ORGANIC
LETTERS

2013
Vol. 15, No. 12
2990–2993

Substituent Effects on “Hyperconjugative” Aromaticity and Antiaromaticity in Planar Cyclopolyenes

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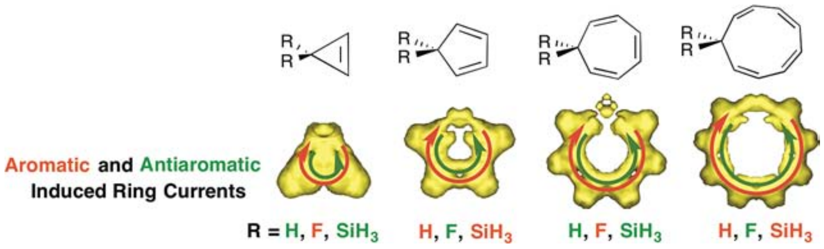
Received April 24, 2013

ABSTRACT



Computed aromatic stabilization energies (ASEs) and dissected nucleus independent chemical shifts (NICS$_{\pi zz}$) quantify the effect of hyperconjugation on the (anti)aromaticities of the planar conformations of three, five, seven, and nine membered (C_nH_n)CR_2 (R = H, SiH_3, F) rings. CH_2 and especially $C(SiH_3)_2$ groups supply two “pseudo” π electrons hyperconjugatively along with the olefinic π electrons in the ring, whereas a CF_2 group acts like a partially vacant p orbital. Following the Hückel rule, compounds with $4n+2$ (or $4n$) pseudo π electrons are “hyperconjugatively” aromatic (or antiaromatic).

Mulliken first considered that cyclopentadiene might be aromatic with 6π electrons,[1a] as the saturated CH_2 group can contribute a pair of “pseudo” 2π electrons by hyperconjugation to the four olefinic π electrons in the ring. Indeed, cyclopentadiene displays a “considerably longer”[1a] UV absorption wavelength than typical open-chain dienes. Nyulászi and Schleyer[2a] confirmed and extended this interpretation. Computed nucleus independent chemical shift (NICS), magnetic susceptibility, and aromatic stabilization energy (ASE) analyses revealed that substitution of the H’s in the saturated CH_2 group by electropositive substituents (e.g., SiH_3, GeH_3, SnH_3) led to enhanced hyperconjugative (pseudo 6π e) aromaticity, while electronegative substituents (e.g., F, Cl) resulted in (pseudo 4π e) antiaromatic five membered ring systems (see Figure 1a).[2c] Similarly, nonatetraenes with electropositive substituents were found to exhibit 10 π electron aromaticity.[2b]

Following Mulliken,[1b] who also applied the hyperconjugation concept to the benzenium ion (i.e., protonated benzene, $C_6H_7^+$), O’Ferrall et al. coined the term “hyperaromaticity”[3] to explain its higher stability than, e.g., the cycloheptadienyl cation. Like cyclopentadiene, the CH_2 group of the benzenium cation can participate hyperconjugatively with the ring π system, resulting in 6π e aromaticity.[1b,3] Thus, the computed dissected NICS, NICS(0)$_{\pi zz}$,[4] for the parent benzenium cation (−18.0 ppm) is half that of benzene (−35.9 ppm). The disilylated benzenium cation,

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(1) (a) Mulliken, R. S. *J. Chem. Phys.* **1939**, *7*, 339. (b) Pickett, L. W.; Muller, N.; Mulliken, R. S. *J. Chem. Phys.* **1953**, *21*, 1400. (c) Also see: Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *115*, 6987.

(2) (a) Nyulászi, L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6872. (b) Schleyer, P. v. R.; Nyulaszi, L.; Kárpáti, T. *Eur. J. Org. Chem.* **2003**, 1923. (c) Stanger’s reservations to the conlusions of ref 2a (see Stanger, A. *Chem.—Eur. J.* **2006**, *12*, 2745) are answered here by employing more sophisticated NICS and energetic evaluations.

(3) (a) Lawlor, D. A.; Bean, D. E.; Fowler, P. W.; Keeffe, J. S.; Kudavalli, J. S.; O’Ferrall, R. A. M.; Rao, S. N. *J. Am. Chem. Soc.* **2011**, *133*, 19729. (b) Kudavalli, J. S.; Boyd, D. R.; Sharma, N. D.; O’Ferrall, R. A. M. *J. Org. Chem.* **2011**, *76*, 9338. We prefer the term “hyperconjugative aromaticity” over “hyperaromaticity.” The latter imposes some ambiguity, as the prefix “hyper-” can imply other terms, e.g. hypervalency, hypercoordinate.

