examination of the NICS values for the substituted ring systems reveals a large difference between the antiaromaticity of 2,7- vs 3,6-disubstituted fluorenylidene dications, with substantially greater antiaromaticity for the 2,7-disubstituted systems. Because of the poor correlation between calculated and experimental ^{1}H NMR shifts for **2b**$^{2+}$, we are reluctant to place much weight on its NICS value. It is difficult to compare individual chemical shifts between the two systems because the shift of each proton is affected both by its position on the cationic ring[19] and by its proximity to the substituent, but the average chemical shifts for the substituted fluorenyl system are revealing. Dications **2**$^{2+}$ are substantially more paratropic than **3**$^{2+}$ and they are more paratropic than the parent unsubstituted dication, **2d**$^{2+}$. Because of concerns that the nature of the substituent might be masking or enhancing paratropic shifts, a more affective measure might be to consider the average of the chemical shift difference between dication and neutral precursor. The chemical shift for each proton for the neutral system is listed in Table 4, with the chemical shift difference from the corresponding dication in Table 5. Again, the larger chemical shift difference for the dications **2**$^{2+}$ indicate greater paratropicity in those systems than in dications **3**$^{2+}$. The differences in the NICS values (Table 3) parallel those of the chemical shifts, but are larger in magnitude. The plot of chemical shift difference vs NICS for the substituted ring systems of **2**$^{2+}$ and **3**$^{2+}$ as well as the parent system, **2d**$^{2+}$, are shown in Figure 1. The good correlation between the calculated NICS values and the experimental chemical shift differences lends confidence to the NICS values. More importantly, the large slope indicates that NICS is a more sensitive measure of antiaromaticity than is the experimental ^{1}H proton shift.

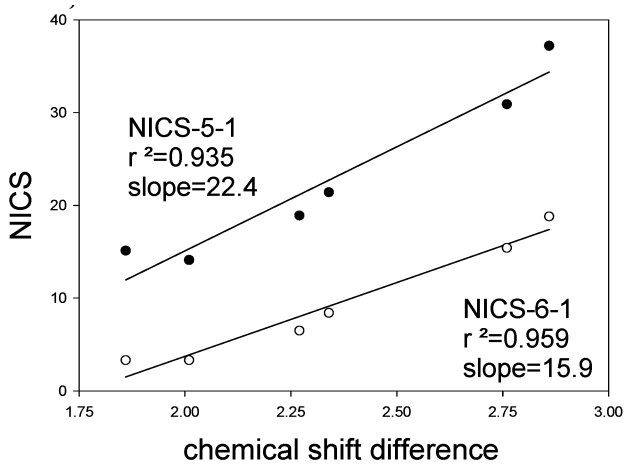


FIGURE 1. Comparison of NICS with chemical shift difference for the substituted ring of **2a**$^{2+}$, **2c**$^{2+}$, **2d**$^{2+}$, and **3**$^{2+}$.

The comparison of either the chemical shifts of **2**$^{2+}$/**3**$^{2+}$ or the chemical shift differences for **2**$^{2+}$/**3**$^{2+}$ with the parent system **2d**$^{2+}$ shows that the degree of paratropicity is affected by placing a substituent on the tetrabenzo[5.5]fulvalene dication, with substituents increasing the paratropicity when placed in the 2,7-positions and decreasing the paratropicity when placed in the 3,6-positions, but the nature of the individual substituent has relatively little effect on the chemical shift with their relatively large error bars.

Why does the position of the substituent have a substantial effect on the antiaromaticity of the substituted ring system in tetrabenzo[5.5]fulvalene dications?

It is important to first establish whether something unusual is occurring in the 2,7-disubstituted systems vs the 3,6-disubstituted systems. A recent study[41] demonstrated a linear correlation between NICS values and σ_{p+} for a series of benzylic cations. The analogous plot for NICS values vs σ_{p+} and σ_m[42] for **2a**$^{2+}$, **2c**$^{2+}$, **2d**$^{2+}$, and **3**$^{2+}$ showed a very poor correlation ($r^2 = 0.24$). The argument could be made that the σ values were chosen inappropriately. A set of new σ values for cationic systems was devised by Brown[43] on the basis of the ^{13}C NMR shifts of a set of para- and meta-substituted *tert*-cumyl cations and validated with other aryl cations. Because of the good correlation between calculated ^{13}C NMR shifts and experimental shifts, which then implied the reliability of the calculated NICS values, we examined the relationship between Brown's $\sigma^{\alpha C+}$ values and the calculated NICS values and observed only marginally better correlation ($r^2 = 0.34-0.36$). However, when the relationship between the NICS values and Brown's $\sigma^{\alpha C+}$ values were compared within similarly substituted systems, the correlation for the 3,6-disubstituted system was substantially better (for NICS-5−1, $r^2 = 0.961$ for **3**$^{2+}$, 0.308 for **2**$^{2+}$; NICS-6−1, $r^2 = 0.838$ for **3**$^{2+}$, 0.243 for **2**$^{2+}$). This suggested that the mode of delocalization of charge in these dications might be different in the two systems, which then affected the degree of antiaromaticity. An examination of resonance forms illustrates this suggestion. As shown in Scheme 3, in the 3,6-disubstituted fluorenyl system, the presence of a substituent in the para-position could act to confine the delocalization primarily to the benzylic system, with the cation behaving more like two benzylic cations held together by a single bond. However, in the 2,7-disubstituted fluorenyl system, delocalization could be forced throughout the entire fluorenyl system. The more complete delocalization in the 2,7-disubstituted system would force upon the system the antiaromatic properties expected with that complete delocalization. We have observed greater antiaromatic properties for fluorenyl systems with more complete delocalization.[23] Rabinovitz et al. have noted that 4nπ dianions gain stability by gaining diatropicity through reorganization of their path of π-delocalization.[44]

