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Antiaromatic ions and their value in quantifying aromaticity, as probes of delocalization, and potential as stable diradicals*

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Abstract: Antiaromatic dications and dianions are available through oxidation or reduction of unsaturated precursors as well as through ionization of diols. Their experimental accessibility allows them to be used to evaluate the effectiveness of theoretical treatments of antiaromaticity such as the nucleus-independent chemical shift (NICS). Because measures of antiaromaticity are generally larger in magnitude than corresponding measures of aromaticity, they demonstrate relationships between different measures of aromaticity–antiaromaticity, such as those based on magnetic and energetic properties, more effectively than do aromatic measures. Antiaromatic species are more sensitive probes of delocalization than are aromatic species, giving the possibility of observation of subtle effects. Antiaromatic species possess a small highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap, giving rise to species with diradical character.

Keywords: antiaromaticity; aromaticity; carbocations; computational chemistry; organic chemistry; stability.

INTRODUCTION

The statement that aromaticity is a key concept in organic chemistry is indisputable. It has served to guide the development of novel aromatic species and has been used to explain the outcome of a number of organic reactions, including the nature of the transition state in Diels–Alder reactions [1]. A researcher who has prepared a compound that possesses a Hückel number of electrons in a cyclically delocalized system must attempt to determine whether the compound is aromatic. Because aromaticity is not a directly observable quantitity [2], it must be probed indirectly. Evidence of aromaticity has come primarily through three characteristics, energetic, structural, and magnetic properties. *Energetic* measures look at the greater stability of aromatic compounds [3,4] including aromatic stabilization energy [5]. *Structural* measures [6] include the assessment of the degree of bond length alternation with the harmonic oscillator model of aromaticity (HOMA) [7]. Finally, magnetic measures [8] examine the effect of the ring current through the diamagnetic shift of protons in an aromatic system [9,10], through the enhancement of magnetic susceptibility, known as magnetic susceptibility exaltation, Λ [11,12], and through calculation of the chemical shift of a probe located in the center of the ring current, the nucleus-independent chemical shift (NICS) [13]. The original description of NICS has been modified to include the suggestion that the probe be placed 1 Å above and below the plane of the ring and that the component of the magnetic shielding tensor perpendicular to the plane of the ring be used [14] to decrease in effect of electrons in the sigma bonds, particularly in small ring systems. A negative value for NICS indicates an aromatic compound; positive values are consistent with the antiaromaticity of a species.

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Our research could use any of these measures to assess the aromaticity of the new compound. It would also be reasonable to ask how aromatic the new species is, and that is where a problem arises. If all of the aforementioned criteria are measuring aromaticity, one would expect a linear relationship between any measure. As Fig. 1a demonstrates for a subset of aromatic compounds [15], there appears to be a trend but there is not a good linear relationship between magnetic susceptibility exaltation and the sum of the NICS values. For this reason, aromaticity has been considered a multidimensional phenomenon [16]. However, upon the addition of antiaromatic species [17], a strong linear correlation is obvious, Fig. 1b. The advantage that the inclusion of antiaromatic species offers is greater dispersion. The magnitudes of the measures of aromaticity, shown as closed circles in Fig. 1b, tend to be clustered. Indeed, one of the greatest values of the similarities of the magnitude for the ^{1}H NMR shift of aromatic species is in its diagnostic reliability as evidence of benzene ring. The greater dispersion for antiaromatic species suggests that they might offer a more sensitive probe of the factors that affect aromaticity.

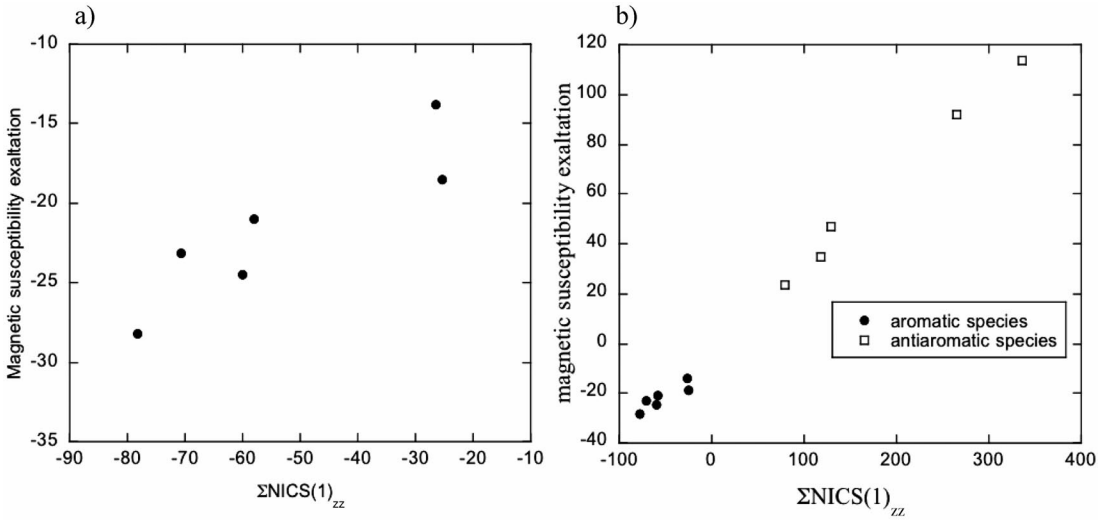


Fig. 1 (a) Magnetic susceptibility exaltation vs. $\Sigma NICS(1)_{zz}$ for aromatic species, see ref. [18] for details of the calculations. (b) Species in (a) plus a set of antiaromatic neutral and cationic species. Used by permission of the American Chemical Society.