(4) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863.

10.1021/ol401154r

$C_6H_5(SiH_3)_2^+$ (NICS(0)$_{\pi zz}$ = −27.9 ppm), exhibits enhanced "hyperaromaticity" while $C_6H_5F_2^+$ (NICS(0)$_{\pi zz}$ = +12.1 ppm) is "hyperantiaromatic."[3a]

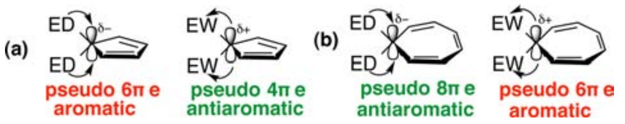


Figure 1. Schematic illustration of "hyperconjugative aromaticity" and "hyperconjugative antiaromaticity" in cyclopentadiene and cycloheptatriene derivatives with electron-withdrawing (EW) or electron-donating (ED) substituents.

This paper examines manifestations of hyperconjugative aromaticity and antiaromaticity in the planar forms of a series of neutral cyclopropene, cyclopentadiene, cycloheptatriene, and cyclononatetraene derivatives $(C_nH_n)CR_2$ (R = H, SiH_3, F, n = 2, 4, 6, 8) (see Figure 2).

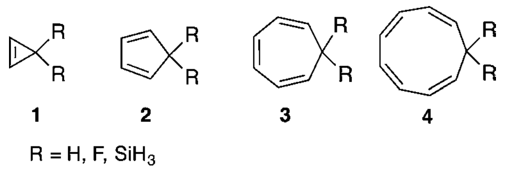
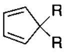
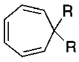
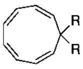


Figure 2. Three (**1**), five (**2**), seven (**3**), and nine (**4**) membered $(C_nH_n)CR_2$ rings (n = 2, 4, 6, 8), with R = H, F, and SiH_3, considered in their planar forms.

We demonstrate conclusively that hyperconjugation involving the σ-C−R bonds of such partially conjugated planar $(C_nH_n)CR_2$ systems can extend π conjugation to complete the cyclic array. This leads to hyperconjugative aromaticity or antiaromaticity depending on the nature of the substituents involved. Following the Hückel rule for monocyclic aromatics, pseudo $4n+2$ π electron systems are aromatic, whereas pseudo $4n$ π electron systems are antiaromatic (see Figure 1).

Our evaluations of the ASEs of **1**−**4**, based on two distinct computational procedures, i.e., the energy decomposition analysis (EDA)[5] (at BP86/TZ2P+)[6] and the block localized wave function (BLW)[7] methods (vertical BLW computations at B3LYP/6-31G*), give highly consistent trends (see Table 1) and correlate excellently (R^2 = 0.97; see Figure 1S in the Supporting Information).[2c] EDA computations examine π interaction energies (ΔE_π)[8] between the manually selected fragments of a molecule. The BLW method[7] evaluates π delocalization energies (DE_π) by comparing the energy difference between the fully delocalized, completely optimized molecule and its most stable resonance contributor under the imposed BLW constraint.

Table 1. Computed EDA-ASE[8] (in kcal/mol, at BP86/TZ2P+), Vertical BLW-ASE[7] (in kcal/mol, at B3LYP/6-31G*), and NICS(0)$_{\pi zz}$[4] (in ppm, at PW91/IGLOIII, *at PW91/IGLOII) Values for Three, Five, Seven, and Nine Membered $(C_nH_n)CR_2$ rings (n = 2, 4, 6, 8), **1**−**4**, R = H, F, and SiH_3

Compound	R	EDA-ASE	BLW-ASE	NICS(0)$_{\pi zz}$
	H	−2.9	+0.4	+2.75
	F	+7.9	+11.3	−1.89
1	SiH_3	−13.0	−8.9	+10.27
	H	+4.2	+3.0	−11.44
	F	−10.1	−7.3	+16.41
2	SiH_3	+11.2	+9.1	−18.33
	H	−6.5	−3.9	+24.42
	F	+5.5	+4.8	−2.42
3	SiH_3	−13.7	−15.7	+55.38
	H	+11.8	+8.6	−19.91*
	F	−9.4	−7.0	+20.71*
4	SiH_3	+25.4	+18.3	−25.35*

