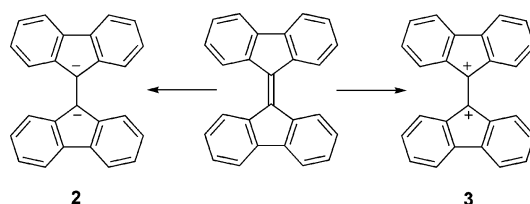# The Aromaticity/Antiaromaticity Continuum. 1. Comparison of the Aromaticity of the Dianion and the Antiaromaticity of the Dication of Tetrabenzo[5.5]fulvalene via Magnetic Measures

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The aromaticity of the dianion (**2**) and the antiaromaticity of the dication (**3**) of tetrabenzo[5.5]fulvalene have been evaluated through magnetic criteria, ^{1}H NMR shifts, nucleus-independent chemical shifts, NICS, and magnetic susceptibility exaltation, Λ. The sum of the NICS values, using the GIAO (gauge-independent atomic orbital) method, for **2** is -35.2; that of **3** is $+38.2$, indicating the aromaticity of **2** and the antiaromaticity of **3**. Calculation of magnetic susceptibility exaltation using the CSGT (continuous set of gauge transformations) method gives a similar result, with Λ of -81.8 ppm cgs for **2** and 95.8 ppm cgs for **3**. The general validity of these values is supported by excellent agreement between the NMR shifts calculated by the GIAO and CSGT methods with experimental shifts. Comparison of ^{1}H NMR shifts with those of model compounds allows evaluation of the magnitude of the diatropic shift in **2** and paratropic shift in **3** and supports their assignment as aromatic/antiaromatic, respectively. The agreement between calculated and experimental ^{1}H NMR shifts is excellent for **3** in the absence of counterions but much better for **2** when counterions are included. Inclusion of counterions in the evaluation of diatropic shift for **2** gave a smaller shift than in the absence of counterions, suggesting a decreased aromaticity. When counterions were included in the calculation of Λ, the value was also decreased, suggesting a decreased aromaticity. This observation has important consequences in the use of experimental data for the evaluation of aromaticity, and presumably antiaromaticity, of anions since, in most cases, there will be close interaction with counterions.

Introduction

Aromaticity, as one of the fundamental concepts in organic chemistry, occupies an interesting position. As a concept it enjoys wide acceptance, but there is widespread disagreement about how it should be measured.[1-5] There are three general categories for the physical properties that have been used to describe aromaticity: magnetic, structural, and energetic. These properties are based on those properties that describe the physical behavior of benzene. The *magnetic* criteria result from the effects of a ring current and include ^{1}H NMR shifts,[6]

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magnetic susceptibility exaltation,[7−9] and nucleus-independent chemical shifts (NICS).[10] The *structural* criteria examine the degree of bond length alternation, normally evaluated through the harmonic oscillator measure of aromaticity (HOMA) and deviations from planarity.[11] Finally, the *energetic* criteria evaluate the stability of the aromatic species compared to localized reference systems.[12]

While all of the characteristics are present in benzene, they are present in varying degrees in both polycyclic and nonbenzenoid aromatic compounds. This has spawned a number of debates about the use of the various criteria in evaluating aromaticity, with some results suggesting that the criteria are orthogonal[13,14] while others show a linear relationship between the criteria.[15] If aromaticity is to be a useful concept, it must have some generality in terms of "molecular response properties",[16] those properties that can be measured or calculated properties that reliably "track" measured properties. If there is no relationship between the various criteria and the properties used to evaluate those, the limitations of each technique must be defined to prevent inappropriate use.

We have become involved in this question through our discovery of a class of fluorenylidene dications, **1**, in which the degree of antiaromaticity was varied by changes in the nature of the substituents R and R′.[17−25] Our intent was to do a

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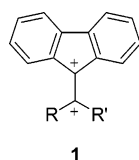
systematic variation through changes in the substituents, to evaluate the antiaromaticity of the fluorenyl cation by as many of the techniques in the three criteria as possible and to look

for internal consistency between the quantitative measures of antiaromaticity. Our premise was that by examining antiaromatic species, species that are far removed from benzene, we would be able to identify those properties that were truly related to antiaromaticity and, by extension, to aromaticity. In these studies, we attempted to include analyses based on both theoretical and experimental results. We are in general agreement with the statement by Lazzaretti that "one should only rely on properties that can actually be measured for the assessment of the vague and controversial concept of aromaticity."[16] We would simply modify this statement by allowing the inclusion of calculated values that cannot be experimentally validated, such as NICS, if those values are related to calculated values that can be experimentally validated. In the case of NICS, since the calculational approaches that give the NICS values also give ^{1}H and ^{13}C NMR shifts, good agreement of those calculated shifts with experimental shifts would serve to validate the NICS calculations.

