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The Effect of Perfluorination on the Aromaticity of Benzene and Heterocyclic Six-Membered Rings

Judy I. Wu,[†] Frank G. Pühlhofer,[†,‡,§] Paul von Ragué Schleyer,[*,†,‡,§] Ralph Puchta,[‡,§] Boggavarapu Kiran,[‡,§,||] Michael Mauksch,[‡,§] Nico J. R. van Eikema Hommes,[§] Ibon Alkorta,[*,⊥] and José Elguero[⊥]

Computational Annex, University of Georgia, Athens, Georgia 30602-2525, Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany, Computer-Chemie-Centrum, Universität Erlangen-Nürnberg, Nägelsbachstrasse 25, D-91052 Erlangen, Germany, and Instituto de Química Médica (CSIC), Juan de la Cierva, 3, E-28006 Madrid, Spain

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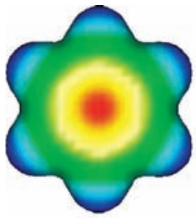
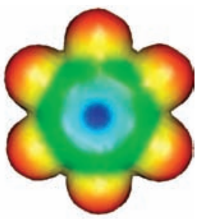
Despite having six highly electronegative F's, perfluorobenzene C_6F_6 is as aromatic as benzene. Ab initio block-localized wave function (BLW) computations reveal that both C_6F_6 and benzene have essentially the same extra cyclic resonance energies (ECREs). Localized molecular orbital (LMO)-nucleus-independent chemical shifts (NICS) grids demonstrates that the F's induce only local paratropic contributions that are not related to aromaticity. Thus, all of the fluorinated benzenes ($C_6F_nH_{(6-n)}$, $n = 1-6$) have similar ring-LMO-NICS$_{\pi zz}$ values. However, 1,3-difluorobenzene **2b** and 1,3,5-trifluorobenzene **3c** are slightly less aromatic than their isomers due to a greater degree of ring charge alternation. Isoelectronic C_5H_5Y heterocycles ($Y = BH^-$, N, NH^+) are as aromatic as benzene, based on their ring-LMO-NICS$_{\pi zz}$ and ECRE values, unless extremely electronegative heteroatoms (e.g., $Y = O^+$) are involved.

Introduction

Perfluorination alters the electrostatic potentials of benzene dramatically. As F's are highly electronegative, C_6H_6 and C_6F_6 display completely opposite molecular electrostatic potential (MEP) maps (below). In particular, the MEP map of C_6F_6 reveals a rather electron-deficient ring center (blue) and an electron-rich exterior (red). Benzene shows the opposite MEP character. Since the aromaticity of benzene arises from its six delocalized π electrons and the C_6F_6 ring center is more "electron deficient" compared to benzene, does this mean that C_6F_6 is less aromatic than benzene?



MEP map of C_6H_6



MEP map of C_6F_6

C_6H_6 and C_6F_6 behave quite differently when used as solvents for NMR measurements. Benzene ring currents[1] produce sizable effects on the proton NMR chemical shifts of nearby solute ^1H nuclei (aromatic solvent induced shifts),[2−5] while C_6F_6 usually seems to be an "inert" solvent in this respect, either because it does not sustain an aromatic ring current[6−8] or because the nature of its association with solute molecules is very different from that of benzene.[9−11] Nikki has argued convincingly that C_6F_6 in certain instances produces ASIS (aromatic solvent induced shifts) in the opposite direction to those produced by benzene as C_6H_6 (−8.7 ± 0.5 DÅ, experimental)[12] and C_6F_6 (+9.5 ± 0.5 DÅ, experimental)[12] have opposite quadrupole moments and may interact with the dipoles of the solute molecules in opposite ways.[9,10] C_6H_6 and C_6F_6 have quite different binding energies to cations and anions.[13−19] The most recent reports support the greater importance of substituent cation[20] or anion[21] interactions over cation/anion−π interactions.

