

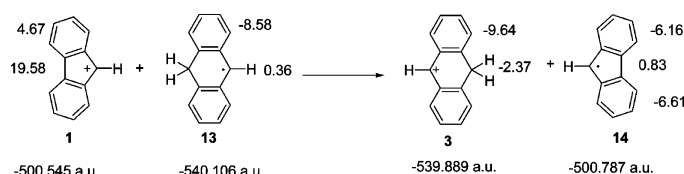
## Aromatic Stabilization Energy Calculations for the Antiaromatic Fluorenyl Cation. Issues in the Choice of Reference Systems for Positively Charged Species

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Aromatic stabilization energy (ASE) calculations for the fluorenyl cation show substantial destabilization in comparison to suitable reference systems ( $16.3 \pm 1.6$  kcal/mol), supporting its categorization as an antiaromatic species. The choice of appropriate reference systems is exacting for cationic systems because of the need to match strain energies, convolved with allylic-type resonance terms and other potential structural effects that stabilize charge. Several homodesmotic ASE reaction systems are examined to demonstrate the role played by these factors in the calculation of an ASE value for the fluorenyl cation. The magnitudes of the derived ASE are quite similar for four very different determinative, homodesmotic reaction systems, giving strong support to the inherent accuracy of the final derived ASE value. The results of nucleus independent chemical shift calculations for the components of each one of the ASE reactions add additional weight to this conclusion.

### Introduction

There is a great deal of current interest in the concept of aromaticity and its evaluation, including full dedicated issues of *Chemical Reviews*<sup>1</sup> and *Tetrahedron*<sup>2</sup> in 2001 and a series of review articles in *Physical Chemistry/Chemical Physics* in 2004.<sup>3–8</sup> Criteria used to evaluate the aromatic character of molecules and ions fall into three primary categories: energetic, structural, and magnetic.<sup>9,10</sup> The energetic criterion may be of greatest

interest because chemical structural factors that govern aromaticity can also determine relative stabilities and influence or control the outcomes of chemical reactions. Within this criterion, the most utilized method of evaluating aromatic stability is through isodesmic and homodesmotic reaction schemes, using nonaromatic reference structures with formal localized single and double bonds. In these reaction schemes, it is well understood that structural factors such as strain can distort the magnitude of a calculated aromatic stabilization energy, and there are several recent suggestions regarding the crucial choice of appropriate reference molecules.<sup>11,12</sup>

We have become involved in the evaluation of aromaticity through our characterization of a suite of fluorenylidene dication, exemplified in the following structure, that appear to be antiaromatic.<sup>13–21</sup> By modifying fluorenylidene dication, the cationic substituent, we are able

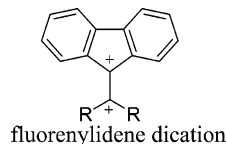
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to modify the antiaromaticity of the fluorenyl cation. Because we would like to use (anti)aromatic (de)stabilization energies to characterize these dication, it was important to ascertain the requirements for the reference systems used in these reaction schemes. Thus, this article describes the use of several homodesmotic, isotopological schemes for evaluating aromatic stabilization energies (ASE) for the fluorenyl cation.



We have chosen to consider the fluorenyl cation rather than the fluorenylidene dication shown above because of its greater simplicity. The antiaromaticity of the fluorenyl cation has been the subject of debate. Friedrich and Taggart<sup>22</sup> concluded that the fluorenyl cation was antiaromatic based on the observation that fluoren-9-yl 3,5-dinitrobenzoate was  $10^9$  less reactive toward solvolysis than would be expected in the absence of antiaromatic effects. Examination of the solvolysis of other fluorenyl derivatives<sup>23,24</sup> showed rate retardation compared to that of the analogous diphenylmethyl analogues, which was attributed to antiaromaticity. This view was challenged by Amyes et al.,<sup>25</sup> based on  $pK_R$  values and calculations that suggested that the fluorenyl cation was not exceptionally unstable. The lack of antiaromatic character in the fluorenyl cation was supported by calculation of magnetic susceptibility exaltation and nucleus independent chemical shifts (NICS) by Jiao et al.<sup>26</sup> More recently, Courtney et al.<sup>27</sup> have used  $pK_R$  values for the anthracenyl cation to argue for destabilization of the fluorenyl cation that is equal in magnitude to the stabilization of the fluorenyl anion. They argue that if the fluorenyl anion is to be considered aromatic on the basis of this stabilization, the fluorenyl cation must be antiaromatic.

