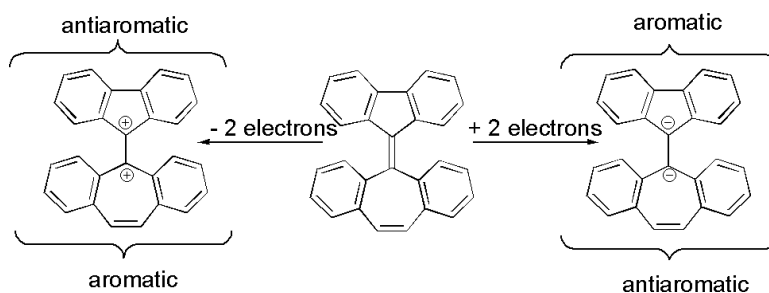**Article**

Dianion and Dication of Tetrabenzo[5.7]fulvalene. Greater Antiaromaticity than Aromaticity in Comparable Systems

Ashley M. Piekarski, Nancy S. Mills, and Abraham Yousef

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Dianion and Dication of Tetrabenzo[5.7]fulvalene. Greater Antiaromaticity than Aromaticity in Comparable Systems

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Abstract: The dianion, 5^{2-}, and dication, 5^{2+}, of tetrabenzo[5.7]fulvalene represent an aromaticity/antiaromaticity continuum in which the fluorenyl system changes from aromatic in 5^{2-} to antiaromatic in 5^{2+}. Conversely, the antiaromatic dibenzotropylium system of 5^{2-} becomes an aromatic system in 5^{2+}, allowing an examination of aromaticity/antiaromaticity within the same carbon framework. Dianion 5^{2-} was prepared and characterized by ^1H NMR spectroscopy. The fluorenyl system of 5^{2-} showed the downfield shifts expected for an aromatic system, while the dibenzotropylium system showed the paratropic shifts expected for an antiaromatic system. The conclusions from ^1H NMR spectroscopy were supported by NICS(1)$_{zz}$ calculations for each system. Comparison of the ^1H NMR spectrum and NICS(1)$_{zz}$ of 5^{2-} with those of 5^{2+} supported the assignments of aromaticity/antiaromaticity for each system. Aromaticity/antiaromaticity were further examined through comparison of the degree of bond length alternation, which showed that the bond length alternation was slightly greater for the antiaromatic ring systems than for the aromatic systems. However, when structures of 5^{2-} and 5^{2+} with no bond length alternation were examined, there was a dramatic increase in the degree of antiaromaticity for the antiaromatic ring systems as evaluated through NICS. This result suggests that a decrease in bond length alternation results in an increase in antiaromaticity as well as an increase in aromaticity. The magnitude of the antiaromaticity of the fluorenyl system in 5^{2+} was greater than the magnitude of the aromaticity in the fluorenyl system of 5^{2-}, with similar effects shown by the analogous tropylium systems. This is consistent with the behavior of the antiaromatic dication of tetrabenzo[5.5]fulvalene, compared to that of its aromatic dianion, and also with the behavior of the cyclopentadienyl cation/anion and tropylium cation/anion.

Introduction

The continuing intense interest in aromaticity[1-10] demonstrates the central nature of the concept in organic chemistry.[11] The primary controversy in the area involves the questions of whether aromaticity can be quantified and, if so, which of the methods commonly used to evaluate aromaticity is most appropriate.[7] We have entered this field through our work with antiaromatic dications, with the intent of using antiaromatic

species to probe the limits of those methods.[12-24] Aromaticity is often manifested within a very small range of values for conjugated cyclic hydrocarbons, i.e., ~6.9-9.0 ppm for ^1H NMR shifts for neutral species. Inclusion of ionic species can expand the range to 10.13 ppm for some dications[25] and 5.73 ppm for the dilithiated cyclooctatetraene in tetrahydrofuran

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(THF).[26] The inclusion of charged antiaromatic species substantially increases the range to 4.97 ppm for the dication of tetrabenzo[5.5]fulvalene[12] and 2.58 ppm for the dianion of tetrabenzo[5.7]fulvalene, *vide infra*. There has been limited use of antiaromatic species to explore aromaticity because the stability of these species has precluded experimental characterization. However, the antiaromatic dications we have examined, shown below as **1** and **2**, are much more stable than previously assumed. Part of their stability may be due to the fact that, as charged species, they are much less susceptible to dimerization.
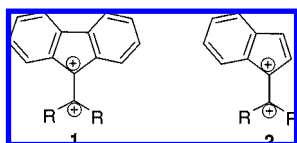

We have documented the antiaromaticity of **1** by using redox potentials to demonstrate the diminished stability of **1** compared to a non-antiaromatic reference system.[17,21] Calculated values of nucleus-independent chemical shifts (NICS) and magnetic susceptibility exaltation, Λ, also support the categorization of the fluorenyl system of **1** and the indenyl system of **2** as antiaromatic.[16−20,22,23] We have demonstrated paratropic ^{1}H NMR shifts for derivatives of **1** and **2** and have used these experimental shifts to document the reliability of calculated ^{1}H NMR shifts.[17,19,21,23] The ability to evaluate the quality of calculated properties through comparison with experimental ones gives additional validity to calculated properties such as NICS.[24]