While various consequences of fluorinated alkanes,[22,23] polycyclic aromatic hydrocarbons,[24−27] cyclacenes,[28] and phenylenes[29] have been reported, there are only a few comparative studies on the aromaticities of C_6H_6 versus C_6F_6 themselves.[30,31] Fowler and Steiner computed the induced π ring current densities of C_6H_6 and C_6F_6 and found no significant differences between the two, except for the six independent local π circulations around the F's in C_6F_6.[30] In contrast, Laali evaluated a set of $C_6H_nF_{(6-n)}$ ($n = 1-6$) compounds based on nucleus-independent chemical shifts (NICS)[32] computations (NICS(1)$_{zz}$) and found diminished ring currents for the more fluorinated species.[31] To reconcile this discrepancy, we re-evaluated the aromaticities of the fluorinated benzenes (**1−6**: $C_6H_nF_{(6-n)}$, $n = 1-6$), employing the more sophisticated NICS$_{\pi zz}$[32c,d] index and the block-localized wave function (BLW)[33] method to characterize their aromatic stabilization energies. In addition, we evaluated the aromaticities of a set of heterocyclic six-membered rings C_5X_5Y ($X = H$, F; $Y = BH^-$, N, NH^+, O^+) isoelectronic to benzene and pentafluorobenzene.

We answer the following questions in this paper: What effect does perfluorination have on the aromaticity of benzene? Can the ASIS effect be due to the absence of ring current in C_6F_6?

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[*] To whom correspondence should be addressed. E-mail: schleyer@chemie.uni-erlangen.de (P.v.R.S.); ibon@iqm.csic.es (I.A.).

[†] University of Georgia.

[‡] Universität Erlangen-Nürnberg.

[§] Universität Erlangen-Nürnberg.

[⊥] Instituto de Química Médica (CSIC).

[||] Present address: Department of Chemistry, McNeese State University, Lake Charles, LA 70609.

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To what extent do heteroring atoms and fluorination perturb the aromaticities of heterocyclic six-membered rings isoelectronic to benzene?

Computational Details

All geometries were optimized at the B3LYP/6-311+G** level as implemented in Gaussian98.[34] Harmonic vibrational frequencies, computed at the same DFT level, established the character of the stationary points. For all NICS computations, we employ the most highly recommended NICS$_{\pi zz}$ index, which extracts the out-of-plane (zz) tensor component of the isotropic NICS and includes only the π MO contributions.[32d] Negative NICS(0)$_{\pi zz}$ values due to diamagnetic shieldings indicate aromaticity. Positive NICS(0)$_{\pi zz}$ values due to paramagnetic shieldings indicate antiaromaticity.

The NICS$_{\pi zz}$ data for the fluorinated benzenes were computed employing both localized molecular orbital (LMO)[35] and canonical molecular orbital (CMO)[36] dissection. LMO-NICS (at the PW91/IGLOIII level) were computed with the individual gauge for localized orbitals (IGLO) method[37] (implemented in the deMon NMR program)[38] utilizing the Pipek−Mezey localization algorithm.[39] CMO-NICS employed the gauge-including atomic orbital (GIAO) method. LMO- and CMO-NICS are complementary, but the former (LMO) separates the total shielding of the molecule into individually localized MO contributions of bonds, lone pairs, and core electrons, while the latter (CMO) dissects the total shielding of the molecule into each canonical MO contributions.

All BLW[33] computations were performed at the B3LYP/6-31G* level as implemented in the GAMESS R5 version.[40] The BLW method is specifically designed for evaluating resonance energies (RE), for cyclic or acyclic conjugated molecules, directly without recourse to reference compounds, but it can also be used to derive the extra cyclic resonance energies (ECREs)[41] of aromatic molecules. Note that the ab initio VB-based BLW computations preserve the concepts of valence bond theory but is more efficient due to its molecular orbital (MO)-based computations.[33]

BLW-computed REs adopt the Pauling−Wheland[42] definition and are the computed total energy difference between the completely delocalized conjugated molecule (fully optimized employing regular canonical molecular orbitals) and that of its most stable resonance contributor. The latter can be optimized by employing BLW orbitals, constructed by partitioning all of the electrons and basis functions into several subspaces to form sets of localized MOs, in which orbitals of the same subspaces are mutually orthogonal but those of different subspaces overlap freely. Depending on the partitioning scheme of the subgroups, the BLW procedure "disables" the intramolecular interactions among the selected subgroups and gives the total energy of the hypothetical resonance structure.[33] The ECREs are derived from the BLW-REs of the aromatic compounds minus that of its acyclic conjugated references with the same number and type of conjugation (see ECRE section).[41]

Results and Discussion

The effect of fluorination on the aromaticity of C_6H_6 and a set of isoelectronic six-membered rings C_5H_5Y (Y = CH, N, NH$^+$, O$^+$), containing first-row heteroatoms, was evaluated both magnetically and energetically. Nucleus-independent chemical shift (NICS) computations characterized the magnetic aromaticity for the sequentially fluorinated benzene analogues as well as the parent and perfluorinated heterocyclic six-membered rings. Their extra cyclic resonance energies (ECREs), related to the aromatic stabilization energies (ASEs), were computed based on Mo's ab initio block-localized wave function (BLW) procedure (see Computational Details).