Experimental measures of aromaticity that can be applied to a diverse group of species are very difficult to identify. Magnetic susceptibility exaltation[7−9] and hardness, a measure of stability via UV/vis spectroscopy,[26−28] are highly dependent on ring size; NICS[10,29] is a local property, making it difficult to compare polycyclic ring systems; and HOMA calculations are relatively insensitive to changes in polycyclic systems.[23] The greatest congruence in properties is found in ring systems of similar sizes[1,15] or those in which there is a mechanism for normalizing ring sizes.[25,27,28] We were anxious to broaden the scope of these investigations by examining systems of the same size but with vastly different degrees of aromaticity/antiaromaticity. That is, by comparing the aromaticity of **2** to the antiaromaticity of **3**, using as many of the techniques in the criteria as possible, we could evaluate the behavior of aromatic/antiaromatic species as shown through the different criteria. Because we have only two species, we cannot examine the linear relationship between the species, but we hoped to define some of the limitations of each technique examined.

Aromaticity/Antiaromaticity Continuum

2   **3**
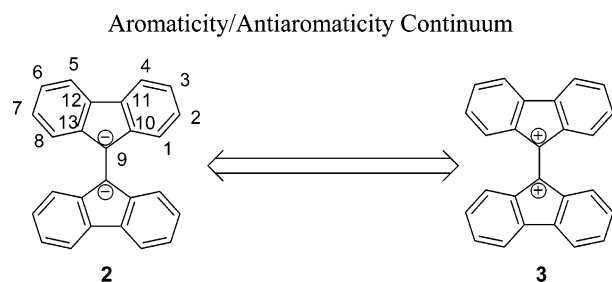
While **2** and **3** are formally the two ends of a continuum, the aromaticity/antiaromaticity continuum, the species that will be experimentally observed will be affected by the associated counterions and the degree of that association. Because chemists are primarily interested in the behavior of "real" species, it is also of value to examine the effects of counterions on moderating the aromaticity/antiaromaticity of these species.