It would seem reasonable to find verification of the different substitution patterns by examination of the difference in the C_{11}–C_{12} bond lengths in the substituted and unsubstituted systems as a function of substitution pattern. Table 6 gives selected computed bond lengths, with a complete listing of computed bond lengths available in the Supporting Information. If the additional resonance forms shown in Scheme 3 for the 2,7-disubstituted fluorenyl system were only utilized by that system, the most obvious difference between the differently substituted fluorenyl systems would be in a shortened bond length for the C_{11}–C_{12} bond of the 2,7-

SCHEME 3. Resonance Forms for 2^{2+} **and 3**$^{2+}$

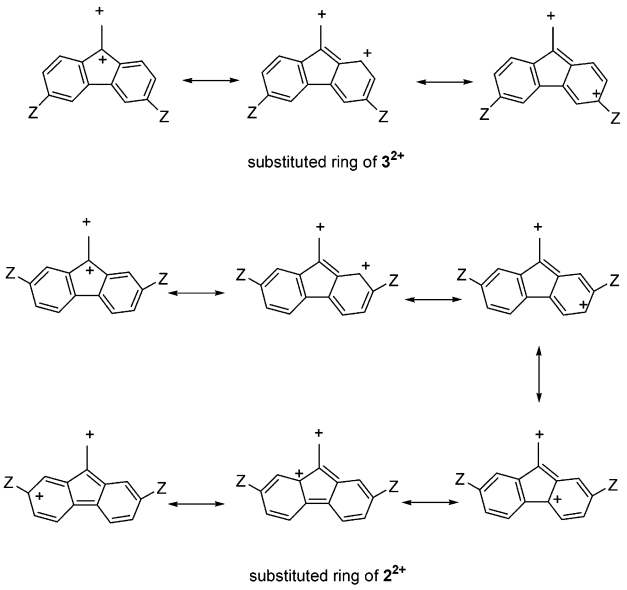


TABLE 6. Selected Bond Lengths from Geometry Optimization, B3LYP/6-31G(d)

compd	C_{11}–C_{12}	C_{11}–$C_{12'}$	C_9–$C_{9'}$	C_9–C_{10}
2a^{2+}	1.4812	1.4824	1.4605	1.4329
2b^{2+}	1.4803	1.4821	1.4610	1.4337
2c^{2+}	1.4830	1.4821	1.4609	1.4337
2d^{2+}		1.4822	1.4609	
3a^{2+}	1.4836	1.4824	1.4604	1.4302
3b^{2+}	1.4820	1.4822	1.4608	1.4305
3c^{2+}	1.4826	1.4824	1.4626	1.4297

(41) Morao, I.; Hillier, I. H. *Tetrahedron Lett.* **2001**, *42*, 4429−4431.
(42) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.
(43) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956−6960.
(44) Rabinovitz, M.; Ayalon, A. *Pure Appl. Chem.* **1993**, *65*, 111−118.

disubstituted fluorenyl system. The analogous bond in the unsubstituted ring was also examined. It is apparent from Table 6 that there is much greater variation in the length of the $C_{11-}C_{12}$ bond in the substituted ring system than in the unsubstituted ring system, which would be consistent with similar patterns of delocalization leading to similar degrees of antiaromaticity in the unsubstituted ring system. Of greater interest, the average $C_{11-}C_{12}$ for the 2,7-disubstituted system is 1.4815 Å, compared to 1.4827 Å for the 3,6-disubstituted systems. The NICS values for **2d**$^{2+}$ and the unsubstituted fluorenyl rings of **2**$^{2+}$ and **3**$^{2+}$ are intermediate in magnitude between the NICS values for the substituted rings. This suggests that the $C_{11-}C_{12}$ bond in the parent system **2d**$^{2+}$ (1.4822 Å) as well as the average length in the unsubstituted systems (1.4823 Å) should be intermediate in length between the average bond length in the 2,7- and 3,6-disubstituted systems, as they are. It is somewhat disturbing that the $C_{11-}C_{12}$ bond length for **3c**$^{2+}$ is slightly shorter than that bond in **2c**$^{2+}$, but the elongation of the bond connecting the two systems, C9−C9′, compared to that bond in other systems suggests that an additional effect may be operating in that system.