**Calculations and Design Protocols for ASE Reactions of Cationic Aromatic Hydrocarbons.** Geometries were optimized at the DFT/B3LYP/6-31G(d) level using Gaussian 03, revision B.03.<sup>28</sup> To provide additional contextual perspective, we also report the results from NICS calculations with the GIAO method at the same theoretical level and B3LYP/6-31G(d) as an additional

assessment of antiaromaticity. NICS<sup>29</sup> has been shown to be an effective measure of aromaticity and antiaromaticity, and NICS values have recently been correlated with experimental measures of aromaticity<sup>30</sup> and antiaromaticity.<sup>18–21</sup> The NICS values are calculated at the center of the ring system of interest and are negative for aromatic ring systems and 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, as is done in the present investigation.<sup>31</sup> We have also shown in previous studies of dication that <sup>1</sup>H and <sup>13</sup>C NMR shifts calculated at the B3LYP/6-31G(d) level on geometries optimized at the same level show a good linear correlation with experimental shifts.<sup>17–21</sup> The excellent agreement between calculated and experimental shifts in other antiaromatic systems suggests that NICS calculations by this method and at this level are reliable aromaticity measures.

In the design of reference structures, the main tools for switching off cyclic resonance are insertions of fully saturated atoms or exocyclic double bonds into the aromatic ring under investigation.<sup>32</sup> In neutral systems, these tools, using reference structures that give an effective overall cancellation of strain energy, are sufficient to deal with a great variety of ASE problems. However, the design of reference systems for charged species presents particular challenges in the choice of reference systems because both aromaticity switches are associated with structural effects that influence charge effects, independent of the effects of cyclic conjugation that give rise to aromaticity. In the case of cationic aromatic systems, both operations can stabilize charge due to well-known classical mechanisms: the first through hyperconjugative effects, and the second by increasing the opportunities for allylic-type resonance stabilization. Finally, an additional factor may simply be the general charge stabilizing effect of increasing molecular size, inferable from studies of gas-phase acidities<sup>33,34</sup> ionization

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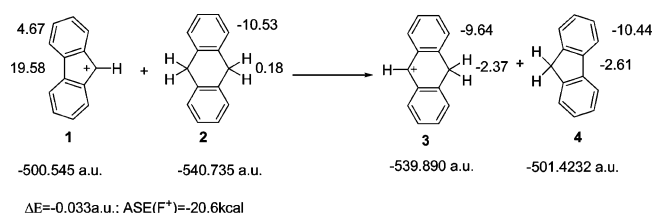
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## SCHEME 1



energies,<sup>35</sup> and proton affinities.<sup>36</sup> Thus, a perfect ASE equation for a charged system would simultaneously match strain energies, nonaromatic resonance effects, and molecular size effects to isolate the aromaticity factor of interest. We propose to deal with these difficulties as follows.

To equate strain, we will construct homodesmotic ASE reactions that duplicate the hybridization and substitution patterns of all atoms in reactants and products, up to and including the neighboring atoms of every atom (nearest-neighbor atom types, NN atoms). Every ring in the ASE reaction can also be exactly matched for size and for the sequence of NN atoms in the ring. Then, in the general case, a requirement of equivalence for twist, curvature, and any other topological distortion present in the optimized molecular frameworks of the products and reactants would be imposed. That is, individual ring topologies and overall three-dimensional geometries are duplicated between the reactants and products of each NN atom homodesmotic ASE reaction.