We became involved in the preparation of dianions while exploring the aromaticity/antiaromaticity continuum of the dications and dianions of tetrabenzo[5.5]fulvalene (**3**).[22] The properties of **3^{2-}**, generally agreed to be aromatic, provided a context for the properties of **3^{2+}**. By all measures examined, **3^{2+}** was slightly more antiaromatic than **3^{2-}** was aromatic, which we had not anticipated. This result raised several questions: Was the enhanced antiaromaticity a result of the dicationic nature of **3^{2+}**? Did the dication possess more effective delocalization which then enhanced the antiaromaticity of the species, and is this more prevalent in dications rather than dianions? Does more effective delocalization result in greater antiaromaticity as well as greater aromaticity?
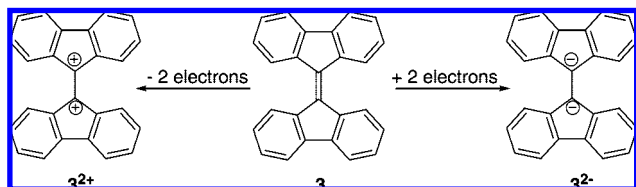
To attempt to answer these questions, we examined the preparation of the dianion of tetrabenzo[5.7]fulvalene (**5^{2-}**), whose properties we describe in this paper. The comparison of the properties of **5^{2-}** with those of **5^{2+}**, which we had prepared previously,[12,13,20] would form a new "aromaticity/antiaromaticity continuum", in which both the fluorenyl and dibenzotropylium systems could be "toggled" back and forth between aromaticity and antiaromaticity through oxidation/reduction (Scheme 1). This redox switch occurs within the same carbon framework, so we can examine the nature of aromaticity and antiaromaticity

Scheme 1. Aromaticity/Antiaromaticity for **5^{2+}** and **5^{2-}**
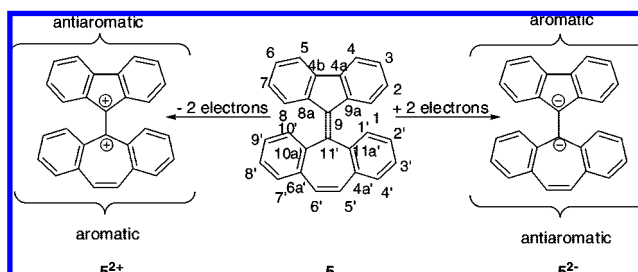
as a function of charge, with minimal changes to the geometry of the species. The extent of delocalization can be probed through the amount of bond length alternation in the optimized geometry.[9,27−29]

The evaluation of the aromaticity/antiaromaticity of **5^{2-}/5^{2+}** is challenging because examination of typical properties that reflect the aromaticity of an entire species would not give an accurate depiction of the aromaticity/antiaromaticity of individual ring systems. Thus, evaluation of stability through experimental determination of stability, calculation of aromatic stabilization energies,[30] or examination of magnetic susceptibility exaltation, Λ, all of which examine the entire system, would be fruitless. The methods that are suitable to probe local aromaticity include ^{1}H NMR chemical shifts,[8] NICS,[31] calculated current density maps,[32−35] and the harmonic oscillator measure of aromaticity (HOMA).[9,27−29] These measures all have some shortcomings. ^{1}H NMR chemical shifts are the traditional magnetic measure of aromaticity, but because the chemical shift is affected by factors other than ring current, its direct relationship to aromaticity measurements has been recently questioned.[2,3] Current density maps show the direction of the circulation of electron density, indicating aromatic or antiaromatic ring currents, but normally do not provide quantitative information. We have found that the HOMA method was less sensitive than other measures,[17] and therefore less indicative of the degree of aromaticity.

NICS values result from the calculated magnetic shielding tensor for a "dummy" atom located in the middle of the ring system under examination.[31] Modifications in the calculation of NICS include positioning the dummy atom 1 Å above the plane of the ring to avoid interaction with the electrons of the σ-system, NICS(1),[36,37] and using only the component of the tensor perpendicular to the plane of the ring system, NICS(1)$_{zz}$.[1,38] However, the use of NICS has been controversial because there is no experimental analogue that can be used to

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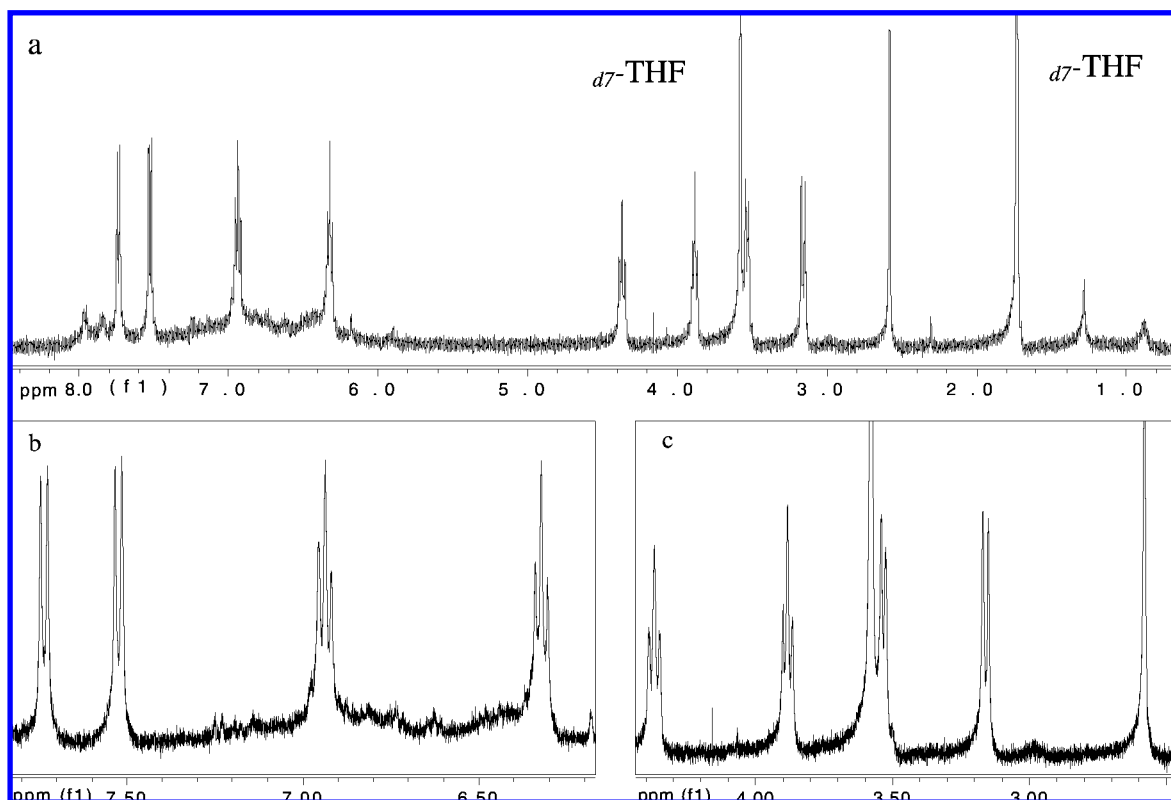
Figure 1. ^{1}H NMR spectrum of 5^{2-} in THF-d_8: (a) full spectrum, (b) downfield region showing the fluorenyl system, and (c) upfield region showing the dibenzotropylium system.