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(29) NICS is technically not an experimental measure, but because the calculations that give NICS values also give chemical shifts that can be compared to experimental shifts, relationships between calculated and experimental chemical shifts also allow the assessment of the quality of the NICS values.
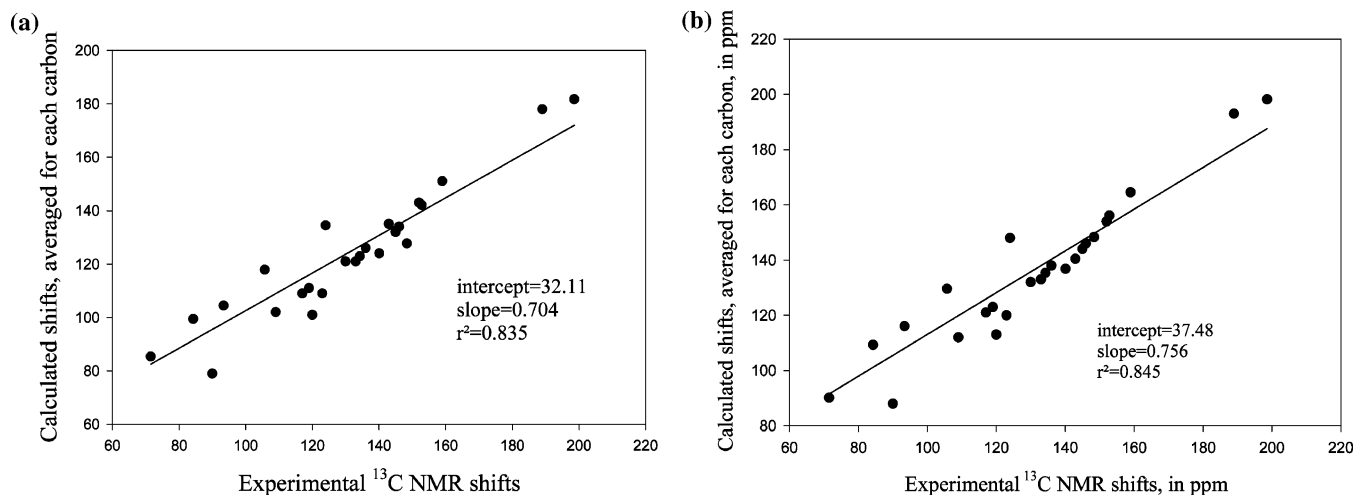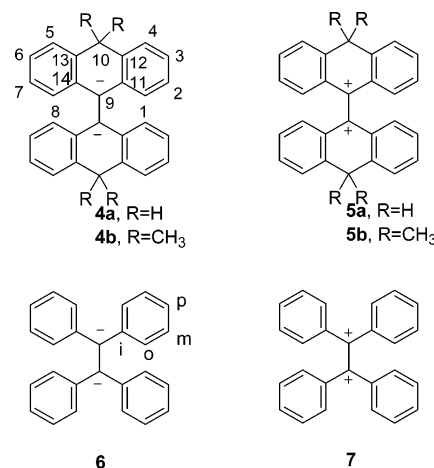
FIGURE 1. Calculated ^{13}C shifts (a, B2LYP/6-31G(d) level; b, B3LYP/6-311+G(d) level) vs experimental shifts for Na_2**2**,[31] **3**,[18] Na_2**6**,[39] and **7**.[34] Calculated shifts for formally equivalent carbons, such as C_1/C_8, of anions were averaged. Calculated geometries are static structures, while the experimental spectra are the result of dynamic structures. See the Supporting Information. The Supporting Information also has plots showing the specific carbon shifts of Na_2**2**, **3**, Na_2**6**, and **7**.

We report the analysis of the aromaticity of **2** and the antiaromaticity of **3** via magnetic criteria (^1H NMR chemical shifts, NICS, and magnetic susceptibility exaltation) in this paper. We include a discussion of the effects of counterions on these properties so that their magnetic behavior can be appreciated in the context of "real" species.

Results and Discussion

Magnetic Criteria: ^1H NMR Spectra. *Magnetic* criteria, based on the special behavior associated with induced ring currents, have been suggested as the most important of the three criteria.[1] The most common measure of ring currents is the ^1H NMR chemical shift,[6] although Schleyer et al. have recently reminded the chemical community of the limitations of proton shifts in the measurement of a ring current.[30] To evaluate the magnitude of the diatropic/paratropic shifts of **2**[31]/**3**,[18] the average chemical shift of the protons was compared to two sets of reference systems, **4b**/**5b** and **6**[32,33]/**7**.[34] Species **4b** and **5b** have methyl substituents because of concerns that rearomatization of **5a** through loss of a proton could be facile. Our initial intent was to compare the experimental ^1H NMR shifts for **2**, **3**, **4b**, and **5b**, but **5b** was impossible to see on the NMR time scale, even at −78 °C. We have observed cyclization of similar dications[35] and believe that this is probably the situation with **5b**. To make comparisons between species, we were forced to rely on calculated NMR spectra. To validate this approach, we examined the relationship between the experimental and calculated spectra for **2**, **3**, **6**, and **7**.

The calculated shifts were obtained on geometries optimized using density functional theory with the GIAO (gauge-

independent atomic orbital) approach in Gaussian03.[36] We examined the calculations at two different levels, with magnetic properties calculated at the B3LYP/6-31G(d) level on geometries optimized at the B3LYP/6-31G(d) level, referred to as B3LYP/6-31G(d)//B3LYP/6-31G(d), and also with diffuse functions in the basis set, B3LYP/6-311+G(d)//B3LYP/6-311+G(d). Our previous experience showed that calculations at the B3LYP/6-31G(d) level gave very good agreement with experimental data[21−23] for dications. Calculations of anions have been known to require inclusion of diffuse functions,[37] and a recent report

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(a)