The EDA/BLW-ASEs are derived by the computed $\Delta E_\pi/DE_\pi$ difference between **1**−**4** (R = H, F, SiH_3) and their appropriate acyclic references, which have the same number and type of conjugative/hyperconjugative interactions (see details in the Supporting Information). For example, the EDA/BLW-ASEs of cyclopentadiene, **2(H)** (EDA-ASE = +4.2, BLW-ASE = +3.0 kcal/mol) are derived by the computed $\Delta E_\pi/DE_\pi$ difference between **2(H)** (ΔE_π = 41.4, DE_π = 27.7 kcal/mol) and 1,3,6-heptatriene (ΔE_π = 37.2, DE_π = 24.7 kcal/mol). As both cyclopentadiene and 1,3,6-heptatriene have one butadiene-type conjugation and two alkene hyperconjugations, the computed $\Delta E_\pi/DE_\pi$ differences give the EDA/BLW-ASEs. Positive ASE values indicate aromaticity while negative ASE values denote antiaromaticity.[9−11]

The BLW procedure has been applied to study the aromatic nature of organic compounds,[9] and recently to quantify the ASEs of porphyrinoids for the first time.[10] The EDA approach also is well-established and has been employed to quantify the ASEs of typical (anti)aromatic organic compounds,[11a] metallabenzenes,[11b] methylenecyclopropane analogues,[11c] and the group 14 homologues of the cyclopropenylium cation.[11d]

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[5] For a recent review on the EDA, see: von Hopffgarten, M.; Frenking, G. *WIREs: Comput. Mol. Sci.* **2012**, *2*, 43.

[6] See computational details in the Supporting Information.

[7] (a) Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687. (b) Mo, Y.; Zhang, Y.; Gao, J. *J. Am. Chem. Soc.* **1999**, *121*, 5737. (c) Mo, Y. *J. Chem. Phys.* **2003**, *119*, 1300. (d) Mo, Y.; Song, L.; Lin, Y. *J. Phys. Chem. A* **2007**, *111*, 8291. (e) Mo, Y.; Hiberty, P. C.; Schleyer, P. v. R. *Theor. Chem. Acc.* **2010**, *127*, 27.

[8] (a) Cappel, D.; Tüllmann, S.; Krapp, A.; Frenking, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 3617. (b) Fernández, I.; Frenking, G. *Chem.—Eur. J.* **2006**, *12*, 3617. (c) Fernández, I.; Frenking, G. *J. Org. Chem.* **2006**, *71*, 2251. (d) Fernández, I.; Frenking, G. *Chem. Commun.* **2006**, 5030. (e) Fernández, I.; Frenking, G. *J. Phys. Chem. A* **2007**, *111*, 8028. (f) Fernández, I.; Frenking, G. *J. Org. Chem.* **2007**, *72*, 7367.

[9] Mo, Y.; Schleyer, P. v. R. *Chem.—Eur. J.* **2006**, *12*, 2009.

[10] Wu, J. I.; Fernández, I.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2013**, *135*, 315.

[11] (a) Fernández, I.; Frenking, G. *Faraday Discuss.* **2007**, *135*, 403. (b) Fernández, I.; Frenking, G. *Chem.—Eur. J.* **2007**, *13*, 5873. (c) Wang, Y.; Fernández, I.; Duvall, M.; Wu, J. I.; Li, Q.; Frenking, G.; Schleyer, P. v. R. *J. Org. Chem.* **2010**, *75*, 8252. (d) Fernández, I.; Duvall, M.; Wu, J. I.; Schleyer, P. v. R.; Frenking, G. *Chem.—Eur. J.* **2011**, *17*, 2215.