validate the calculated values.[5] NICS values reflect local aromaticity because magnetic shielding is proportional to the inverse third power of the distance of the electrons from the probe, but the NICS values may also include contributions from adjacent ring systems.[39,40] We have recently examined the relationship between the summation of NICS$(1)_{zz}$ and Λ for a diverse group of aromatic and antiaromatic neutral and charged species.[24] Magnetic susceptibility exaltation is known to be related to the square of the ring area,[41] and we showed an excellent correlation between $\sum$NICS$(1)_{zz}$/ring area^2 and Λ/ring area^2, which suggests that NICS can be summed as a reliable measure of aromaticity in a polycyclic system. That is, the contributions to NICS from the ring currents of adjacent ring systems are negligible. The excellent correlation between ^{13}C NMR shifts calculated by the same method used to calculate NICS and the experimental shifts for a variety of species also provides support for the use of NICS as an accurate measure of aromaticity/antiaromaticity. The bottom line, however, is that aromaticity/antiaromaticity is most reliably evaluated using a variety of criteria, including both experimental and calculated values. We have approached the examination of the aromaticity/antiaromaticity of the dianions and dications of tetrabenzo[5.7]-fulvalene from this vantage point.

Results and Discussion

Spectral Evidence for Formation of 5^{2-}. The ^{1}H NMR spectrum of the dianion that resulted from treatment of tetrabenzo[5.7]fulvalene (**5**) with lithium, according to the

Table 1. Experimental and Calculated^a ^{1}H NMR Shifts for 5^{2-}

protons	experimental shifts,^{b} ppm	multiplicity and coupling constants, Hz	shifts calculated without lithium counterions, ppm	shifts calculated with lithium counterions,^{c} ppm
1,8	7.736	d, 7.22	8.759, 8.758	7.563, 8.614
2,7	6.936	d, 7.45	6.921	7.248, 7.592
3,6	6.323	t, 6.79	6.007	7.042, 6.971
4,5	7.524	t, 8.07	7.545	8.288, 8.493
1′,10′	3.158	d, 8.62	1.273, 1.283	5.022, 6.204
2′,9′	4.368	t, 7.91	2.780, 2.783	5.992, 6.227
3′,8′	3.881	d, 6.87	2.426, 2.433	5.722, 5.858
4′,7′	3.532	t, 7.08	1.384, 1.391	5.429, 6.355
5′,6′	2.581	NA	0.226, 0.230	5.493, 5.898

^{a} Shifts calculated using the GIAO method with the B3LYP/6-311+g(d,p) basis set on geometries optimized using the B3LYP/6-31g(d) basis set. ^{b} Spectra taken at -10 °C, referenced to THF-d_8, upfield protons, 1.727 ppm. ^{c} The calculation gives a geometry that is effectively frozen, as opposed to the averaged values for these protons seen in the experimental spectra which have nuclear motion at -10 °C.

method of Rabinovitz and Scott,[42] is shown in Figure 1, with the experimental and calculated shifts in Table 1. The proton assignments were made by a combination of COSY spectroscopy and comparison with calculated shifts. We were unable to obtain the ^{13}C NMR spectrum, which then meant that we were unable to obtain the HETCOR data that would allow us to make complete assignments through experimental data alone. The spectrum clearly shows the diatropic shifts expected for the aromatic fluorenyl system and the paratropic shifts of the antiaromatic dibenzotropylium system.

The relationship between the experimental ^{1}H NMR shifts and the shifts calculated with and without lithium counterions