Our original interest in exploring the linearity of the relationship between magnetic susceptibility exaltation and the summation of NICS values was to determine whether the sum of NICS accurately measured global aromaticity [18]. There had been suggestions in the literature that the NICS values might also reflect the contribution from neighboring ring systems [19,20]. The linear correlation for a variety of polycyclic aromatic and antiaromatic species, Fig. 1b, indicated that if there is a contribution from neighboring rings, it must be small. At the time that we initiated the work, we were planning to examine antiaromatic dianions so it seemed appropriate to include representatives of those species. As is clear from Fig. 2a, there is a linear relationship between these two measures of aromaticity–antiaromaticity, but it is not the same as for neutrals and cations. Anions are normally larger than cations, and it was known that magnetic susceptibility exaltation is related to the square of the ring area. When $\Sigma NICS(1)_{zz}$ was also divided by the area squared, the linear relation shown in Fig. 2b was obtained. Again, the inclusion of antiaromatic species revealed a relationship that would not have been apparent when only aromatic species were used, e.g., the behavior of the aromatic systems with negative values for magnetic susceptibility exaltation and $\Sigma NICS(1)_{zz}$.

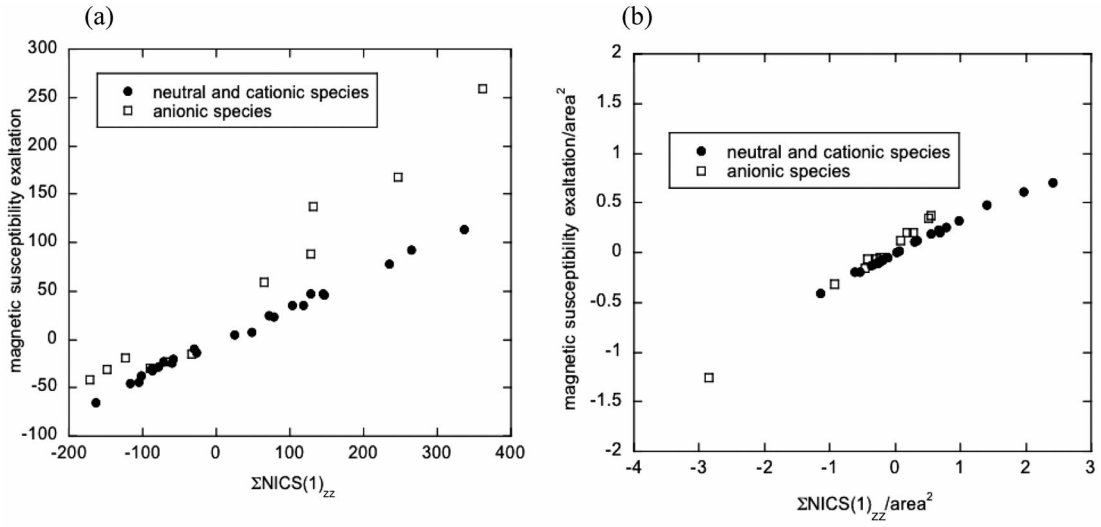


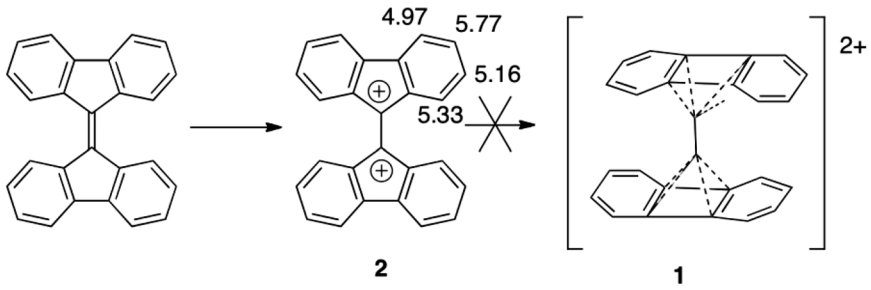
Fig. 2 (a) $\Sigma NICS(1)_{zz}$ vs. magnetic susceptibility exaltation for aromatic and antiaromatic dications and dianions. (b) $\Sigma NICS(1)_{zz}$ /area^2 vs magnetic susceptibility exaltation/area^2. Taken from ref. [18]. Used by permission of the American Chemical Society.