As shown in Table 1, the involvement of the pseudo 2π electrons of the CH$_2$ groups result in alternating effects on the aromaticities and antiaromaticities of the parent unsubstituted **1(H)**−**4(H)** series. Cyclopentadiene and cyclononatetraene, **2(H)** (EDA/BLW-ASE: +4.2/+3.0 kcal/mol, pseudo 6π e) and **4(H)** (+11.8/+8.6 kcal/mol, pseudo 10π e), have positive EDA/BLW ASEs and are aromatic. Conversely, cyclopropene **1(H)** (−2.9/+0.4 kcal/mol, pseudo 4π e) and cycloheptatriene **3(H)** (−6.5/−3.9 kcal/mol, pseudo 8π e) have negligible positive to modestly negative EDA/BLW-ASEs and are nonaromatic or weakly antiaromatic. In **1(SiH$_3$)-4(SiH$_3$)**, the greater hyperconjugative donor power of the C−SiH$_3$ bonds leads to more positive EDA/BLW-ASE values for the hyperconjugatively aromatic **2(SiH$_3$)** (+11.2/+9.1 kcal/mol) and **4(SiH$_3$)** (+25.4/+18.3 kcal/mol) and more negative values for the hyperconjugatively antiaromatic **1(SiH$_3$)** (−13.0/−8.9 kcal/mol) and **3(SiH$_3$)** (−13.7/−15.7 kcal/mol).

The magnitudes of the EDA/BLW-ASEs of **1(H)**−**4(H)** and **1(SiH$_3$)**−**4(SiH$_3$)** depend also on the number of pseudo π electrons. For the $4n$+2 π electron systems, both **4(H)** and **4(SiH$_3$)** (pseudo 10 π e) have much more positive ASE values compared to **2(H)** and **2(SiH$_3$)** (pseudo 2π e). Likewise, for the 4n π electron systems, both **3(H)** and **3(SiH$_3$)** (pseudo 8π e) have much more negative ASE values compared to **1(H)** and **1(SiH$_3$)** (pseudo 4π e). The computed magnetic NICS(0)$_{\pi zz}$ values (see below and Table 1) for **1**−**4** follow the same trend.

In sharp contrast, the difluorinated **1(F)**−**4(F)** compounds display reversed hyperconjugative (anti)aromaticity trends relative to their **1(H)**−**4(H)** and **1(SiH$_3$)**−**4(SiH$_3$)** analogs. As the F's are strongly electron withdrawing, the CF$_2$ groups do not contribute any pseudo π electrons to the ring systems, but resemble partially "empty" p orbitals with carbocationic character. Hence, the π conjugation in **1(F)**, **2(F)**, **3(F)**, and **4(F)** involve only two, four, six, and eight formal π electrons, respectively, and their (anti)aromaticities follow the Hückel rule. The three and seven membered rings, **1(F)** (+7.9/+11.3 kcal/mol, pseudo 2π e) and **3(F)** (+5.5/+4.8 kcal/mol, pseudo 6π e), have positive EDA/BLW ASEs and are $4n$+2 π aromatic, while the five and nine membered rings, **2(F)** (−10.7/−7.3 kcal/mol, pseudo 4π e) and **4(F)** (−9.4/−7.0 kcal/mol, pseudo 8π e), have negative EDA/BLW-ASEs and are $4n$ π antiaromatic. Compared to **1(F)**, the cyclopropenylium cation has much higher positive EDA-ASE (+33.2 kcal/mol) and BLW-ASE (+34.0 kcal/mol) values.[11d]

Computed dissected NICS(0)$_{\pi zz}$[4] and the anisotropy of the induced current density (ACID)[12] plots of **1**−**4** (R = H, F, SiH$_3$) agree qualitatively with the EDA/BLW-ASE findings. The dissected NICS(0)$_{\pi zz}$ values, computed at the heavy atom centers of **1**−**4**, are based on the out-of-plane (zz) tensor components of the isotropic NICS and include only the π-contributions. Negative NICS(0)$_{\pi zz}$ values indicate aromaticity whereas positive NICS(0)$_{\pi zz}$ values indicate antiaromaticity. As shown in Table 1, the NICS(0)$_{\pi zz}$ for **2(H)** (−11.4 ppm), **4(H)** (−19.9 ppm), **1(F)** (−1.9 ppm), **3(F)** (−2.4 ppm), **2(SiH$_3$)** (−18.3 ppm), and **4(SiH$_3$)** (−25.4 ppm) are all negative and indicate pseudo $4n$+2 π electron hyperconjugative aromaticity. In contrast, **1(H)** (+2.8 ppm), **3(H)** (+24.4 ppm), **2(F)** (+16.4 ppm), **4(F)** (+20.7 ppm), **1(SiH$_3$)** (+10.3 ppm), and **3(SiH$_3$)** (+55.4 ppm) have positive NICS(0)$_{\pi zz}$ values and are pseudo $4n$ π electron hyperconjugative antiaromatic compounds.