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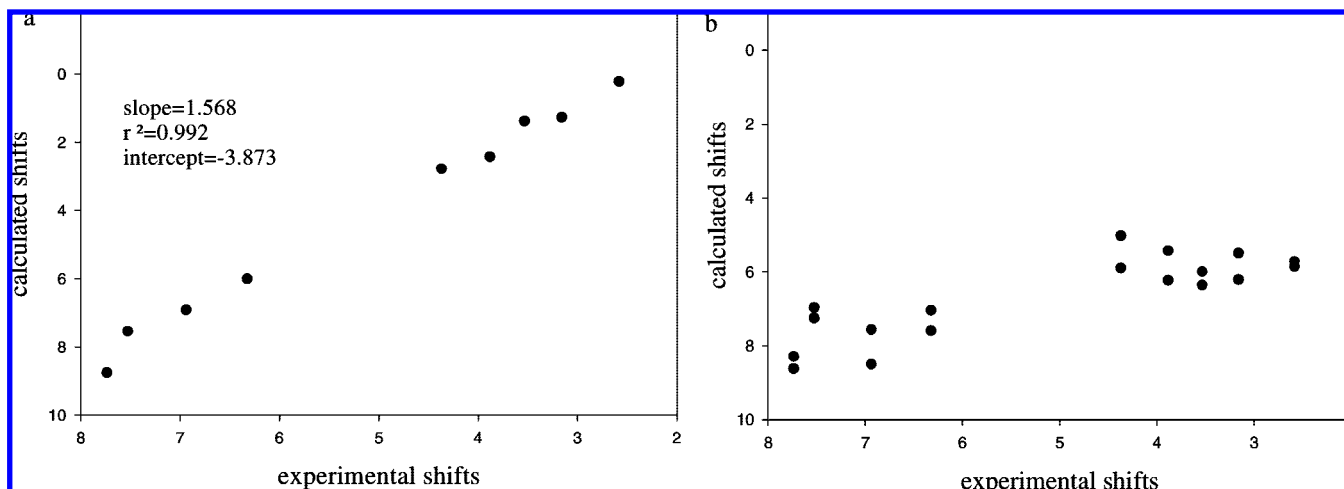
Figure 2. Calculated vs experimental ^{1}H NMR shifts for 5^{2-}. (a) Shifts calculated without lithium counterions. (b) Shifts calculated with lithium counterions. Shifts were calculated with the GIAO method at B3LYP/6-311+g(d,p) on geometries optimized at the B3LYP/6-31g(d) level. Optimized geometries available in the Supporting Information.
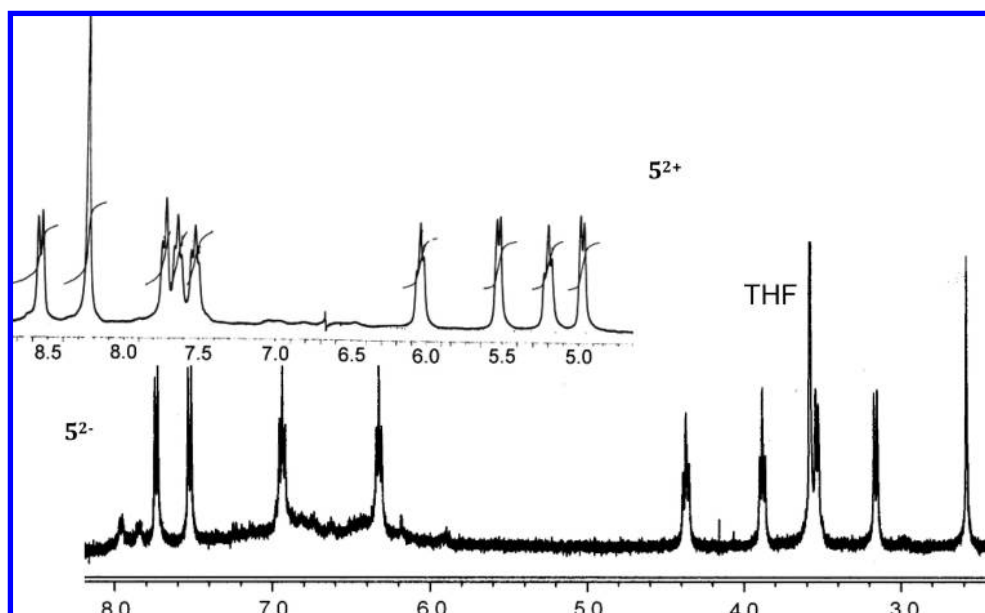

Figure 3. Comparison of ^{1}H NMR shifts for 5^{2+} and 5^{2-}. THF-d_7 is visible as a singlet at ~3.6 ppm.

is shown in Figure 2. It is apparent that the agreement is much better with the chemical shifts calculated without lithium counterions, suggesting that the association between the lithium counterions and the anionic systems is very weak. We also compared the experimental ^{1}H NMR shifts of dilithiated 3^{2-} with the NMR shifts calculated with and without lithium counterions, to demonstrate that the agreement shown in Figure 2a was not limited to 5^{2-}. The agreement between experimental shifts and those calculated without lithium counterions for 3^{2-} and 5^{2-} is almost as good, $r^2 = 0.982$, as that for 5^{2-} alone (see Supporting Information), while that with the inclusion of lithium counterions is substantially worse. There are no literature reports of contact ion pairs for lithiated 3^{2-}, but the related lithiated fluorene has been shown to exist as a solvent-separated ion pair in THF at ambient and lower temperatures.[43] We therefore have calculated other values for 5^{2-} without the inclusion of lithium counterions, *vide infra*.

Comparison of 5^{2-} with 5^{2+}. a. ^{1}H NMR Shifts. Figure 3 shows a comparison of the change in the ^{1}H NMR chemical shifts of **5** when oxidized to 5^{2+} [12,13] and reduced to 5^{2-}. The singlet for protons 5′/6′ are the signature for the dibenzotropylium system. As the figure demonstrates, the dibenzotropylium protons are shifted downfield in 5^{2+}, consistent with development of an aromatic system, while the analogous protons of 5^{2-} show the paratropic shift consistent with an antiaromatic system. The protons of the fluorenyl systems of 5^{2+} and 5^{2-} show the opposite shifts, consistent with the antiaromaticity and aromaticity of the respective species.

The analysis of the shifts is complicated by the charge of each system. The protons of anionic species are shifted upfield because of increased electron density, while those of cationic species are shifted downfield. Thus, anionic systems always

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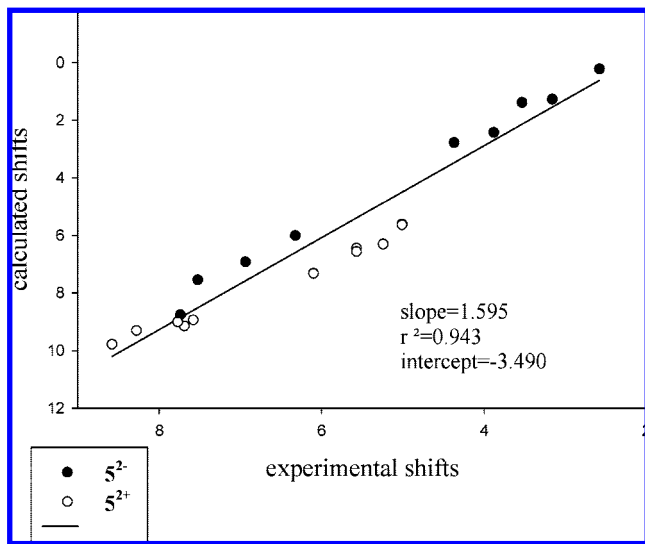
Figure 4. Experimental and calculated shifts for 5^{2-} (●) and 5^{2+} (○). Shifts calculated with the GIAO method at B3LYP/6-311+g(d,p) on geometries optimized at the B3LYP/6-31 g(d) level. No counterions were included in calculations of either 5^{2-} or 5^{2+}.