Others have observed a linear relationship between different measures of aromaticity when antiaromatic species were included. In a paper that attempted to determine "To what extent can aromaticity be determined uniquely?" [2], a set of five-membered ring compounds was examined using a variety of the measures of aromaticity. When antiaromatic species were included, there were statistically significant correlations between the various measures. However, the paper concluded with dissenting opinions. The majority opinion felt that when the comparison was restricted to aromatic compounds, "the energetic, structural, and magnetic descriptors of aromaticity do not speak with the same voice". The reluctance to include antiaromatic species in this comparison can arise from a number of factors, but a reluctance to place much value on a class of compounds whose calculated properties cannot be verified by comparison with experiment must play a role. Thus, the value of antiaromatic species in an understanding of aromaticity must be legitimized through their creation in the laboratory.

EXPERIMENTAL EXAMINATION OF ANTIAROMATIC DICATIONS

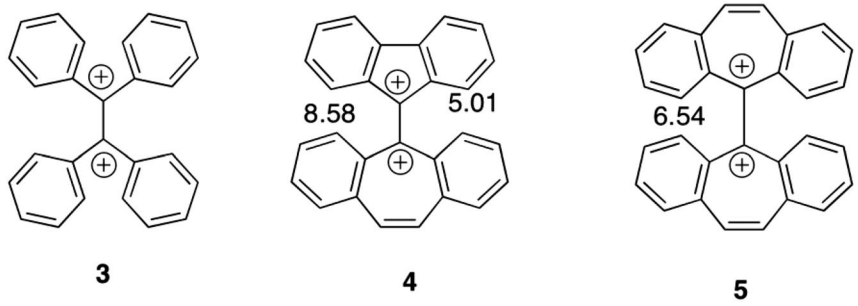
Our entré into this field began with an attempt to prepare a 3D aromatic species. Oxidation of tetrabenzo[5.5]fulvalene was anticipated to result in formation of the tetrabenzannulated derivative of a pyramidal dication **1** whose non-benzannulated parent [21] was predicted to possess the stability anticipated for a 3D aromatic compound, Scheme 1. However, oxidation stopped with **2**, which is formally an antiaromatic dication [22].

Verification of its antiaromatic character came from two experiments [22]. The average chemical shift of **2** was compared with that of the non-antiaromatic dication **3** and was shown to be 3.34 ppm upfield, a substantial paratropic shift. In addition, because calculations showed a large dihedral angle between the planar ring systems, the ortho proton on **2** impinges on the opposing ring system. Just as the bridgehead protons of the aromatic-1,6-methano[10]annulene are shifted upfield [23], the protons on the ortho position should be shifted downfield. To make this comparison, dications of tetrabenzo[5.7]fulvalene **4**, and of tetrabenzo[7.7]fulvalene, **5**, were synthesized. A comparison of the ortho proton on the fluorenyl systems of **2** and **4** reveals a shift that is slightly further downfield for **2** compared to **4**, 5.33 compared to 5.01 ppm. A more dramatic shift is seen for the ortho proton on the



Scheme 1 Formation of antiaromatic dication **2** by oxidation. ^{1}H NMR chemical shifts shown on species **2**.

dibenzotropylium system of **4**, which lies over the antiaromatic fluorenyl ring system, compared to the analogous proton of **5** (Scheme 2). The greater difference for the proton on the seven-membered ring is probably primarily due to the larger angle in that ring, which forces the ortho proton more completely into the magnetic environment of the opposing ring system.



Scheme 2 Dications **3–5**. Structures **4** and **5** showing ^{1}H NMR chemical shifts for the ortho protons of the 5- and 7-membered rings, respectively.

Thus, **2** is behaving as one would expect an antiaromatic species to behave in terms of magnetic properties, but was it unusual? We compared it to the substituted fluorenyl cations studied by Olah and Schleyer [24] who found a much smaller paratropic shift for the fluorenyl monocation compared to a diphenylmethyl derivative. We believe that the presence of the positively charged substituent on the fluorenyl ring diminished the ability of the antiaromatic ring system to "borrow" electron density from the substituent and therefore enhanced the aromaticity. This suggested that it would be possible to probe antiaromaticity in a systematic way by adjusting the nature of that charged substituent. Our recent work in this area in four systems is described below.