We have suggested that two mechanisms may operate to allow one perpendicular ring system to affect the other.[20,23] In the first, electron density from one system is donated into the π system of the other, σ to p donation.

σ to p donation,
benzene rings not shown for clarity

Evidence for this donation comes from a consideration of the ^{13}C shifts for C_9 of **2d**$^{2+}$, 189 ppm, which are substantially shielded, compared to the same carbon of the fluorenyl monocations, 218−224 ppm. Alternatively, the magnitude of the positive charge on the atom attached to C_9 of the fluorenyl system may act to force greater delocalization of charge in the fluorenyl system. Our discussion to date has focused on delocalization effects, but σ to p donation may also be playing a role. Focusing on the substituted ring systems, the consequences of this interaction would be to decrease the length of the bond connecting the two ring systems, $C_{9-}C_{9'}$, and increase the $C_{9-}C_{10}$ bond length. Those bond lengths are also given in Table 6. A second consequence would be to decrease the magnitude of the ^{13}C NMR shift for C_9, because of the increased electron density at that carbon. We are unable to assess this effect for **2a**$^{2+}$ and **3a**$^{2+}$ because we do not have ^{13}C NMR shift data for **3a**$^{2+}$. The similarities of bond lengths for $C_{9-}C_{9'}$ for **2b**$^{2+}$ and **3b**$^{2+}$ suggest that this effect does not play a major role in these dications. However, comparison of **2c**$^{2+}$ with **3c**$^{2+}$ shows a decrease in the $C_{9-}C_{9'}$ bond length and an increase in the $C_{9-}C_{10}$ bond length for **2c**$^{2+}$, which is consistent with greater σ to p donation. These results from calculated bond lengths receive some experimental validation from the decrease in chemical shift for C_9 of **2c**$^{2+}$ compared to **3c**$^{2+}$, 186.0 ppm (**2c**$^{2+}$) vs 188.7 ppm.

Finally, the HOMO/LUMO gap for an antiaromatic species should be smaller than for an aromatic species and has been used to evaluate relative antiaromaticity.[45]

TABLE 7. Calculated Total Energies for 2^{2+} and 3^{2+}, Singlets and Triplets, and the HOMO/LUMO Gap[a]

	singlet energy	triplet energy	energy difference		HOMO/LUMO gap
			hartrees	kcal/mol	
2a^{2+}	−1078.4536	−1078.4482	−0.0054	−3.4	0.0490
2b^{2+}	−1918.9814	−1918.9795	−0.0019	−1.2	0.0426
2c^{2+}	−1198.2573	−1198.2546	−0.0028	−1.7	0.0486
2d^{2+}	−999.8094	−999.7806	−0.0288	−18.1	0.0622
3a^{2+}	−1078.4631	−1078.4455	−0.0176	−11.0	0.0581
3b^{2+}	−1918.9959	−1918.9744	−0.0215	−13.5	0.0602
3c^{2+}	−1198.2726	−1198.2547	−0.0180	−11.3	0.0639

[a] Geometries optimized with B3LYP/6-31G(d) and UB3LYP/6-31G(d), respectively.

Particularly in the highly rigid benzenoid skeleton of polycyclic aromatic compounds, which enforces planarity in the fused ring systems and the relative lack of bond length alternation shown in the calculated geometries, the lack of geometrical distortion should lead to a perturbance of a triplet configuration to the singlet ground state as the excited triplet lies closer to the ground state configuration. We have calculated the difference in energy between the singlet and triplets of these dications, and those results are given in Table 7. As expected, the singlet is lower in energy than the triplet for all dications. However, there is a dramatic decrease in the singlet/triplet energy gap for the 2,7-disubstituted dications, supporting the suggestion of greater antiaromaticity in these dications. The calculated HOMO/LUMO gap is also reasonably consistent with the singlet/triplet gap. Again, the smaller HOMO/LUMO gap for the 2,7-disubstituted dications supports their greater antiaromaticity. The increase in triplet character should be visible experimentally as a broadening of the NMR signal. While broadening of an NMR signal can result from a variety of sources, a comparison of the ^{1}H NMR spectrum of **2c**$^{2+}$ with **3c**$^{2+}$ shown in Figure 2 is consistent with the calculated NICS values and experimental proton shifts.[46]