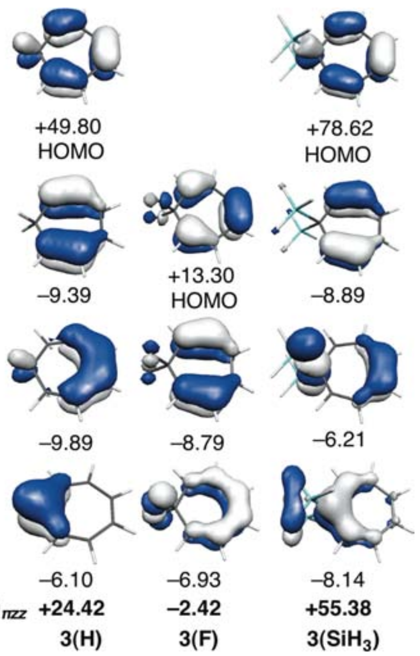

Figure 3. Dissected MO-NICS(0)$_{zz}$ contributions for substituted cycloheptatriene analogs, **3(H)**, **3(F)**, and **3(SiH$_3$)**, at PW91/IGLOIII.

Dissected NICS(0)$_{zz}$ contributions of the individual canonical π molecular orbitals (MO) of the parent **3(H)**, difluoro **3(F)**, and disilylated **3(SiH$_3$)** cycloheptatriene are illustrative. As shown in Figure 3, differences in the signs of the NICS(0)$_{\pi zz}$ values of **3(F)** (pseudo 6π e, three π MOs) vs both **3(H)** and **3(SiH$_3$)** (pseudo 8π e, four π MOs) arise predominately from variations in the HOMO contributions. Thus, the HOMO NICS(0)$_{zz}$ contributions of the antiaromatic **3(H)** (+49.8 ppm) and **3(SiH$_3$)** (+78.6 ppm) are highly paratropic and offset the diatropic contributions of the three lower π MOs. Conversely, in **3(F)**, the paratropic HOMO NICS(0)$_{zz}$ contribution (+13.3 ppm) is rather modest, and the diatropic NICS(0)$_{zz}$ contributions of the two lower π MOs (−8.8 and −6.9 ppm) result in the net negative NICS(0)$_{\pi zz}$ value (−2.4 ppm).

Nevertheless, planar **3(H, F, SiH$_3$)** only are saddle points on the potential energy surfaces. Their nonplanar C_s minima, featuring puckered "bridging" CR$_2$ units, are 5.8, 0.5, and 2.9 kcal/mol lower in energy (B3LYP/6-311+G**, no ZPE). Rather than being "hyperconjugated" (anti)aromatic, the nonplanar **3(H, F, SiH$_3$)** minima prefer

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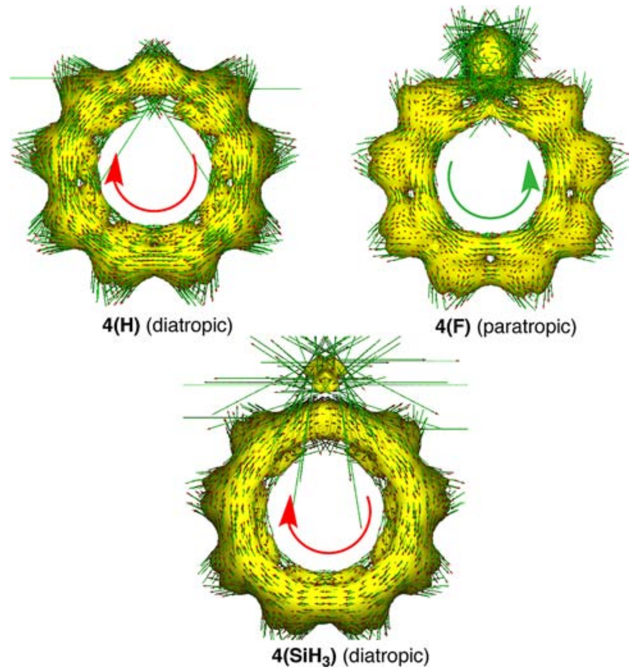
(12) (a) Herges, R.; Geuenich, D. *J. Phys. Chem. A* **2001**, *105*, 3214. (b) Geuenich, D.; Hess, K.; Köhler, F.; Herges, R. *Chem. Rev.* **2005**, *105*, 3758.

to be 6π e homoaromatic, as exemplified by their computed negative $\text{NICS}(0)_{\pi}$ values (NICS point at the center of the six unsaturated carbon atoms), **3(H)**[13] (−16.0 ppm), **3(F)** (−13.1 ppm), and **3(SiH$_3$)** (−6.8 ppm).