DICATIONS OF BENZYLIDENE FLUORENE: THE RELATIONSHIP BETWEEN MAGNETIC AND ENERGETIC MEASURES OF AROMATICITY

The antiaromaticity of the dications of benzylidene fluorenes **6** was examined by adjusting the electronic nature of the phenyl substituent through the electronic character and placement of substituents on it [25]. The argument previously made was that experimental properties could support the calculated measures of aromaticity. In the case of NICS, there is no experimental analogue but the same process by which NICS are calculated also calculates the ^{1}H and ^{13}C NMR shifts. The correlation between the calculated and experimental shifts for the dications that could be prepared by oxidation with

SbF_5/SO_2ClF is shown in Fig. 3. The good correlation suggests that the calculation of the chemical shifts and therefore the NICS are reliably measuring the magnetic environment. Table 1 shows the calculated $NICS(1)_{zz}$ for para-substituted **6** [25] and for the dications of para-substituted diphenylmethylidene fluorene **7** [26]. While the antiaromaticity of **7** is smaller than for comparable dications **6**, because the positive charge can be delocalized more effectively in **7**, it is clear that the greater the electron-withdrawing ability of the substituent, the larger the antiaromaticity of the fluorenyl system, as predicted.

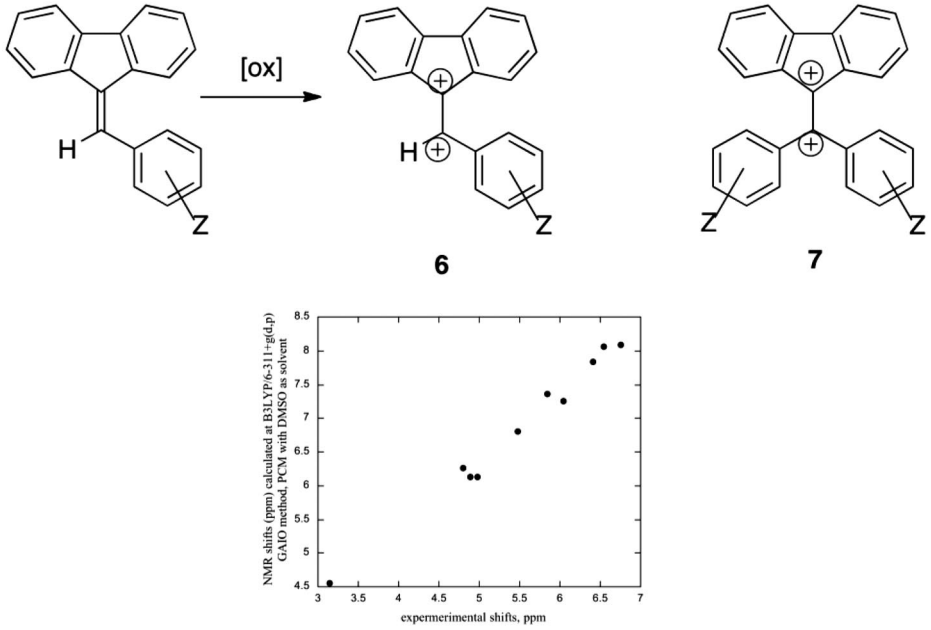


Fig. 3 Calculated vs. experimental ^{1}H NMR shifts for **6**, Z = *p*-OCH_3, see ref. [23] for details of the calculation. Used by permission of the American Chemical Society.

Table 1 Calculated $\Sigma NICS(1)_{zz}$ for *p*-substituted **6** and **7**, as well the $\Sigma NICS(1)_{zz}$ normalized by the square of the fluorenyl ring area.[a]

	6		**7**	
Z	$\Sigma NICS(1)_{zz}$	$\Sigma NICS(1)_{zz}$/area^2	$\Sigma NICS(1)_{zz}$	$\Sigma NICS(1)_{zz}$/area^2
CF_3	204.99	1.255	145.18	0.782
H	191.17	1.087	126.92	0.706
F	170.59	0.993	139.94	0.733
CH_3	155.36	0.907	129.85	0.681
OCH_3	145.37	0.842	98.64	0.649

[a]For details of the calculations, see refs. [25,26].

We also sought evidence of the instability of these dications by determination of the oxidation potential for their formation through cyclic voltammetry. The more positive the oxidation potential, the more difficult is the formation of the species. We compared the experimental oxidation potential with a calculated measure of stability, the difference in energy between the dications and their neutral precursors, ΔE. That comparison is shown in Fig. 4a for the species for which oxidation potentials could be observed. The relationship between a magnetic measure, $NICS(1)_{zz}$, and a measure of stability, ΔE, is