Conclusion. The antiaromaticity of substituted dications of tetrabenzo[5.5]fulvalenes was evaluated experimentally through the paratropicity of their ^{1}H NMR shifts and through NICS calculations. The antiaromaticity of these dications can be adjusted through the position of the substituent. Fluorenyl cations with substituents in the 2,7-positions demonstrate greater antiaromaticity for the substituted ring system than do fluorenyl cations with substituents in the 3,6-positions. Substituents in the 3,6-positions fix the delocalization of the positive charge to the benzylic system, while delocalization in the 2,7-disubstituted fulvalenes dications occurs throughout the entire fluorenyl system, resulting in the increase in antiaromaticity. Neither the nature of the substituent nor its position causes much change in the antiaromaticity of the unsubstituted fluorenyl cationic system.

Experimental Section

General Methods. ^{1}H, ^{13}C, COSY, and HETCOR NMR spectra were recorded on a 400 MHz instrument. ^{1}H and ^{13}C

(45) Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *Tetrahedron* **1985**, *41*, 785−791.
(46) Shenhar, R.; Beust, R.; Hagen, S.; Bronstein, H. E.; Willner, I.; Scott, L. T.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* **2002**, 449−454.

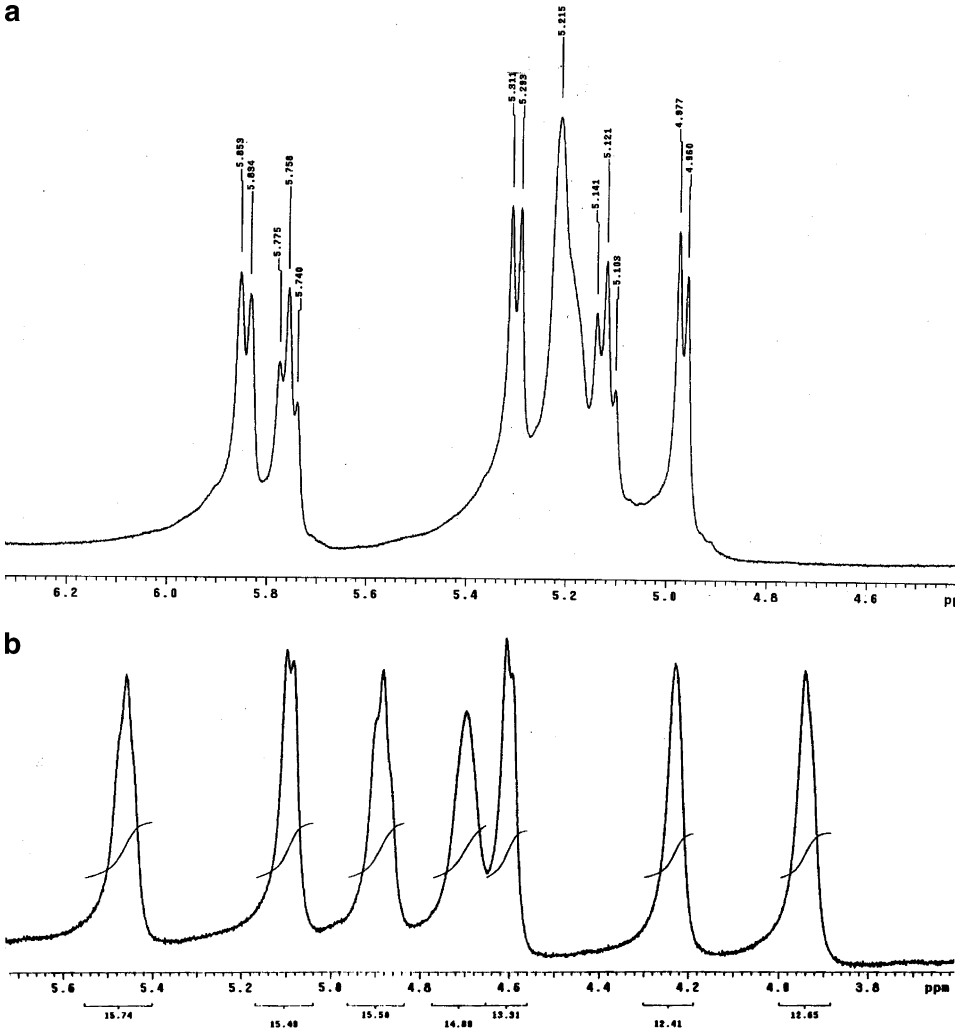


FIGURE 2. (a) ^{1}H spectrum of $\mathbf{3c}^{2+}$. (b) ^{1}H spectrum of $\mathbf{2c}^{2+}$.