appear more paratropic/antiaromatic and cationic systems more diatropic/aromatic. It is apparent from Figure 3 that the average chemical shift of 5^{2-} is farther upfield than the average chemical shift of 5^{2+}. Thus, the average chemical shift for the dibenzotropylium system of 5^{2-}, Trop-5^{2-}, suggests greater antiaromaticity because the shifts are farther upfield due to the excess charge on the carbons of the system. At the same time, the apparent aromaticity of the fluorenyl system of 5^{2-}, Fl-5^{2-}, is diminished because the diatropic shift due to the aromatic ring current is affected by the upfield shift due to the increase in electron density in the system. Similarly, the apparent antiaromaticity of Fl-5^{2+} is decreased by the decrease in electron density in the system, while the apparent aromaticity of Trop-5^{2+} is increased. The ^{1}H NMR shifts support the characterization of the ring systems shown in Scheme 1, particularly when the effects of the electron density of the system are taken into account.

The relationship between calculated and experimental ^{1}H NMR shifts is shown in Figure 4 for 5^{2-} and 5^{2+}. While the correlation is not as good as that shown in Figure 2, the calculated shifts are gas-phase values, while the experimental shifts were obtained in solvents with fairly different dielectric constants, THF-d_8 for 5^{2-} and SO$_2$ClF for 5^{2+}. One additional issue in comparing experimental and calculated spectra for 5^{2-} and 5^{2+} is the known temperature dependence for ionic species.[44] Because the spectra were obtained at different temperatures, −50 °C for 5^{2+} and −10 °C for 5^{2-}, it is not surprising that the agreement is poorer for the two species.

b. Nucleus-Independent Chemical Shifts. Table 2 shows the NICS(1)$_{zz}$ values for the ring systems of 5^{2-} and 5^{2+}, with optimized geometries and with geometries with no bond length alternation, *vide infra*. The negative signs of the NICS values for Fl-5^{2-} and Trop-5^{2+} clearly support the conclusions from the experimental ^{1}H NMR data for the aromaticity of each system. Similarly, the positive NICS values support the assignment of Fl-5^{2+} and Trop-5^{2-} as antiaromatic. The excellent quality of the correlation of experimental and calculated ^{1}H

NMR shifts for 5^{2+} and 5^{2-} gives support to the NICS(1)$_{zz}$ values calculated in the same manner.

Effect of Bond Length Alternation on Aromaticity/Antiaromaticity. We began this study to understand why the antiaromaticity of 3^{2+}, as measured by NICS values, was greater than the aromaticity of 3^{2-}. Did the charge type matter? Were dications more effectively delocalized than dianions? What is the relationship between delocalization and aromaticity/antiaromaticity? We felt that an effective probe for this would be the degree of bond length alternation.

We chose to evaluate bond length alternation by using the GEO term of the harmonic oscillator measure of aromaticity.[9,28,29,45] The complete equation, shown below, probes the effect of bond length alternation, the GEO term, and the deviation from optimal bond length, the EN (energetic) term, on aromaticity.

$$\begin{aligned} \text{HOMA} &= 1 - \left[\alpha(R_{opt} - R_{av})^2 + \frac{\alpha}{n}\sum(R_{av} - R_i)^2 \right] \\ &= 1 - \text{EN} - \text{GEO} \end{aligned} \quad (1)$$

For benzene, the bond length alternation and the deviation from the optimal bond length would be zero, and HOMA would be 1; the factor α was chosen so that the HOMA value for a non-aromatic species would be 0. The GEO term sums the square of the difference in bond length of each bond from the average bond length for the system under examination and multiplies it by a ratio of α and the number of bonds in the system, n. The HOMA equation also includes an energetic term (EN) to account for factors that increase the energy of the system, such as deviations from the optimal bond length. We do not include this term because we know that anions are larger than cations, which will inherently affect the EN term. Since we are interested in delocalization, the GEO term, which deals with bond length alternation, is appropriate for this examination.

The GEO terms for each ring and ring system of 5^{2-} and 5^{2+} are shown in Table 3, with the bond lengths tabulated in the Supporting Information. The aromatic systems, Fl-5^{2-} and Trop-5^{2+}, show less bond length alternation—a smaller GEO term—than do the corresponding antiaromatic systems. Antiaromatic systems have been shown to possess greater bond length alternation.[46] The dibenzotropylium systems show greater bond length alternation than do the fluorenyl systems, suggesting more effective delocalization in the fluorenyl systems. *There is no indication of more effective delocalization in cations over anions by this measure.*

Change in Aromaticity/Antiaromaticity as a Function of Bond Length Equalization. While the GEO term shows greater bond length alternation in the antiaromatic systems, the magnitude of that alternation in these systems is similar to that shown in such aromatic species as the external ring of naphthalene (0.245) or of tetracene (0.310).[47,48] The relative lack of bond length alternation for the antiaromatic systems of 5^{2-} and 5^{2+} suggested that both aromatic *and* antiaromatic species might show a lack of bond length alternation. The NICS(1)$_{zz}$ values were calculated for geometries of 5^{2-} and 5^{2+} in which the bond lengths of the fluorenyl and tropylium systems were equal,

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Table 2. NICS(1)$_{zz}$[a] for $\mathbf{5^{2-}}$ and $\mathbf{5^{2+}}$, for the Optimized Geometry and the Geometry with No Bond Length Alternation[b]

	fluorenyl system			dibenzotropylium system			
	5-ring	6-ring	ΣNICS(1)$_{zz}$	7-ring	6-ring	ΣNICS(1)$_{zz}$	total ΣNICS(1)$_{zz}$
$\mathbf{5^{2-}}$, optimized geometry	−35.38	−26.81	−89.00	106.03	38.15	182.33	93.32
equal bond lengths	−35.38	−26.00	−87.38[c]	178.08	82.81	343.71	256.33
$\mathbf{5^{2+}}$, optimized geometry	65.34	21.18	107.70	−21.16	−30.68	−82.52	25.18
equal bond lengths	96.86	38.44	173.74	−21.10	−31.78	−84.66	89.08

[a] Calculated by the GAIO method, with basis set B3LYP/6-311+g(d,p); using the magnetic shielding tensor perpendicular to the planar ring system, for a dummy atom 1 Å above the plane of the ring. [b] Bond lengths were set to the average bond length of the optimized geometry for each system. [c] See footnote 49.