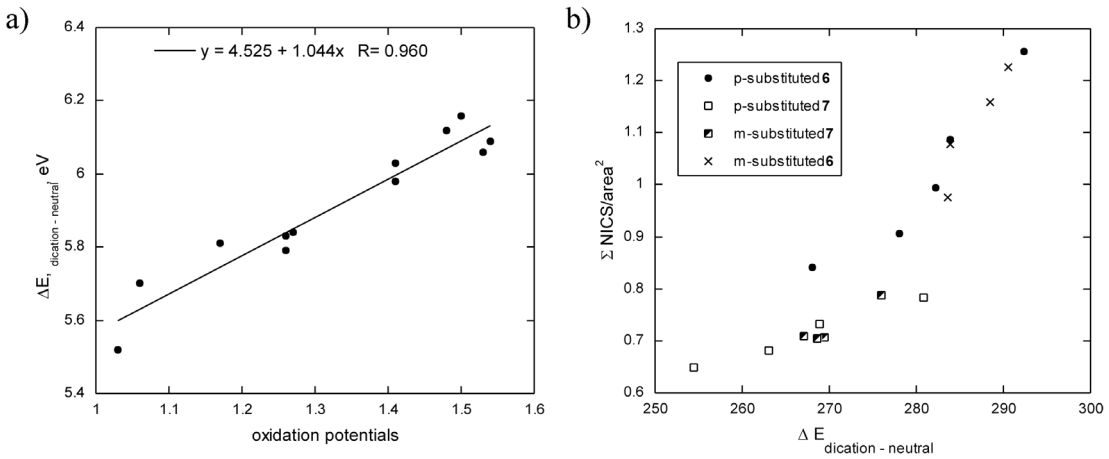
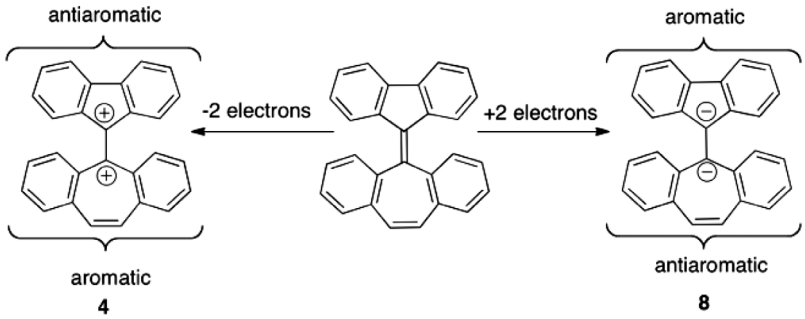


Fig. 4 (a) $\Delta E_{dication\text{-}neutral}$, in eV vs. oxidation potentials in eV. (b) $\Delta E_{dication\text{-}neutral}$, in eV vs. $\Sigma NICS(1)_{zz}$. See ref. [25]. Used by permission of the American Chemical Society.

given in Fig. 4b, and shows that, in general, there is a linear relationship between magnetic and energetic measures of antiaromaticity, and presumably aromatic measures, within similar systems. The ability to support calculated measures of aromaticity with experimental measures also means that we are able to then include in the comparison in Fig. 4a of species that could not be prepared experimentally, such as the electrochemical oxidation of the meta-substituted dication of **6**.

AN AROMATICITY–ANTIAROMATICITY CONTINUUM: DICATIONS AND DIANIONS OF TETRABENZO[5.7]FULVALENE

Oxidation of tetrabenzo[5.7]fulvalene to give dication **4** has already been discussed [27], but we were interested in the reduction with lithium or potassium to give the dianion **8** [28]. As is clear from Scheme 3, examination of the fluorenyl systems of **4** and **8** allows the comparison of an antiaromatic and an aromatic fluorenyl ion. In addition, the dibenzylcycloheptatrienyl systems of **4** and of **8** show the properties of an aromatic and an antiaromatic system, respectively. In essence, we can "toggle" back and forth between aromaticity and antiaromaticity in the same system, and do so in a way that allows both aromaticity and antiaromaticity to exist in the same charge state. The ^{1}H NMR spectra of **4** and **8** are given in Fig. 5 and demonstrate that antiaromatic species can be particularly well behaved spectroscopically. The examination of NICS as a function of bond length alternation, discussed in ref. [28], suggests the power of antiaromatic systems to reflect small changes in delocalization.



Scheme 3 Oxidation and reduction of tetrabenzo[5.7]fulvalene.

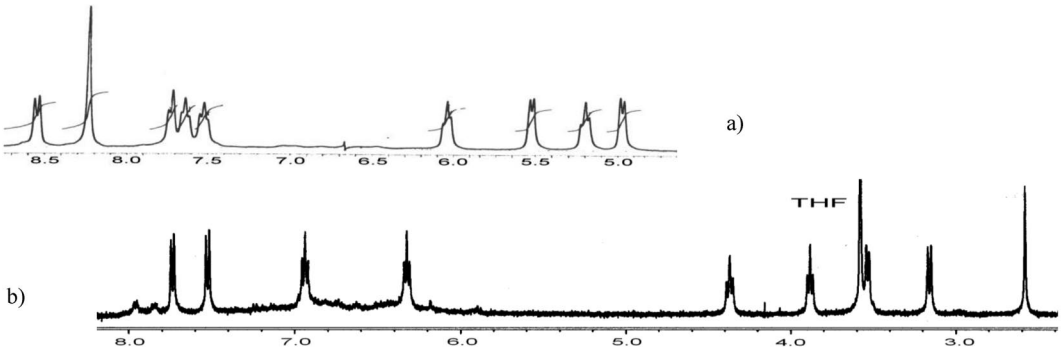


Fig. 5 (a) ^{1}H NMR spectrum of **4**. (b) ^{1}H NMR spectrum of **8**. See ref. [28]. Used by permission of the American Chemical Society.