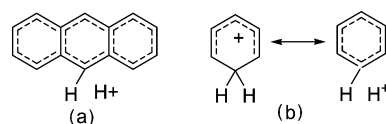
These restrictions on the molecular structures can be taken to rigorously define a class of isotopological homodesmotic (IHD) ASE reactions.<sup>37</sup> The topology and geometry isometries in an IHD/ASE chemical equation make it unnecessary to calculate or estimate strain energies. The issues related to charge stabilization and destabilization are more difficult to summarize succinctly and will be, therefore, exemplified and discussed in the context of several examples to be presented in the next section.

## Results and Discussion

The first system examined is shown in Scheme 1, with the NICS values shown adjacent to the appropriate ring system. Reasonable cancellation of the strain energies of reactants and products should be obtained due to the overall equivalence of ring types and sizes. Thus, this seems to be a good quality homodesmotic reaction, and the mismatches of exact sequences of atom types in the five- and six-membered rings should have little effect on the ASE estimate. There is a strong inference that the antiaromaticity energy for **1** is substantial. The NICS values of 19.58 for the five-membered ring and 4.67 for the six-membered ring support this conclusion. Jiao et al.<sup>26</sup> concluded that the NICS values for the fluorenyl cation (NICS-5, 24.7; NICS-6, 1.9) suggested that the fluorenyl cation was nonaromatic. However, these cal-

culations were done at the Hartree–Fock level, which does not include electron correlation. Our density functional calculations on fluorenyl cations<sup>17</sup> showed better agreement between experimental and calculated chemical shifts for calculations done at B3LYP/6-31G(d) than with RHF/6-31G(d), suggesting that the NICS values with the density functional method are more accurate.<sup>37</sup> The NICS values for the six-membered rings of **2** and **4** are negative and show that the aromaticity of the benzene rings in those species is affected very little by the ring size. The smaller value of NICS for the six-membered ring of **3** suggests that there is some decrease in aromaticity in this benzylic cation, which is not unexpected.<sup>38</sup>

However, two molecular structural elements suggest that the  $-20.6$  kcal antiaromaticity value is probably an overestimate. Both factors are associated with excess stabilization of the cationic reference structure **3** compared to that of **1**. The first stabilizing factor is simply the larger size of **3**, and the second is the cation stabilizing effect of the methylene alkyl group in the central ring. In fact, as depicted in the structure below in (a), if one models either hyperconjugation or the general inductive effect of the methylene group by using no-bond resonance structures, the **3** system can be depicted as possessing three six-membered aromatic rings, with a no-bond to  $\text{H}^+$  on the central ring.



The six-membered ring of (b) in the above structure is similar to the central ring of (a). The NICS value for (b),  $-5.61$ , gives support to the latent aromaticity of the six-membered ring of (b). The small negative NICS values for the central ring of **3** also lend modest support for this rationale, and as expected, C–C bonds to the methylene group in **3** are shorter, and the C–H bonds longer, than the respective corresponding bonds for neutral reference compound **2** in Scheme 1. Also, in two related ASE studies on the parent  $\text{C}_6\text{H}_7^+$ , the cyclohexadienyl cation is found to have an average total calculated stabilization energy of  $4.0 \pm 0.5$  kcal/mol, for which the simplest and most reasonable explanation is a homoconjugative effect as pictured in (b).<sup>39</sup>

Addition of a methyl group to the fluorenyl system will increase the size of the fluorenyl system so that it is closer to that of the anthracenyl system and, if properly placed, will allow additional opportunities for hyperconjugation. These structural variations are exemplified in Scheme 2, and just as anticipated, there is a reduction in the calculated antiaromaticity term for the fluorenyl cation from Scheme 1 of 5.0 kcal due to the sum of two factors outlined in the earlier discussion. The capability of the methyl substituent to replicate inductive and homoconjugation effects of the aliphatic methylene (Scheme 1) is difficult to judge. The value of 5.0 kcal is close to the 4.0 kcal value attributable solely to homoconjugative stabi-