Table 3. Bond Length Alternation, the GEO Term, for $\mathbf{5^{2--}}$ and $\mathbf{5^{2+}}$ by Ring System[a]

fluorenyl ring system	5-ring	6-ring	entire fluorenyl system
$\mathbf{5^{2-}}$	0.057	0.136	0.120
$\mathbf{5^{2+}}$	0.103	0.090	0.183

| dibenzotropylium system	7-ring	6-ring	entire dibenzotropylium system
$\mathbf{5^{2-}}$	0.405	0.149	0.287
$\mathbf{5^{2+}}$	0.183	0.282	0.199

[a] Bond lengths from geometries optimized at the B3LYP/6-31g(d) level.

GEO = 0. The average bond length was used so that the area of each ring system was basically the same as for the optimized geometry. The results from these calculations are shown in Table 2. The NICS(1)$_{zz}$ values for the aromatic systems, Fl-$\mathbf{5^{2-}}$ and Trop-$\mathbf{5^{2+}}$, showed little change when the geometry was altered from the optimized geometry to that of the symmetrical system.[49] Aromatic systems have been shown to be very resistant to changes in the π-electron structure.[50] However, the change in the antiaromatic systems, Fl-$\mathbf{5^{2+}}$ and Trop-$\mathbf{5^{2-}}$, was dramatic. This is particularly striking when systems with similar GEO terms for the optimized geometry, Trop-$\mathbf{5^{2+}}$ (0.1992) and Fl-$\mathbf{5^{2+}}$ (0.1830), are compared. The change in NICS(1)$_{zz}$ for aromatic Trop-$\mathbf{5^{2+}}$ is very small; the change for antiaromatic Fl-$\mathbf{5^{2+}}$ is very large. At the very least, this suggests that, in systems of this type, aromatic ring systems are much less sensitive to changes in bond length alternation than antiaromatic ring systems, and it may indicate that bond length alternation is a less viable method for evaluation of aromaticity. Aihara has expressed concern about the use of bond length alternation in the categorization of charged species as aromatic because "negative and positively charged π-systems have too many and too few π-electrons, respectively, to form the maximum number of localized bonds."[6] In effect, the presence of excess charge or "holes" in the π-system forces greater delocalization in the π-system, artificially lessening the degree of bond length alternation.

Comparison of the Magnitude of Aromaticity/Antiaromaticity in Similar Ring Systems. We have used three measures to evaluate aromaticity/antiaromaticity in the ring systems of $\mathbf{5^{2-}}$ and $\mathbf{5^{2+}}$: ^{1}H NMR shifts, NICS(1)$_{zz}$, and bond length alternation. The average ^{1}H NMR shift for each ring system cannot be compared because the increase in electron density in $\mathbf{5^{2-}}$ artificially enhances the paratropic shift of the antiaromatic

(49) While the NICS values for the fluorenyl anion suggest that aromaticity decreases upon a decrease in bond length alternation, the similarity of the NICS(1)$_{zz}$ values suggests that it would be inappropriate to place a great deal of weight upon the difference between them.

(50) Krygowski, T. M.; Ejsmont, K.; Stepie, B. T.; Cyrasnki, M. A.; Poater, J.; Solà, M. *J. Org. Chem.* **2004**, *69*, 6634–6640.
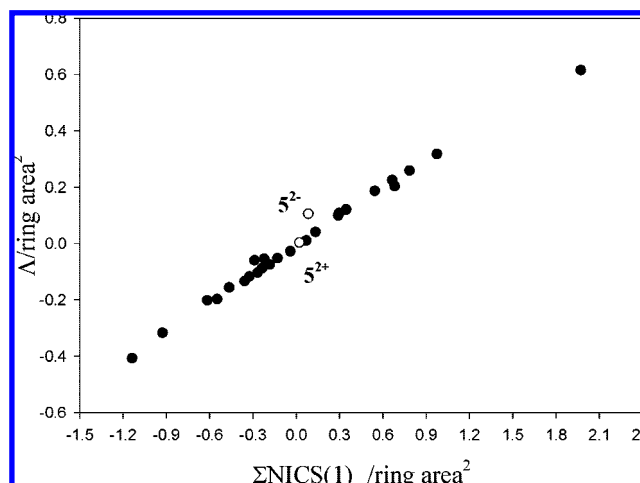
Figure 5. Λ/ring area^2 vs ΣNICS(1)$_{zz}$/ring area^2 for $\mathbf{5^{2-}}$, $\mathbf{5^{2+}}$, and a variety of aromatic and antiaromatic hydrocarbons and ions from ref 24.

tropylium system and diminishes the diatropic shift of the aromatic fluorenyl system. HOMA calculations show greater bond length alternation in antiaromatic ring systems than in aromatic systems, regardless of charge type. Thus, the delocalization seen is not related to charge type.