(b)
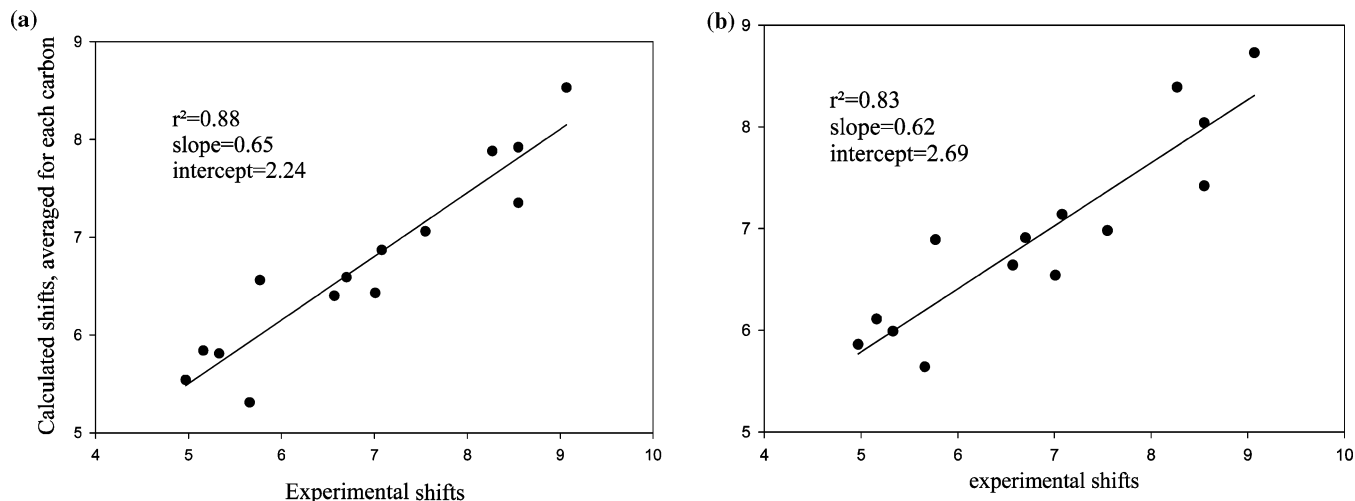
FIGURE 2. Calculated ^1H NMR shifts (a, B3LYP/6/31g(d) level; b, B3LYP/6-311+G(d) level) vs experimental shifts for $Na_2$2,[31] 3,[18] $Na_2$6,[32,33] and 7.[34] Calculated shifts for formally equivalent carbons, such as C_1/C_8, of anions were averaged. Calculated geometries are static structures, while the experimental spectra are the result of dynamic structures. See the Supporting Information for plots in which the calculated spectra were not averaged. The Supporting Information also has plots showing the specific proton shifts of $Na_2$2, 3, $Na_2$6, and 7.

emphasized the importance of incorporating diffuse functions in the calculations of polycyclic aromatic hydrocarbon dianions.[38] We have chosen to evaluate the quality of the calculations by a plot of the experimental shift vs the calculated shift. The plots of the ^{13}C NMR shifts for $Na_2$2/3/$Na_2$6[39]/7 at both levels of theory are shown in Figure 1. While 2 and 6 have been prepared both with lithium and with sodium counterions, we have chosen to include the data with sodium counterions because the lithium counterion is "intimately involved" in stabilizing polyanions in lithiated hydrocarbons,[40,41] and we wanted to minimize the effect of the counterion, vide infra. The overall agreement for comparisons is basically the same for the calculations without diffuse functions and with diffuse functions and is improved when the sodium counterions are included in the calculation.

Agreement is better when similar systems are compared, for $Na_2$2 and 3, $r^2 = 0.97$ (0.98), slope = 1.01 (1.05) for calculations without and with diffuse functions, values for diffuse functions shown in parentheses; for $Na_2$6 and 7, $r^2 = 0.91$ (0.92), slope = 0.65 (0.74).