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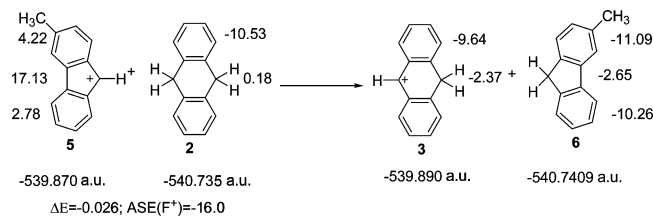
(37) Numerous examples of IHD/ASE methodology have been designed and evaluated in our previous ASE studies (unpublished), presented at three international symposia (WATOC, Imperial College, London, August, 1999; EUOC-CC3, Budapest, 2000; ISNA 2001, San Diego, CA, July, 2001).

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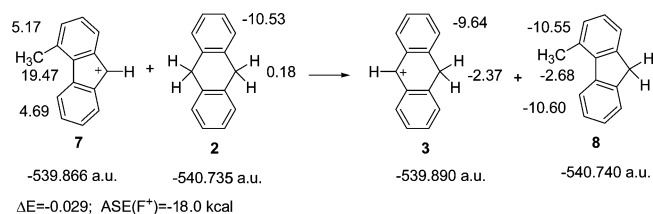
(39) See Supporting Information.



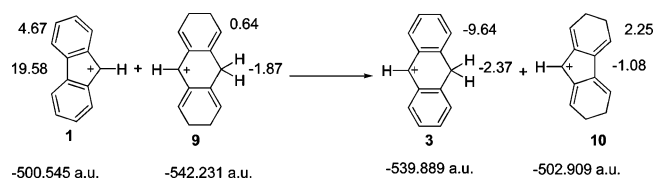
## SCHEME 2



## SCHEME 3



## SCHEME 4

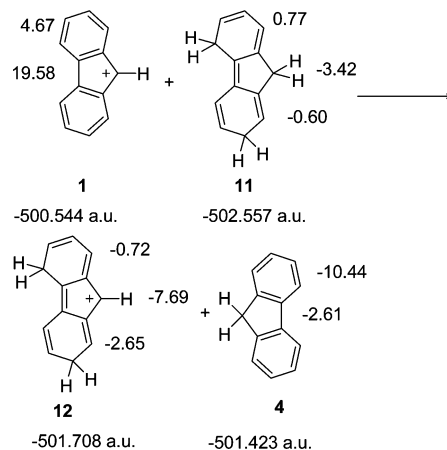


lization of structure (b), the analogous monocyclic cation. This does not imply that the cation molecular size factor is an unessential part of the design of an accurate ASE equation. The more reasonable explanation is simply that homoconjugation is more important in the small monocyclic cation than in the larger tricyclic cation. This would, of course, be due to the average 3-fold larger density of positive charge on the atoms of the smaller cation. Be that as it may, all major molecular structure restrictions required to give an accurate value of the ASE antiaromaticity component have certainly been met in this chemical equation. Thus, the  $-16.0$  kcal ASE value should be a good estimate for the antiaromaticity component of the fluorenyl cation.

Some confirmation of the importance of the size of the molecular system independent of hyperconjugation comes from the ASE shown in Scheme 3, in which a methyl substituent has been added to **1** in a position in which it cannot interact as effectively via hyperconjugation. The difference in the ASE antiaromaticity component in Scheme 3 from that in Scheme 2 is 2.0 kcal, which suggests this value as a lower bound on the stabilization due to hyperconjugation in this system. The presence of a methyl substituent on the fluorenyl system decreases the antiaromaticity of the five- and six-membered rings in **5** compared to the unsubstituted fluorenyl cation **1**, while the six-membered rings of **7** show a slight increase in antiaromaticity relative to **1**. These changes would be consistent with more effective hyperconjugation in **5**, resulting in greater stabilization, and a decrease in antiaromaticity.