NMR spectra of neutral compounds were obtained in $CDCl_3$, and chemical shifts are expressed in parts per million (δ) relative to internal TMS. ^{19}F NMR were recorded at 376.5 MHz using $CDCl_3$ as a solvent and $CFCl_3$ as external standard δ = 0 ppm. Dication spectra were referenced to external acetone-d_6. Purification of reagents and solvents was effected according to standard methods.[47] All extracts were dried ($MgSO_4$) prior to concentration under reduced pressure. Elemental analyses were performed by Desert Analytics in Tucson, AZ.

Synthesis of 3a, 3b. Ethyl 2-(4-methylphenyl)-2-ketoacetate (4a). Following the procedure of Creary et al.,[48] a solution of 4-bromotoluene (6.10 g, 36.0 mmol) in 45 mL of ether was added to Mg (1.10 g, 45.2 mmol) in 20 mL under argon and allowed to react for 30 min. The Grignard solution was cooled to −78 °C and added by cannula to a solution of diethyl oxalate (4.8 mL, 36 mmol) in 75 mL of ether at −78 °C. The reaction mixture was stirred for 2 h and then at 0 °C for 2 h. The reaction was quenched with 50 mL of saturated NH_4Cl solution and extracted with 10% HCl, distilled water, and saturated NaCl. The organic layer was dried and the solvent removed under vacuum, giving a yellow oil, **4a** (5.38 g, crude yield, 83%).

^{1}H NMR ($CDCl_3$): δ 1.42 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 4.45 (q, J = 7.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H).

4b[49] was prepared in analogous fashion (yield 67%).

^{1}H NMR (400 MHz,$CDCl_3$): δ 1.42 (t, J = 7.0 Hz, 3H), 4.45 (q, J = 7.1 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.1 Hz, 2H).

Ethyl 2,2-Bis(4-methylphenyl)-2-hydroxyacetate (5a).[50] To 1.23 g of Mg (42.3 mmol) in 30 mL of ether was added 4-bromotoluene (7.32 g, 42.3 mmol) in 50 mL of ether, and the mixture stirred for 1 h at room temperature. The Grignard reagent was added by Teflon cannula to 6.02 g of **4a** (31.3 mmol) in 50 mL of ether at −78 °C. The reaction mixture was stirred for 5 h in the temperature range −78 to 0 °C. The reaction was quenched with 50 mL of NH_4Cl and the aqueous layer was extracted with ether twice. The combined organic layers were dried and solvent removed under vacuum, giving a yellow oil (4.88 g, yield 88%).^{1}H NMR ($CDCl_3$): δ 1.27 (t, J = 7.2 Hz, 3H), 1.58 (bs, 1H), 2.36 (s, 6H), 4.31 (q, J = 7.2 Hz, 2H), 7.14 (d, J = 8.4 Hz, 4H), 7.31 (d, J = 8.4 Hz, 4H).

^{13}C NMR ($CDCl_3$): δ 14.02, 21.06, 62.78, 80.66, 127.29, 128.72, 137.65, 139.32, 174.68.

5b[50] was prepared analogously (crude yield 88%).^{1}H NMR ($CDCl_3$): δ 1.25 (t, J = 7.2 Hz, 3H), 4.25 (bs, 1H), 4.36 (q, J = 7.2 Hz, 2H), 7.28−7.38 (m, 8H).

3,6-Dimethyl-9-carboxethoxyfluorene (6a). To polyphosphoric acid (77.5 g) at 75 °C was added 10 mL of phosphoric acid. To this mixture of acids was added hydroxy ester **5a**

(47) Perrin, D. D.; Armarego, W. F. L.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1980.
(48) Creary, X. *J. Org. Chem.* **1987**, *52*, 5026−5030.
(49) Nimitz, J. S.; Mosher, H. S. *J. Org. Chem.* **1981**, *46*, 211−213.
(50) von Voegtli, W.; Lauger, P. *Helv. Chim. Acta* **1955**, *38*, 46−69.

(0.428 g, 1.51 mmol), giving a deep red solution that became purple within 5 min. The reaction was stirred at 75−80 °C for 1 h, during which time the color faded. The reaction mixture was poured into 300 mL of ice and extracted with CH_2Cl_2, which was washed with an equal volume of water and with saturated NaCl solution. After drying with $MgSO_4$, solvent was removed under vacuum, giving 3.129 g of a yellow/brown oil (crude yield, 0.388 g, 97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, J = 7.0 Hz, 3H), 2.43 (s, 6H), 4.19 (q, J = 7.1 Hz, 2H), 5.24 (s, 1H), 7.12 (dd, J = 7.6, 1.0 Hz, 2H), 7.51 (d, J = 8.0, 2H), 7.53 (bs, 2H).