While agreement for ^{13}C NMR shifts is important, the crucial question involves the agreement for ^1H shifts, which is often poorer than for ^{13}C shifts because absolute errors in ^1H shifts are a much larger fraction of the overall shift. The plots of experimental vs calculated ^1H NMR shifts at the two levels are shown in Figure 2. Calculations for 2 and 6 showed that the inclusion of counterions improved the quality of the correlation; see the Supporting Information. The association of counterions with anions has a much greater effect on NMR shifts than does the association of counterions with cations.[42,43] Rabinovitz et

TABLE 1. Average Calculated and Experimental ^1H NMR Shifts for 2−7

	exptl shifts[a] (ppm)		calcd shifts, without counterion (ppm)	calcd shifts with sodium counterions (ppm)
2	7.28b[b]		6.35	7.10
4b[c]			5.32	5.96
6	6.56[d]	6.52[e]	5.59	6.19
3	5.31[f]		5.94	
5b[a]			7.83	
7	8.65[g]		7.81	

[a] In THF and THF-d_8. [b] Reference 31. [c] Protons on the aromatic ring system only. [d] Reference 32. [e] Reference 33. [f] Reference 17. [g] Reference 34.

al.[38] have observed that agreement between calculated and experimental shifts is improved with the inclusion of basis sets with diffuse functions. Because the correlation of shifts calculated using B3LYP/6-311+G(d) is very similar to that for shifts calculated using B3LYP/6-31G(d), we have chosen to calculate magnetic properties, such as proton shifts and nucleus independent chemical shifts, vide supra, using that basis set because it is calculationally more efficient.

The average ^1H NMR shifts, calculated and experimental where available, are listed in Table 1. The calculations show that the dihydroanthracenylideneanthracene systems (4a and 5a) and tetraphenylethylene systems (6 and 7) function very similarly as model systems for ^1H NMR shifts.

Comparison of the calculated spectra for 5 and 7 show effectively no difference in the chemical shift. Comparison of calculated proton shifts for 4 and 6 without counterions shows a difference of less than 0.3 ppm, as does the calculation with counterions.

Our intent was to use these model systems to assess the degree of aromaticity/antiaromaticity of 2/3. Looking first at the experimental data, which requires reliance on the data for 6/7 only, dication 3 is substantially more antiaromatic (3.34 ppm upfield) than $Na_2$2 is aromatic (∼0.7 ppm downfield). Because the association of the counterion with anions is known to be stronger than the association of counterions with cations,[42,43] it is possible that the effect of the sodium counterion was to remove some electron density from 2, potentially decreasing its aromaticity. Complexation of benzene with $Cr(CO)_3$ has been

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TABLE 2. Calculated and Experimental ^{1}H NMR Spectra for 2 and 4a

position	exptl shift (ppm), Na$_2$**2**[a]	calcd shift (ppm), Na$_2$**2**	calcd shift (ppm), **2**	calcd shift (ppm), Na$_2$**4a**	calcd shift (ppm), **4a**	$\Delta\delta_{2-4a}$ (ppm), no counterion
1	7.46	6.59	6.92	4.95	5.51	1.41
8	7.46	7.54	6.92	5.73	6.27	0.65
avg	7.46	7.06	6.92	5.34	5.89	1.03
2	6.93	6.82	5.91	6.40	5.35	0.56
7	6.93	6.92	5.91	6.43	5.44	0.47
avg	6.93	6.87	5.91	6.42	5.40	0.51
3	6.56	6.53	5.45	5.67	4.60	0.85
6	6.56	6.65	5.45	5.77	4.60	0.85
avg	6.56	6.59	5.45	5.72	4.60	0.85
4	8.17	7.92	7.14	6.40	5.39	1.75
5	8.17	7.85	7.14	6.32	5.36	1.78
avg	8.17	7.88	7.14	6.36	5.38	1.76
10				4.18	2.70	
10				3.53	3.70	

[a] Reference 31.

shown to reduce the aromaticity of the benzene ring.[44] We have examined this through the calculation of atomic charges for **2**, with and without sodium counterions, using natural population analysis. Details on the calculations can be found in the Supporting Information. The sum of the atomic charges for the carbons and hydrogens of Na$_2$**2** is -1.91, compared to the sum for **2**, which is of necessity -2.00; thus, the sodium counterion has removed some electron density. We can use the calculated ^{1}H NMR shifts to evaluate the aromaticity/antiaromaticity of the "naked" di-ions. By this measure, **3** is still substantially more antiaromatic (-1.9) than **2** is aromatic (1.0 in comparison to **4**; 0.8 in comparison to **6**).