The third method of comparison uses the NICS(1)$_{zz}$ value of each ring system. We have chosen to represent the aromaticity/antiaromaticity of each ring system by a summation of the NICS(1)$_{zz}$ value for each individual ring. Such a summation would require that the NICS(1)$_{zz}$ values accurately reflect the local aromaticity/antiaromaticity of the ring system probed by that NICS(1)$_{zz}$ value, without sensing the aromaticity/antiaromaticity of adjacent rings. If the NICS(1)$_{zz}$ values included contributions from adjacent rings, the summation would be too large. As alluded to earlier, the effectiveness of the summation as a measure of the aromaticity of the system can be determined through the relationship between the summation of NICS(1)$_{zz}$ and a measure of the aromaticity/antiaromaticity of the entire system, such as magnetic susceptibility exaltation, Λ. If the relationship shows good linearity for a diverse group of compounds, then the summation of NICS(1)$_{zz}$ values is a reliable measure of the aromaticity/antiaromaticity of the system as a whole. Analogously, if the summation corresponds to a measure of the aromaticity/antiaromaticity of the system as a whole, then the NICS(1)$_{zz}$ for each individual ring must be reliable.[24] As noted previously, both NICS(1)$_{zz}$ and magnetic susceptibility exaltation, Λ, depend on the square of the ring area.[41] Figure 5 shows the relationship between ΣNICS(1)$_{zz}$/ring area^2 and Λ/ring area^2 for a variety of aromatic and antiaromatic hydrocarbon molecules and ions, including $\mathbf{5^{2-}}$ and $\mathbf{5^{2+}}$ (see Supporting Information).[24] The excellent relationship between ΣNICS(1)$_{zz}$ and Λ supports the premise that the NICS(1)$_{zz}$ value for each individual ring system reflects its aromaticity/antiaromaticity.

Table 4. NICS(1)$_{zz}$/Ring Area^2 for **5**$^{2-}$ and **5**$^{2+}$,^{a} for the Optimized Geometry and the Geometry with Constant Bond Lengths^b

|	fluorenyl system			dibenzotropylium system		
	5-ring	6-ring	∑NICS(1)$_{zz}$/ ring area^2	7-ring	6-ring	∑NICS(1)$_{zz}$/ ring area^2
5^{2-}, optimized geometry	−2.79	−1.00	−0.46	1.87	1.42	0.57
structure with equal bond lengths	−3.06	−0.48	−0.42	4.58	2.15	1.52
5^{2+}, optimized geometry	5.11	0.81	0.56	−0.39	−1.14	−0.26
structure with equal bond lengths	7.95	0.69	0.88	−0.37	−0.59	−0.26

^{a} Calculated by the GAIO method, with basis set B3LYP/6-311+g(d,p); using the magnetic shielding tensor perpendicular to the planar ring system, for a dummy atom 1 Å above the plane of the ring. ^{b} Bond lengths were set to the average bond length of the optimized geometry for each system.

Because NICS(1)$_{zz}$ is affected by ring area and because anions are generally larger than cations[24] (see Supporting Information for ring sizes of each system of **5**$^{2-}$ and **5**$^{2+}$), we show the values of ∑NICS(1)$_{zz}$/ring area^2 for the individual ring systems, along with the ∑NICS(1)$_{zz}$/(∑individual ring areas)^2 for the fluorenyl and dibenzotropylium systems of **5**$^{2-}$ and **5**$^{2+}$ in Table 4. It is apparent that, when the effect of ring area is included, the absolute magnitude of ∑NICS(1)$_{zz}$/ring area^2 for the antiaromatic fluorenyl system in **5**$^{2+}$ is still greater than that for the aromatic fluorenyl system in **5**$^{2-}$, and similarly for comparison of Trop-**5**$^{2-}$ with Trop-**5**$^{2+}$. When systems with identical bond lengths, and presumably equal delocalization, are examined, the absolute magnitude of the ∑NICS(1)$_{zz}$/ring area^2 is even greater for antiaromatic systems than for aromatic systems.

Comparison of Aromaticity/Antiaromaticity. There are at least two concerns with this approach. The first involves whether summation of NICS is really appropriate in a polycyclic system, and the second asks whether there are other measures of aromaticity/antiaromaticity that also show an increase in magnitude of the measure for antiaromatic systems over aromatic systems. The comparison of the aromaticity of benzene with the antiaromaticity of cyclobutadiene and with planar cyclooctatraene with D_{4h} symmetry provides answers to both concerns. As monocyclic systems, if they show the same linear relationship as seen in Figure 5, this would support the summation of NICS(1)$_{zz}$ for polycyclic systems.[24] Figure 6 shows that the linear relationship holds true.

The examination of monocyclic systems would not be complete without the inclusion of the cyclopentadienyl ions and the tropylium ions. NICS(1)$_{zz}$/ring area^2 and Λ/ ring area^2 are shown in Scheme 2, and again, the systems with 4n π-electrons show greater antiaromaticity than do the comparable systems with 4n +2 π-electrons.

However, we need to insert a cautionary note here. When the charged species are included in the plot of ∑NICS(1)$_{zz}$/ring area^2 vs Λ/ring area^2, the cyclopentadienyl anion and tropylium anion do not show the same type of linear relationship as the other species, which include anionic species (see Figure 7). We believe that charge density may play a role in these magnetic manifestations of aromaticity/antiaromaticity, with the most obvious effects in anions of smaller ring systems. It is difficult to determine whether the discrepancy is found in NICS or Λ. We considered the possibility that, for an anionic system which contains more diffuse orbitals, the appropriate distance
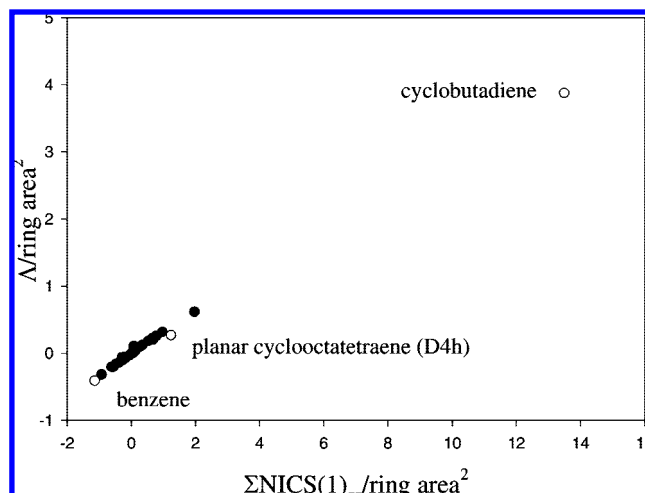
Figure 6. Λ/ring area^2 vs ∑NICS(1)$_{zz}$/ring area^2 for benzene, cyclobutadiene, cyclooctatetraene, and a variety of aromatic and antiaromatic hydrocarbons and ions from ref 24.
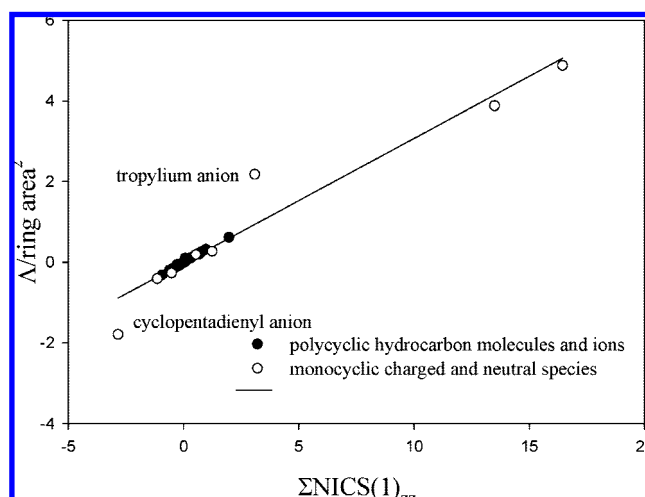
Figure 7. Plot of magnetic susceptibility exaltation (Λ)/ring area^2 vs ∑NICS(1)$_{zz}$ including tropyliun cation and anion and cyclopentadieryl cation and anion.