3,6-Dichloro-9-carboxethoxyfluorene (6b). Hydroxy ester **5b** (4.88 g, 15 mmol) was dissolved in 24 mL of acetic acid. Concentrated H_2SO_4 (50 mL, 900 mmol) was added dropwise, with every drop creating a deep maroon color until all the solution became deep maroon. The reaction was stirred at room temperate for 5 h, with the color deepening to dark brown. The reaction mixture was poured into ice, extracted with CH_2Cl_2, and washed with water, 10% $NaHCO_3$, and again with water. After drying with $MgSO_4$, solvent was removed under vacuum, giving 3.13 g of an orange red oil (crude yield, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, J = 7.0 Hz, 3H), 4.18 (q, J = 7.1 Hz, 2H), 4.79 (s, 1H), 7.34 (dd, J = 8.0, 2.0 Hz, 2H), 7.59 (d, J = 8.0, 2H), 7.68 (d, J = 2 Hz, 2H).

3,6-Dimethyl-9*H*-fluorenone (8a).[51] Fluorene ester **6a** (0.388 g, 1.46 mmol) was refluxed in 15 mL of 2-propanol and 0.250 g (4.46 mmol) of KOH for 75 min. The reaction was cooled and O_2 was bubbled through the solution for 2.5 h to oxidize the fluorene **7a**. Methylene chloride was then added to increase the reaction volume to 50 mL, and the reaction mixture was extracted with water and with saturated NaCl. The organic phase was passed through a short column of alumnia and dried, and the solvent was removed under vaccum, giving a yellow solid (0.271 g, crude yield 89%). The product was purified on silica with hexanes and ethyl acetate (yield, 0.086 g, 28%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 6H), 7.08(d, J = 7.7 Hz, 2H), 7.31 (s, 2H), 7.53 (d, J = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 22.06, 121.00, 124.05, 129.39, 132.36, 144.64, 145.39, 193.27.

3,6-Dichloro-9*H*-fluorene (7b). Fluorene ester **6b** (3.120 g, 10 mmol) was refluxed with 70 mL of distilled water and 0.672 g (12 mmol) of KOH for 5 h. The cooled reaction mixture was extracted with 3 × 50 mL of CH_2Cl_2. Then 20% HCl (50 mL) was added to the aqueous layer, which was extracted with 2 × 50 mL of CH_2Cl_2. The combined organic layers were dried, and the solvent was removed under vacuum. Column chromatography of the crude product on silica gel with petroleum ether/CH_2Cl_2 (98:2) yielded 0.295 g of a white solid (12%).

^{1}H NMR ($CDCl_3$): δ 3.80 (s, 2H), 7.29 (dd, J = 8.0, 2.0, 2H), 7.45 (d, J = 8.0, 2H), 7.70 (d, J = 2.0, 2H).

3,6-Dichloro-9*H*-fluoren-9-one (8b).[52] To fluorene **7b** (0.865 g, 3.68 mmol) in 20 mL of benzene was added 0.45 g of KOH (8.0 mmol) and 18-crown-6 (0.050 g, 0.49 mmol). After the solution became light purple, oxygen was bubbled into the reaction mixture overnight, giving a yellow, insoluble solid. The solid was dissolved three times in a 1:1 mixture of hot benzene and CH_2Cl_2 and filtered hot, giving 0.270 g yellow crystals (29% yield).

^{1}H NMR ($CDCl_3$): δ 7.32 (d, J = 8, 1.6 Hz, 2H), 7.45 (d, J = 1.6 Hz, 2H), 7.70 (d, J = 8 Hz, 2H).

3,6-Dimethyltetrabenzo[5.5]fulvalene (3a). To 9-trimethylsilylfluorene (0.207 g, 0.870 mmol) in 10 mL of THF at −78 °C under nitrogen was added 1.0 mL of *n*-butyllithium (1.6 mmol, 1.6 M in hexanes). After 10 min, the reaction was warmed to 0 °C and stirred for 2 h. The reaction mixture was cooled again to −78 °C and the ketone **8a** (0.171 g, 0.820 mmol) in 10 mL of THF was added. The reaction mixture was allowed to warm to room temperature and stir overnight. The reaction mixture was quenched with 50 mL of 10% HCl solution and ether was added to increase the volume of the organic phase to 100 mL. The organic layer was extracted with 10% HCl, water, and saturated NaCl. Removal of solvent under vacuum gave a reddish orange solid that was purified by chromatography on silica gel with hexanes, giving 0.260 g of a red powder (purified yield, 0.098 g, 33%). Mp: 176−180 °C. Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 93.73; H, 6.27.