This evaluation of aromaticity/antiaromaticity is oversimplified, however. The parent olefin of **2/3** has a severely twisted central double bond because of steric interactions between the ortho protons. Calculations suggest that upon oxidation or
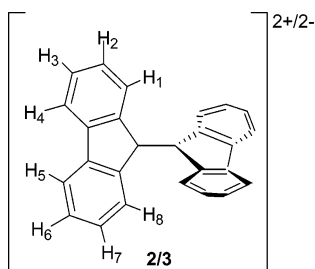
reduction of this olefin, the two ring systems become almost perpendicular[21] and a similar situation occurs for **4/5**. The optimized geometries for **2** and **3** have dihedral angles between the fluorenyl ring systems of approximately 60° with a point group of D_2; the optimized geometries of **4/5** have dihedral angles of 90° between the ring systems and a point group of C_1 because the methylene groups force the center ring to be nonplanar, decreasing the symmetry. One consequence of this change in the dihedral angle of the carbons of the central bond is that the ortho protons now feel the effects of the opposing ring system, as shown above. For **3**, this means that H$_1$ and H$_8$ are positioned close enough to the center of the antiaromatic fluorenyl cationic ring system to be shifted downfield in comparison to H$_1$ and H$_8$ of **5**.[17] Specifically, H$_1$/H$_8$ of **3** have a calculated shift of 5.81 ppm, see Table 3, but would have been expected to show a smaller value of δ (more upfield) in

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TABLE 3. Calculated and Experimental ^{1}H NMR Spectra for 3 and 5a

position	exptl shift (ppm), **3**[a]	calcd shift (ppm), **3**	calcd shift (ppm), **5a**	$\Delta\delta_{3-5}$
1/8	5.33	5.81	7.24	−1.43
2/7	5.16	5.84	7.42	−1.58
3/6	5.77	6.56	8.74	−2.18
4/5	4.97	5.54	7.92	−2.38
10			3.56	

[a] Reference 17.

the absence of this effect. We have seen that this effect is strongest for H$_1$/H$_8$ but falls off with distance and is virtually nonexistent for H$_3$/H$_6$ and H$_4$/H$_5$5.[18] A corresponding effect should be felt for **2** in comparison with **4a**, with H$_1$ and H$_8$ of **2** shifted upfield in comparison with H$_1$/H$_8$ of **4a**. Specifically, the calculated shift, 6.92 ppm, see Table 2, for H$_1$/H$_8$ of **2** would have been expected to be larger (further downfield) in the absence of this effect. Thus, the apparent aromaticity of **2** and antiaromaticity of **3** is diminished for protons H$_1$/H$_8$ and, to a lesser extent, for H$_2$/H$_7$. Because it is difficult to evaluate how much of a change these effects cause in the shifts of H$_1$/H$_8$ and H$_2$/H$_7$, the most reliable method of comparison would be between those protons least affected, H$_3$/H$_6$ and H$_4$/H$_5$.[18] By that measure, the average difference between **2** and **4a** for H$_3$/H$_6$ and H$_4$/H$_5$ is 1.31; that between **3** and **5** is -2.28. Thus, dication **3** is antiaromatic and dianion **2** is aromatic.

Magnetic Criteria: NICS. The second measure of aromaticity/antiaromaticity used in this study is the nucleus-independent chemical shift (NICS).[10] NICS values have recently been correlated with experimental measures of aromaticity[45] and antiaromaticity.[22−24] NICS values are calculated using the GIAO method for dummy atoms at the center of the ring system of interest and are negative for aromatic ring systems, positive for antiaromatic systems. Because "local shielding effects" influence the magnitude of NICS, particularly for small rings, it has been recommended that they be calculated 1 Å above the plane of the ring.[46,47] The GIAO calculations also gave the calculated chemical shifts reported in Table 1 and in the Supporting Information. The observed correlation between experimental

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(46) 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.

TABLE 4. NICS[a] Values for 2−5a

species	NICS-5(1)	NICS-6(1), benzene ring	NICS-6(1), central ring	sum per ring system
2	−14.0	−10.6		−35.2
3	21.4	8.4		38.2
4a		−6.5	−0.7	-
5a		−9.1	2	-

[a] Calculated at B3LYP/6-31G(d)// B3LYP/6-31G(d). Dummy atom 1 Å above the plane of the ring, average of ring positions.

shifts and those calculated at the B3LYP/6-31G(d) level shown in Figures 1 and 2 suggests similar reliability for the NICS values.