for the position of the ghost atom for the NICS calculations should be greater. Aromatic species show a minimum for the NICS value at 1 Å which supports the use of a ghost atom at that distance. However, a scan of NICS[40] from 0.5 to 1.5 Å showed that the minimum was still at 1 Å for the aromatic cyclopentadienyl anion.

Summary

The dianion of tetrabenzo[5.7]fulvalene, **5**$^{2-}$, has been prepared, and the ^{1}H NMR shifts and NICS(1)$_{zz}$ values of the fluorenyl system are consistent with it being categorized as aromatic, while the paratropic shifts of the dibenzotropylium system are consistent with those of an antiaromatic species. The experimental ^{1}H NMR shifts show an excellent relationship with the chemical shifts calculated for **5**$^{2-}$ without lithium counterions and a much poorer correlation with lithium counterions, suggesting that there is little association with the lithium counterion.

Assessment of bond length alternation showed that there was greater bond length alternation for antiaromatic systems than for the corresponding aromatic system of **5**$^{2-}$ and **5**$^{2+}$, demon-

Scheme 2. Comparison of Aromaticity and Antiaromaticity for Cyclopentadienyl and Tropylium Ions
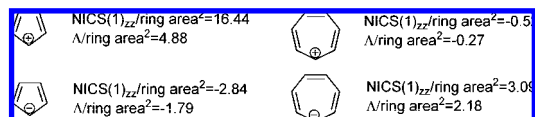
strating that the effectiveness of the delocalization was not a function of the charge type. When the structures of 5^{2-} and 5^{2+} were constrained so that there was no bond length alternation, the result was a substantial increase in the magnitude of NICS(1)$_{zz}$ for the antiaromatic systems. This would appear to suggest that a lack of bond length alternation is related to an increase in antiaromaticity.

Comparison of the NICS values for 5^{2-} with 5^{2+}, which has an antiaromatic fluorenyl system and an aromatic dibenzotropylium system, shows that, when the individual systems are examined, the antiaromatic system has a larger absolute value of NICS than the aromatic system. This relationship was maintained when the effect of the size of the ring was taken into account. A similar relationship was demonstrated for the cyclopentadienyl cation/anion and tropylium cation/anion.

Experimental Section

The neutral precursor **5** was prepared according to literature procedures.[51]

Preparation of 5^{2-}. Neutral **5** was reduced with lithium following a variation of the procedure of Rabinowitz.[42] A piece of fresh lithium wire was placed in the upper part of an extended NMR tube which contained ~5 mg of **5**. THF-d_8 was transferred to the evacuated tube. The solution was degassed using the freeze−pump−thaw technique and flame-sealed. The solution was brought into contact with the lithium by inverting the tube. The inverted tube was then sonicated at 0 °C to remove the oxidized layer on the lithium. Sonication continued until the solution turned to a deep red.

Quenching of 5^{2-}. After completion of NMR analysis, the solution was quenched with oxygen to regenerate the starting material and to demonstrate that 5^{2-} was the only species present

in solution. The NMR tube was opened and a gentle stream of oxygen introduced into the NMR tube. The deep color of the solution gradually disappeared. The resulting material was identified by NMR and TLC analysis through comparison with a known sample of **5**.

Computational Details. Geometries of 5^{2-}, Li$_2$5, 5^{2+}, and **5** were optimized using density functional theory at the B3LYP/6-31g(d) level in Gaussian03,[52] and frequency calculations indicated that the geometries represented energy minima. Geometries for hydrocarbons calculated with density functional theory at this level have been shown to agree well with experimental data.[53−55] NMR/NICS calculations for all species were done using the GIAO method in Gaussian03 with basis set B3LYP/6-311+g(d,p). NICS(1)$_{zz}$ was calculated using the component of the magnetic shift tensor in the z direction, perpendicular to the plane of the ring, for a dummy atom 1 Å above the plane of the ring.[1]

Supporting Information Available: Plot of experimental vs calculated ^{1}H NMR shifts for 3^{2-} and 5^{2-}, with and without lithium counterions; the geometries for 5^{2-} and 5^{2+}; ring areas for optimized geometries of 5^{2-} and 5^{2+} and for geometries with equal bond lengths; species included in the comparison of ΣNICS(1)$_{zz}$ with magnetic susceptibility exaltation, Λ; bond lengths for optimized geometries of 5^{2-} and 5^{2+}; calculated total energies; [x,y,z] coordinates for **5**, 5^{2-}, and 5^{2+}; complete ref 52. This material is available free of charge via the Internet at http://pubs.acs.org.

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