4(H) (diatropic)

4(F) (paratropic)

4(SiH$_3$) (diatropic)

Figure 4. Computed ACID plots for **4(H)**, **4(F)**, and **4(SiH$_3$)** with a 0.04 au isosurface value. Aromatic species exhibit clockwise diatropic circulations (red); antiaromatic species have anticlockwise paratropic circulations (green).

The ACID method[12] illustrates the induced diatropic (clockwise vectors) and paratropic (anticlockwise vectors) circulations of aromatic and antiaromatic compounds pictorially. As shown in Figure 4 for the planar forms of **4(H, F, SiH$_3$)**, the pseudo $4n+2$ π electron hyperconjugative aromatic **4(H)** and **4(SiH$_3$)** have distinct diatropic (clockwise) currents. This contrasts with their pseudo $4n$ π electron hyperconjugative antiaromatic analog, **4(F)**, which exhibits a paratropic (anticlockwise) circulation. See Supporting Information for ACID plots for **1**−**4** (R = H, F, and SiH$_3$).

In summary, hyperconjugative effects involving the σ-bonds of saturated linkages in partially π conjugated planar neutral $(\text{C}_n\text{H}_n)\text{CR}_2$ (n = 2, 4, 6, 8; R = H, SiH$_3$, F) rings can effectively influence π conjugation[14,15] and result in distinct hyper(anti)aromatic features that follow the Hückel $4n+2/4n$ π electron count rule for monocyclic compounds. The "pseudo 2π electron" character and degree of hyperconjugation of the C−R bonds depend on their electron donating ability: C−SiH$_3$ > C−H ≫ C−F.

While *hyperconjugative aromaticity* and *homoaromaticity* both pertain to partially π-conjugated cyclic molecules containing saturated linkages, the two terms refer to different phenomena and should be distinguished from one another. *Homoaromaticity* arises when homoconjugation in molecules can operate "through-space," despite the presence of a saturated linkage, due to the proximity of overlapping p_{π} orbitals. The homotropylium cation, triscyclopropenylium cation, "homobenzene" (nonplanar cycloheptatriene),[13] and the nonplanar **3(H, F, SiH$_3$)** minima are exemplary.[13,16] *Hyperconjugative aromaticity* refers to molecules in which the saturated linkages interact with the formal π electrons via hyperconjugation. Examples include the benzenium ion[1b,3] and the neutral cyclic $(\text{C}_n\text{H}_n)\text{CR}_2$ (n = 2, 4, 6, 8; R = H, SiH$_3$) compounds considered here.

Acknowledgment. This work was supported by the USA NSF Grant CHE-105-7466 and by the Spanish MINECO and CAM (Grant Nos. CTQ2010-20714-C02-01, CSD2007-00006, S2009/PPQ-1634). We thank Rainer Herges for providing us with the ACID program and László Nyulászi for stimulating discussions and his involvement with these topics.

Supporting Information Available. Details of the computed EDA and BLW results, dissected $\text{NICS}(0)_{zz}$ MO plots, and ACID plots for **1**−**4** (R = H, F, and SiH$_3$). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Chen, Z. F.; Jiao, H.; Wu, J. I.; Herges, R.; Zhang, S. B.; Schleyer, P. v. R. *J. Phys. Chem. A*. **2008**, *112*, 10586.

(14) (a) Wu, J. I.; Fernández, I.; Mo, Y.; Schleyer, P. v. R. *J. Chem. Theor. Comput*. **2012**, *8*, 1280. (b) Alabugin, I. V.; Gilmore, K. M.; Peterson, P. W. *WIREs: Comput. Mol. Sci.* **2011**, *1*, 109. (c) Wu, J. I.; Schleyer, P. v. R. *Pure Appl. Chem.* **2013**, *85* (dx.doi.org/10.1351).

(15) Steinmann, S. N.; Mo, Y.; Corminboeuf, C. *Phys. Chem. Chem. Phys*. **2011**, *13*, 20584.

(16) (a) Herrero-García, N.; Fernández, I.; Barcina, J. O. *Chem.—Eur. J.* **2011**, *17*, 7327. (b) Williams, R. V. *Chem. Rev.* **2001**, *101*, 1185.

The authors declare no competing financial interest.