The NICS values, calculated 1 Å above the plane of the ring, for the 5- and 6-membered rings of **2** and **3** and the central 6-membered ring and benzene rings of **4a** and **5a** are given in Table 4. It is apparent that all rings of **2** demonstrate appreciable aromaticity because the NICS values are negative, while those of **3** demonstrate appreciable antiaromaticity, with positive values of NICS. The central rings of **4a** and of **5a** have small values of NICS, suggesting little aromaticity or antiaromaticity, as expected, while the aromaticity of the benzene rings is slightly reduced over that of benzene,[48] reflecting the decreased aromaticity in a benzylic cation.[49]

As mentioned in the Introduction, it is difficult to know how to use NICS values for different ring systems to handle a global property like aromaticity. Schleyer has recently made the suggestion that the summation of the NICS values reflects global aromaticity/antiaromaticity.[50] We have observed that the summation of NICS values shows a linear correlation with hardness, a measure of stability.[25] The summation of the NICS values is also given in Table 4 for **2** and **3**. Dication **3** is again shown to be antiaromatic and dianion **2** aromatic.

Magnetic Criteria: Magnetic Susceptibility Exaltation. Magnetic susceptibility exaltation (Λ) evaluates the effect of a ring current by comparing the bulk magnetic susceptibility (χ) to the susceptibility of a localized ring system.[7−9] The susceptibility of the localized ring system is estimated from an increment system. Aromatic compounds are characterized by negative Λ; antiaromatic systems by positive Λ, and the magnitude of the value is a measure of the magnitude of the ring current, and therefore of relative aromaticity/antiaromaticity.

The susceptibilities of **2** and of **3** were calculated using the CSGT method at the B3LYP/6-31g(d) level on geometries optimized at B3LYP/6-31g(d). Because the calculation also gives chemical shifts, it is possible to evaluate the quality of the calculation by comparing experimental ^{13}C and ^{1}H NMR shifts with calculated shifts. While we are interested in Λ for **2** and **3** without counterions, we calculated those chemical shifts for Na$_2$**2**, **3**, Na$_2$**6** and **7**, species for which we had experimental chemical shifts. The chemical shifts calculated with the CSGT method are listed in the Supporting Information. The correlation

(47) The NICS values reported in Table 4 are averaged values. A reviewer expressed concern that NICS calculated 1 Å above the plane of the ring could feel effects from the opposing ring system, but the unaveraged NICS values 1 Å above the plane of the ring, see the Supporting Information, show very little deviation, so interaction with the opposing ring system, if it occurs, is slight. We also report the NICS values in the plane of the ring for **2** and for **3** for comparison in the Supporting Information.

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(49) Morao, I.; Hillier, I. H. *Tetrahedron Lett.* **2001**, *42*, 4429−4431.

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TABLE 5. Magnetic Susceptibility,[a] χ, and Magnetic Susceptibility Exaltation,[b] Λ, of 2, 3, and Na$_2$2

| compd	χ (ppm cgs)	χ_{ref} (ppm cgs)	Λ (ppm cgs)
2	−219.2	−137.4	−81.8
3	−36.2	−132.0	95.8
Na$_2$2[b]	−214.5	−204.0	−10.5
Na$_2$2[c]	−214.5	−162.0	−52.5

[a] Calculated with the CSGT method in Gaussian 98 and 03 using B3LYP/6-31g(d) on geometries optimized at the same level. [b] Magnetic susceptibility for the reference system was calculated from the summation of magnetic susceptibilities for increments; reference system for **2** = $\Sigma 8(cis\text{-}CH{=}CH)$ + $4(>C{=}C<)$ + $2(>C{-}C<)^{2-}$; reference system for **3** = $\Sigma 8(cis\text{-}CH{=}CH)$ + $4(>C{=}C<)$ + $2(>C{-}C<)^{2+}$. See the Supporting Information for details for the reference systems. [c] See discussion in the text and the Supporting Information for details of the reference systems. The reference system here is for

$$Na_2\mathbf{2} == \Sigma\ 8(cis\text{-}CH{=}CH) + \left[\begin{array}{c} \text{structure} \end{array} \right] Na_2$$
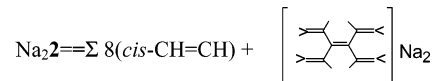
between experimental and calculated shifts is good, with r^2 = 0.923 for carbon spectra and 0.837 for proton spectra. The ^{1}H shifts calculated by this method are generally about 2 ppm upfield from experimental shifts but, since the magnetic susceptibility exaltation is evaluated by the difference in magnetic susceptibility of a delocalized and a localized system, the upfield shift will be canceled out.