OVER-REDUCTION OF BENZYLIDENE DIBENZOCYCLOHEPTATRIENES

The successful formation of **8** suggested that additional antiaromatic dianions might be accessible through reduction with alkali metals [29]. The reductions of the neutral precusors to **9** were monitored by ^{1}H NMR spectroscopy. Although color was seen in the reaction mixture within 5 min of contact with lithium, no spectrum was apparent until an hour after reduction, at which time the spectrum shown in Fig. 6 was obtained. Quench of the reaction mixture at that time with either D_2O or $(CH_3)_3SiCl$ revealed a substantial amount of product from **10**, as well as product from **9**, which was present in about 30 % of the abundance of **10**. The quench results suggested that both **9** and **10** should be visible in the NMR spectrum. Comparison of the calculated chemical shifts for **10** and **9** with the experimental shifts in Fig. 6 showed good agreement with **10** and no evidence of **9**, in contradiction to the evidence from the quench studies. Formation of **10** must involve formation of **9**, Scheme 4, yet the first species visible in the NMR spectrum was **10**. An explanation for the failure to observe the antiaromatic dianion might lie in the diminished highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap anticipated for antiaromatic species [30–32], which would allow access to diradical species and a broadened NMR spectrum. Dications **2**, **4**, and **6**, Z=OCH_3, and dianion **8** showed well-behaved ^{1}H NMR spectra; why would the spectrum of **9** be so broadened as to be invisible? Figure 7 shows that

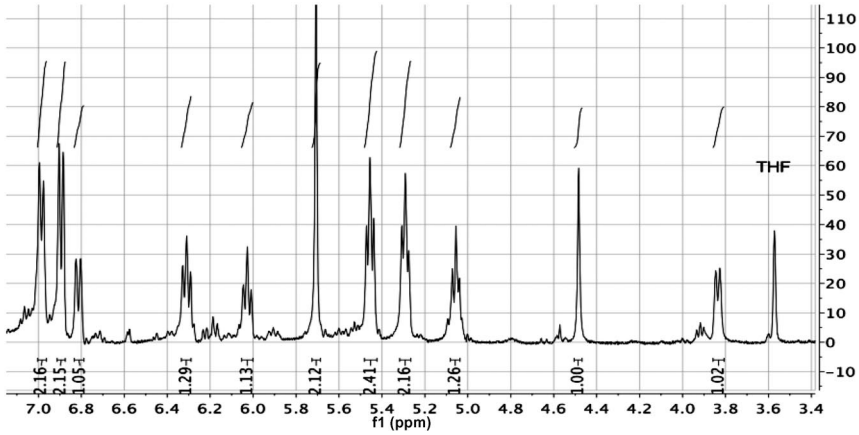
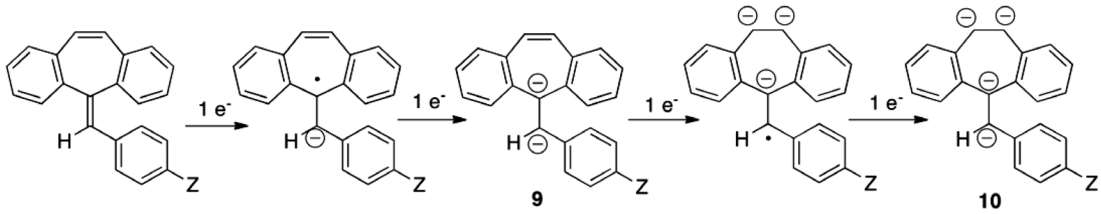


Fig. 6 ^{1}H NMR spectrum of **10**, R=H. See ref. [29]. Used by permission of the American Chemical Society.



Scheme 4 Reduction of substituted benzylidene cycloheptatrienes.

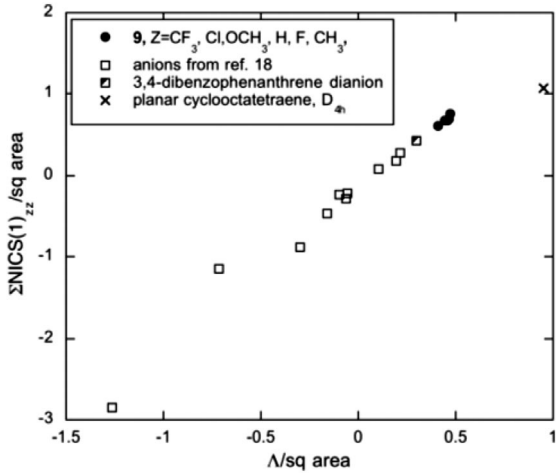


Fig. 7 $\Sigma NICS(1)_{ZZ}$ per square area vs. magnetic susceptibility exaltation, Λ, per square area. See ref. [29]. Used by permission of the American Chemical Society.

the dianions of **9** are the most antiaromatic species we and others have examined and should have the smallest HOMO–LUMO gap.