^{1}H NMR ($CDCl_3$): δ 7.01 (d, J = 6.4 Hz, $H_{2'}$, $H_{7'}$), 7.21 (d, J = 8.0 Hz, H_2, H_7), 7.31 (t, J = 7.4 Hz, $H_{3'}$, $H_{6'}$), 7.48 (s, H_4, H_5), 7.71 (d, J = 7.2 Hz, $H_{4'}$, $H_{5'}$), 8.26 (d, J = 7.9 Hz, $H_{1'}$, $H_{8'}$), 8.37 (d, J = 8.4 Hz, H_1, H_8). ^{13}C NMR ($CDCl_3$): δ 120.12 ($C_{4'}$, $C_{5'}$), 120.32 (C_4, C_5), 126.73 ($C_{1'}$, $C_{8'}$), 127.08 ($C_{2'}$, $C_{7'}$), 127.35 (C_2, C_7), 127.50 (C_1,C_8), 129.70 ($C_{3'}$, $C_{6'}$), 134.93, 136.75, 137.89, 138.23, 141.40, 141.56.

3,6 Dichlorotetrabenzo[5.5]fulvalene (3b). To 9-trimethylsilylfluorene (0.260 g, 1.1 mmol) in 20 mL of THF at −78 °C under nitrogen was added 1.375 mL of *n*-butyllithium (2.2 mmol, 1.6 M in hexanes). After 0.5 h the reaction was warmed to 0 °C and stirred for 2 h. The reaction mixture was cooled again to −78 °C and the ketone **8b** (0.273 g, 1.1 mmol) in 10 mL of THF was added after 10 min. After 0.5 h the reaction warmed to 0 °C and was stirred overnight. The deep red reaction mixture was quenched with 50 mL of saturated NH_4Cl solution and extracted with ether. Trituration with hot ethanol gave 0.317 g of the desired compound, which was purified by chromatography on silica gel with petroleum ether/CH_2Cl_2 (98:2), giving 0.260 g of a red powder (65%). Mp: 266−268 °C. Anal. Calcd for $C_{28}H_{18}Cl_2$: C, 78.60; H, 3.55; Cl, 17.85. Found: C, 78.27; H, 3.55; Cl, 18.18.

^{1}H NMR ($CDCl_3$): δ 7.19 (d, $H_{2'}$, $H_{7'}$), 7.20 (d, H_2, H_7), 7.34 (t, J = 8.0 Hz, $H_{3'}$, $H_{6'}$), 7.63 (d,J = 1.6 Hz, H_4, H_5), 7.68 (d, J = 7.2 Hz, $H_{4'}$, $H_{5'}$), 8.23 (d, J = 7.9 Hz, $H_{1'}$, $H_{8'}$), 8.29 (d, J = 8.4 Hz, H_1, H_8). ^{13}C NMR ($CDCl_3$): δ 120.12 ($C_{4'}$, $C_{5'}$), 120.32 (C_4, C_5) 126.73 ($C_{1'}$, $C_{8'}$), 127.08 ($C_{2'}$, $C_{7'}$), 127.35 (C_2, C_7), 127.50 (C_1,C_8), 129.70 ($C_{3'}$, $C_{6'}$), 134.93, 136.75, 137.89, 138.23, 141.40, 141.56.

Synthesis of 3c. Benzophenone 9a and 9b. The Friedel−Crafts reaction was performed according to the literature method.[53−55] To 1-bromo-3-fluorobenzene (12 mL, 109 mmol) at 0 °C was added 4-fluorobenzoyl chloride (1.036 mL, 8.64 mmol) followed by 0.63 g of $AlCl_3$ (4.75 mmol) after 15 min. The reaction mixture was warmed to room temperature after 10 min, stirred for 15 min, refluxed for 4 h, and then stirred overnight. The reaction mixture was added to 100 g of ice and 5 mL of concentrated HCl. The organic phases were extracted with CH_2Cl_2, and the solvent was removed under vaccum, giving a brown oil (2.30 g, yield 89%). NMR showed the two isomers in the ratio of 1:1.

9a ^{19}F NMR ($CDCl_3$, $CFCl_3$ = 0.0 ppm): 24.74, 29.07 ppm.

9b, ^{19}F NMR ($CDCl_3$, $CFCl_3$ = 0.0 ppm): 24.36, 28.70 ppm.

3,6-Difluoro-9*H*-fluoren-9-one (8c). The palladium coupling reaction was performed according to the literature method.[30] Dimethylacetamide (DMA, 10 mL) was added to the mixture of **9a**/**9b**, (2.296 g, 7.73 mmol), along with Na_2CO_3 (0.699 g) and $Pd(OAc)_2$ (0.136 g, 0.606 mmol), and the reaction refluxed for 2.5 h. After the mixture cooled to room temperature, water was added and a precipitate was obtained. The precipitate was isolated by filtration and mixed with silica gel for chromatography on silica gel with a petroleum ether/CH_2Cl_2 gradient (10−40%). The fraction that came in 30−40% CH_2Cl_2 was the ketone. Removal of solvent under vacuum gave light yellow crystals [0.337 g, 20% yield (based on half of the mixture **9a** and **9b**)]. Mp: 250−252 °C.[56] ^{1}H NMR: δ 7.00 (dt, J = 8.2 Hz, J = 2.2 Hz), 7.18 (dd, J = 8.2 Hz, J = 2.2 Hz) 7.66 (dd, J = 8.2 Hz, J = 5.2 Hz).