We propose that calculated ASE values can be assessed as reliable when a number of alternative, distinctly dissimilar, isotopological homodesmotic equations give markedly similar ASE results. The remaining examples will illustrate this viewpoint. First, in Scheme 4, we examine the antiaromaticity of cationic fluorenyl ion by

## SCHEME 5



designing an ASE equation scheme in which all species are cationic, including all of the reference structures. This can be done by using saturated dimethylene bridges to interrupt cyclic delocalization, as shown in Scheme 4. This latter design feature should lead to an efficient cancellation of molecular size dependent charge effects. The validity of the overall approach and the methodology for designing both types of ASE equations is supported by the good agreement of the calculated  $\Delta E$  values for the antiaromaticity component of the fluorenyl cation in Schemes 2 and 4, respectively.

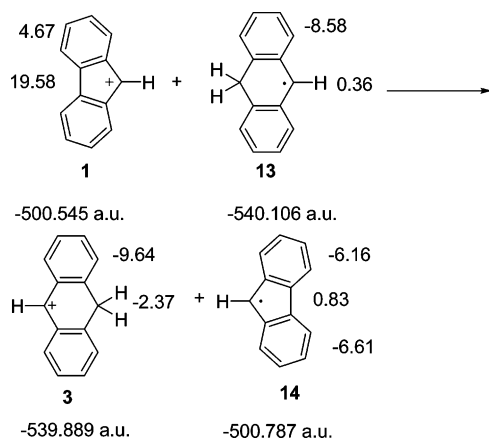
Another example of an ASE reaction for the antiaromaticity character of fluorenyl cation, using a completely different design restriction, is given in Scheme 5. The reaction in Scheme 5 has a property that none of the other examples possess. Aromaticity, following from the valence bond representations of the various reference structures, is only present in one of the reference structures, and that structure (**4**) is a typical, neutral, simple aromatic compound, containing two typical aromatic benzene rings. The calculated ASE for the fluorenyl cation, once again, denotes an antiaromatic structure, consistent with the other calculations that have been presented.

Radical species offer an alternative way of ensuring a match of strain energy, nonaromatic resonance effects, and molecular size, as shown in Scheme 6.<sup>40</sup> Radical species such as the cyclopropenyl radical have been suggested to be nonaromatic rather than aromatic or antiaromatic.<sup>41</sup> The calculated geometries of **1/14** and **3/13** are highly congruent, which argues for an effective cancellation of strain. Yet again, the ASE value for the fluorenyl cation is within the narrow range of calculated antiaromaticity seen from Schemes 2, 4, and 5. The NICS values for **3** and **13** are also quite similar and suggest that the stabilization present in this reference cation and radical is similar, and in this respect the systems are well matched and relatively similar to those in **14**. However, the comparison of NICS values for **1** with those of **14** again supports the classification of **1** as antiaromatic.

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## SCHEME 6



## Conclusion

The average value from Schemes 2, 4–6 is  $-16.3 \pm 1.6$ , illustrating the antiaromaticity of the fluorenyl cation. The close agreement between the values for the ASE for the antiaromatic fluorenyl cation from four very different ASE systems suggests that the value is reliable. The NICS values in general support the assumptions in the choice of compounds for Schemes 1–6, with **1** clearly

antiaromatic, while the formal benzene rings of the remaining compounds show the expected NICS aromaticity. Rings that are not completely conjugated show NICS values that are close to zero, as anticipated. The only unanticipated result is for the central ring of **12**, which shows a somewhat larger negative value of NICS than anticipated.

This is the first use of radical species in aromatic stabilization energy calculations of charged species. The consistency of the ASE value from Scheme 6 with that found from more “traditional” isodesmic, homodesmotic reactions suggests that radical species should be considered more widely for inclusion in ASE calculations of charged species.

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**Supporting Information Available:** A table of calculated symmetries, total energies, and  $[x,y,z]$  coordinates for **1–14**; ASE calculations for  $C_6H_6^+$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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