ANTIAROMATIC SPECIES AS PROBES OF DELOCALIZATION: DICATIONS OF PHENYL-SUBSTITUTED INDENYLIDENE FLUORENES WITH PHENYL SPACERS

The $NICS(1)_{ZZ}$ values for a series of phenyl-substituted indenylidene fluorenes with phenyl spacers **11–15** are shown in Table 2 along with data for the unsubstituted dication **16** [33]. The presence of a phenyl substituent would be expected to stabilize the cationic indenyl system, reducing its antiaromaticity. This is seen to be the case for **13–16**, compared to unsubstituted **11**, which have similar geometries; the phenyl substituent in the 2-position of **12** forces the phenyl spacer to assume a greater dihedral angle with the indenyl system.

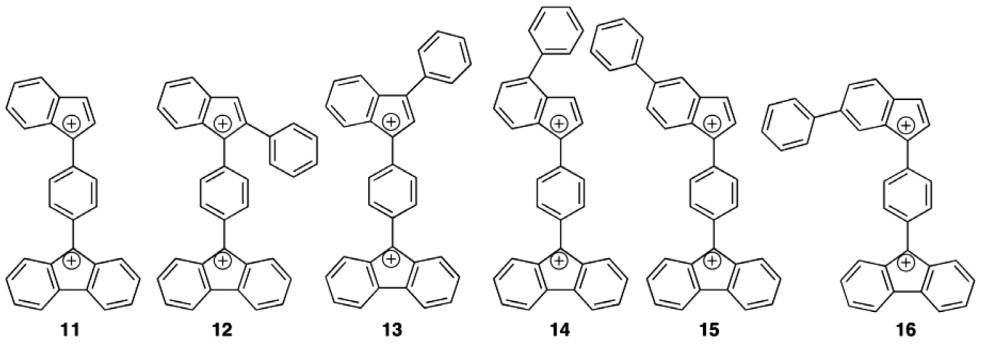
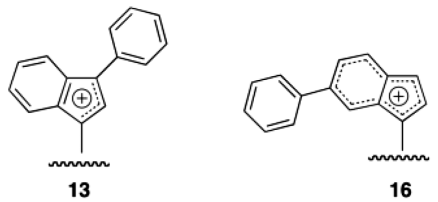


Table 2 $\Sigma NICS(1)_{zz}$ values for **11–15**.

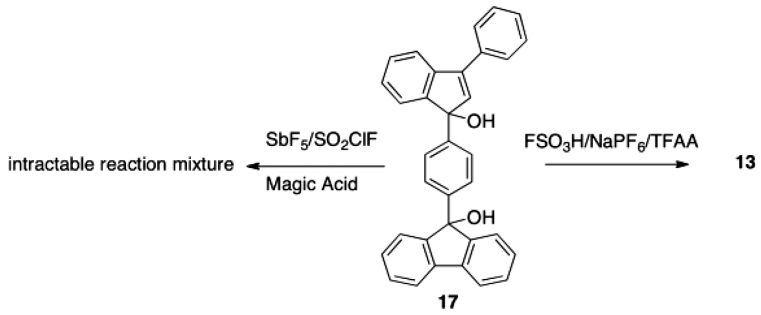
	11	**12**	**13**	**14**	**15**	**16**
$\Sigma NICS(1)_{zz}$ indenyl	101.87	152.86	43.22	57.35	75.79	79.22
$\Sigma NICS(1)_{zz}$ fluorenyl	105.98	90.84	86.57	86.14	90.47	79.50

If there is no change in geometry, what is the explanation for the diminished antiaromaticity of the indenyl system of **13** compared to that of **14–16**? We believe that the delocalization of the charge in **13** occurs primarily in the five-membered ring to give an allylic cation with a substantially intact benzene ring, see Scheme 5. However, if the phenyl substituent is located on the six-membered ring, the delocalization is forced to extend throughout the indenyl system, Scheme 4. The involvement of the phenyl substituent enhances the antiaromaticity of the system by promoting more extensive delocalization. This extensive delocalization is clearly visible in the greater antiaromaticity of the indenyl system of **14–16**, and should be evident in the ^{1}H NMR shifts of the indenyl system.



Scheme 5 Modes of delocalization promoted by the position of the phenyl substituent.

We have become involved in the preparation of antiaromatic dications with phenyl spacers related to **13–16** through ionization of the appropriate diol precursor with Magic Acid [34,35]. However, when diol **17** was reacted with Magic Acid, SbF_5/FSO_3H, the resulting ^{1}H NMR spectrum was sufficiently broad to prevent definitive assignment, see Scheme 6 and Fig. 8a. It seemed possible that the SbF_5 was capable of oxidizing the double bond of the five-membered ring of the indenyl alcohol. FSO_3H with trifluoroacetic anhydride (TFAA) had been reported to ionize alcohols to cations [36]. While this superacid gave ionization, we found that we had superior stability and resolution, as shown in Fig. 8b, when PF_6^-, was used as a stabilizing counterion [37]. The plot of calculated vs. experimental chemical shift, Fig. 9, showed that the new superacid had indeed doubly ionized the diol, to give the desired doubly antiaromatic dication. The ionization of other indenylidene fluorene diols with phenyl spacers with phenyl substituents is being examined, along with indenylidene fluorene diols with methyl substituents. With the aid of this new "super" acidic system, we anticipate the ability to form dications previously inaccessible.