(51) Chardonnens, L.; Wurmli, A. *Helv. Chim. Acta* **1946**, *29*, 922−928.

(52) Guinot, S. G. R.; Hepworth, J. D.; Wainwright, M. *J. Chem. Res. Syn* **1997**, 183.

(53) US Patent No. 3,475.

(54) US Patent No. 3,959,475, 1976.

(55) PCT Int. Appl. 2000, WO00/3163, p 36−37.

(56) Balasubramanian, N.; Brown, P. J.; Parker, R. A.; Wright, J. J. *Bioorg, Med. Chem. Lett.* **1992**, *2*, 99−104.

^{13}C NMR: δ 108.74 (J = 24.4 Hz), 116.25 (J = 23.2 Hz), 126.45 (J = 10.3 Hz), 145.84 (J = 10.4 Hz), 167.20 (J = 351.7 Hz), 190.29. ^{19}F NMR ($CDCl_3$, $CFCl_3$ = 0.0 ppm): 30.11 ppm.

3,6-Difluorotetrabenzo[5.5]fulvalene, **3c.** The reaction was carried out analogously to the preparation of **3a** and **3b**. The desired compound **3c** was obtained as red powder (0.307 g, yield 88%). Purification by column chromatography on silica gel with petroleum ether gave 0.271 g (78%). Mp: 239−245 °C. Anal. Calcd for $C_{28}H_{18}F_2$: C, 85.70; H, 3.88; F, 10.42. Found: C, 85.33; H, 4.00; F, 10.49.

^{1}H NMR ($CDCl_3$): δ 6.92 (td, J = 8.7 Hz, J = 2.4 Hz, H_2, H_7), 7.19 (dt, J = 7.7 Hz, $H_{2'}$, $H_{7'}$), 7.315−7.326 (m, H_4, H_5, $H_{3'}$, $H_{6'}$), 7.68 (d, J = 7.5 Hz, $H_{4'}$, $H_{5'}$), 8.24 (d, J = 7.5 Hz, $H_{1'}$, $H_{8'}$), 8.31 (dd, J = 7.5 Hz, 5.4 Hz, H_1, H_8). ^{13}C NMR ($CDCl_3$): δ 107.16, 114.41, 120.04, 126.53, 126.96, 128.2, 129.13, 129.30, 134.82, 137.99, 138.23, 141.30, 142.30, 163.52.

^{19}F NMR ($CDCl_3$, $CFCl_3$ = 0.0 ppm): 21.77 ppm.

Dication Preparation. 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[57] (1.3 mL, 17.8 mmol) at −78 °C was transferred in 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 (∼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 a chilled 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.

Calculational Methods. Geometries were optimized at B3LYP/6-31G(d) density functional theory level for singlets and the UB3LYP/6-31G(d) level for triplets with the Gaussian 98 program package.[58] Stability calculations for the singlets of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ were done at the B3LYP/6-31G(d) level and showed that that singlet wave functions were stable. The nucleus-independent chemical shifts 1 Å above the ring centers were calculated at B3LYP/6-31G(d) using the GIAO approach with the Gaussian 98 program package.

Acknowledgment. We gratefully acknowledge the Welch Foundation (Grant 794) and the National Science Foundation (CHE-9820176, REU site) for their support of this work.

Supporting Information Available: Tables of ^{13}C NMR data for $\mathbf{2}^{2+}$, $\mathbf{3b,c}^{2+}$, experimental and calculated; ratios of calculated and experimental ^{1}H NMR shifts; Cartesian coordinates and zero point energies for singlets and triplets of $\mathbf{2}^{2+}$, $\mathbf{3}^{3+}$; HOMO and LUMO energies for the singlets of $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$; experimental spectra for $\mathbf{3a}^{2+}$ (^{1}H), $\mathbf{3b}^{2+}$ (^{1}H/^{13}C), $\mathbf{3c}^{2+}$ (^{1}H/^{13}C), and **3** (^{1}H/^{13}C); preparation of SO_2ClF. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026924H

(57) Reddy, V. P.; Bellew, D. R.; Prakash, G. K. S. *J. Fluorine Chem.* **1992**, *56*, 195−197.

(58) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98,* A.7 ed.; Gaussian, Inc.: Pittsburgh, PA, 1998.