The values for χ and Λ for **2**, Na$_2$**2**, and **3** are reported in Table 5. The negative value of Λ for **2** indicates its aromaticity, while the positive value for **3** supports its antiaromaticity.

When counterions are present for anions, there is a marked effect on Λ. That is, Λ for Na$_2$**2** is diminished with respect to the value calculated for **2**. We have calculated the magnetic susceptibility exaltation using two different reference systems. In the first, we have used neutral increments except for the increment including carbon 9 from each fluorenyl system, **8**; see the Supporting Information for all increments used in the summation of incremental magnetic susceptibilities. In this reference system, the sodium counterions are of necessity closely associated with the two carbon atoms, as represented below. In
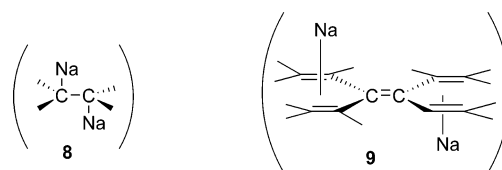
the second, we used a reference system that included vinyl substituents on the ethylene dianion increment, **9**, a divinylhexatrienyl increment. In this system, the sodium counterions are associated with the five carbons of the divinylhexatrienyl dianion, as represented in the structure shown. The optimized geometry of Na$_2$**2** shows an association of counterions that is more similar to **9** than to **8**. This increment of necessity contains more extended conjugation. Since the intent of the localized reference system is to prevent delocalization, **8** is a better model. To the extent that the coordination of sodium more closely represents the coordination found in Na$_2$**2**, **9** is a more appropriate increment. For reference systems utilizing either increment, the magnetic susceptibility exaltation is less than that for **2**, which has no counterions. Thus, the counterion affects this measure of aromaticity. We have shown that the presence of the counterion affects the amount of charge on the anionic system of **2** and the magnitude of the diatropic ^{1}H NMR shift

**TABLE 6. Summary of Assessment of Aromaticity/
Antiaromaticity by Magnetic Criteria for 2 and 3**

	2	3
avg ^{1}H NMR shift for H-3/H-6; H-4/H-5 vs analogous shifts for **4** or **5**	1.31	−2.28
Σ NICS 1 Å above the plane of the ring	−35.2	38.2
Λ	−81.8	95.8

that is indicative of its aromaticity. Since the majority of the experimental data for hydrocarbon dianions will involve species with close interaction with counterions, the diminished aromaticity, and potentially antiaromaticity, seen in these species must be considered when experimental data is used for the assessment of aromaticity/antiaromaticity.

Summary. The results from the application of magnetic criteria to the assessment of aromaticity in **2** and antiaromaticity in **3** are summarized in Table 6. They show that not only do magnetic criteria demonstrate the aromaticity of **2** and the antiaromaticity of **3** but by all three measures, **3** is more antiaromatic than **2** is aromatic.

Counterions play a more important role in the behavior of dianions than dications as shown by the improvement in the agreement of experimental and calculated shifts for dianions with the inclusion of counterions; the agreement for dications is very good without the inclusion of counterions. The magnitude of the diatropic shift and of Λ for the aromatic dianion **2** was decreased for species with sodium counterions, suggesting that experimental evaluation of the aromaticity/antiaromaticity of anions must reflect the role of the counterion in affecting the magnitude of its aromaticity/antiaromaticity.

Supporting Information Available: Synthesis of precursors to **2/3** and **4b/5b**; calculated and experimental ^{1}H and ^{13}C NMR shifts for Na$_2$**2**, **3**, Na$_2$**6**, and **7**; calculated ^{1}H and ^{13}C NMR shifts for **2**, **4a**, **5a**, and **6**; plot of experimental vs calculated ^{13}C and ^{1}H NMR shifts for Na$_2$**2**, **3**, Na$_2$**6**, and **7**; selected dihedral angles for **2**, **3**, **4a**, and **5a**; increments for reference systems for magnetic susceptibility exaltation; atomic charges from natural population analysis for **2** and Na$_2$**2**; total energies and Cartesian coordinates for structures optimized at B3LYP/6-31G(d) and B3LYP/6-311+G-(d). This material is available free of charge via the Internet at http://pubs.acs.org.

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