Scheme 6 Effectiveness of ionization of diol **17** to give **13** in two different strong acids.

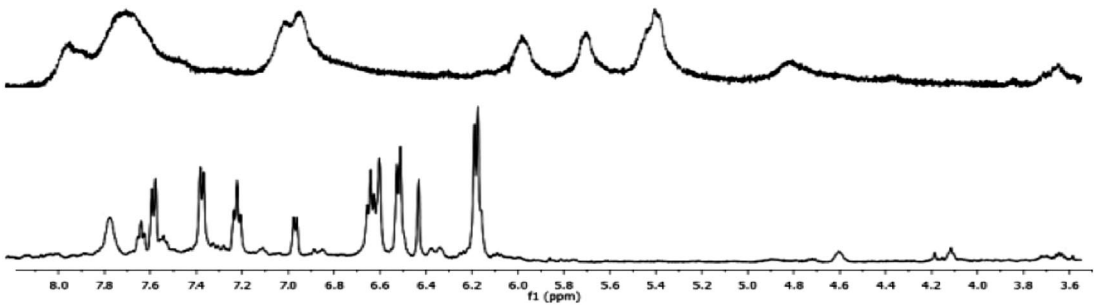


Fig. 8 (a) Ionization in Magic Acid. (b) Ionization in FSO_3H, $NaPF_6$,$(CF_3CO)_2O$.

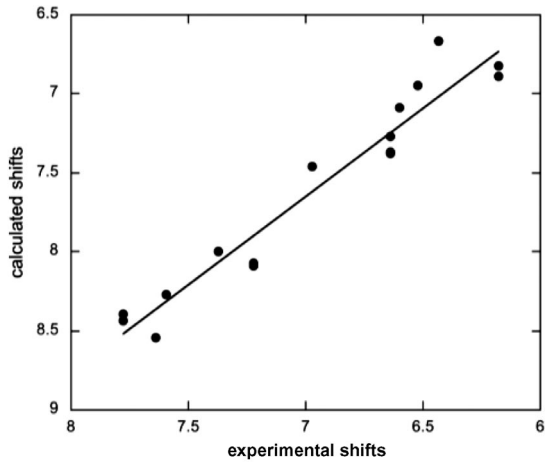


Fig. 9 Experimental vs. calculated shifts for **13**. Chemical shifts calculated with the GIAO method, B3LYP/6-311g(d,p)//B3LYP/6-31g(d). Solvent was included through use of the polarization continuum method (PCM) (solvent = DMSO).

CONCLUSIONS

Our research has shown that antiaromatic dications and dianions are much more accessible than previously believed. These antiaromatic species can be characterized by traditional methods such as NMR spectroscopy, which then allows an assessment of theoretical methods for the evaluation of anti-

aromaticity. That is, the linear relationships shown in Figs. 3 and 9 for species that contain both antiaromatic ring systems and benzyl cations or dications demonstrate that the chemical shifts calculated by the gauge-independent atomic orbital (GIAO) method with an appropriate basis set provide an accurate measure of the magnetic properties of antiaromatic species. Because NICS values are also calculated by the same method, this then provides a link between NICS and an experimental measure, the chemical shift. The linear relationship between ΣNICS/area^2 and the calculated magnetic susceptibility exaltation/area^2 further extends the connection between theoretical values, NICS and magnetic susceptibility, and experiment for antiaromatic species.

The accessibility of these species means that they can be prepared by alternative methods, such as electrochemical oxidation. Again, it is possible to identify a link between experimental and theoretical values, and to obtain some evidence for a link between different measures of aromaticity and antiaromaticity, although that link may depend on the system under study.

Reduction by electron transfer from an alkali metal can result in over-reduction to a more stable species, such as the reduction of benzylidene dibenzocycloheptatrienes to a tetraanion containing a tropenide trianion. The NMR spectral invisibility of the intermediate dianion can be rationalized as due to a small HOMO–LUMO gap for this highly antiaromatic dianion.

Finally, antiaromatic dications have been suggested as more sensitive probes to delocalization than aromatic ions [38]. Additional support for this suggestion has been shown by the generation of species like **13**, aided by the development of a new, non-oxidizing strong acid system.

The stability of antiaromatic dications and dianions is presumably enhanced by their charged natures, which diminished the amount of self-reaction. As discussed previously, their accessibility allows them to be considered as potential sources of diradicals because of their small HOMO–LUMO gaps and as very sensitive probes of electron delocalization, rather than simply as theoretical curiosities.

ACKNOWLEDGMENTS

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