TABLE 1: CMO- and LMO-NICS(0)$_{\pi zz}$ Data for the $C_6F_nH_{(6-n)}$ Compounds (Both Computed at the PW91/IGLOIII Level)[a] (See Chart 1)

		LMO-NICS(0)$_{\pi zz}$		
compound	CMO-NICS(0)$_{\pi zz}$	total	ring	F's
benzene	−35.9	−36.9	−36.9	
1	−34.0	−34.8	−36.6	1.8
2a	−33.1	−33.9	−37.1	3.2
2b	−31.7	−32.2	−35.8	3.6
2c	−33.1	−33.4	−36.9	3.5
3a	−31.7	−32.3	−36.9	4.6
3b	−31.2	−31.9	−36.7	4.8
3c	−29.3	−29.5	−34.6	5.1
4a	−30.7	−31.5	−37.4	5.9
4b	−29.5	−30.0	−36.1	6.1
4c	−30.3	−31.0	−37.2	6.2
5	−29.3	−30.1	−37.1	7.0
6	−28.6	−29.3	−37.7	8.4

[a] In the LMO-NICS$_{\pi zz}$ column, F's refers to contributions from the p$_z$ lone pairs of the F substituents only; ring refers to contributions from the three π MOs of the C_6 ring; and total refers to the total contributions from all π MOs (includes both F and ring) and may be compared to the CMO-NICS$_{\pi zz}$ results.

1. Nucleus-Independent Chemical Shifts. *C_6F_6 and C_6H_6.* We evaluated the nucleus-independent chemical shifts of C_6H_6 and C_6F_6, based on the most sophisticated NICS$_{\pi zz}$ index,[32] employing both LMO- and CMO-NICS (see Computational Details). The LMO-NICS is especially useful for comparing the aromaticity of C_6F_6 versus C_6H_6 as it can distinguish the NICS$_{\pi zz}$ contributions of the ring from those of the F lone pairs (see Computational Details).[35] The "ring"-LMO-NICS(0)$_{\pi zz}$ values include only the contributions of the three double bonds within the six-membered ring; "F"-LMO-NICS(0)$_{\pi zz}$ values include only the contributions of the F's. The total-LMO-NICS(0)$_{\pi zz}$ includes both the ring and F contribution and may be compared with the canonical molecular orbital (CMO)-NICS(0)$_{\pi zz}$ data, which dissects the total shielding of the molecule into each canonical MO contribution but cannot identify contributions coming from the ring and F's for C_6F_6 separately.

Remarkably, the ring-LMO-NICS(0)$_{\pi zz}$ values of C_6H_6 (−36.9 ppm) and C_6F_6 (−37.7 ppm) are very similar (Table 1). Despite having six highly electronegative F's, C_6F_6 is as aromatic as C_6H_6! The six peripheral F's induce sizable paramagnetic shielding at the C_6F_6 ring center (F-LMO-NICS(0)$_{\pi zz}$ = +8.4 ppm), but these are only local effects and do not perturb the aromaticity of the benzene ring (see discussion below). For this reason, the total-LMO-NICS(0)$_{\pi zz}$ (the sum of both ring and F contributions) of C_6F_6 (−29.3 ppm) is quite different from that of C_6H_6 (−36.9 ppm), which, when interpreted superficially, may suggest erroneously that C_6F_6 is less aromatic than benzene. The CMO-NICS(0)$_{\pi zz}$ results for C_6F_6 (−28.9 ppm) and C_6H_6 (−36.2 ppm) are also misleading for the same reason.

The in-plane NICS$_{\pi zz}$ grids for C_6F_6 and C_6H_6 (see Figure 1), with NICS points placed at positions radiating out from the ring center at 1 Å intervals through the ring C−C bonds, characterize the local effects of the F's (see Figure 1c). Aromatic molecules should not only be characterized by a negative NICS$_{\pi zz}$ value at the ring center, they also exhibit paramagnetic deshielding outside of the ring as well. The NICS$_{\pi zz}$ values for each of the NICS grid points of C_6F_6 and C_6H_6 have similar magnitudes both inside (diatropic, red dots) and outside (paratropic, green dots) of the ring. However, the F-LMO-NICS$_{\pi zz}$ grids for C_6F_6 reveal large parat-

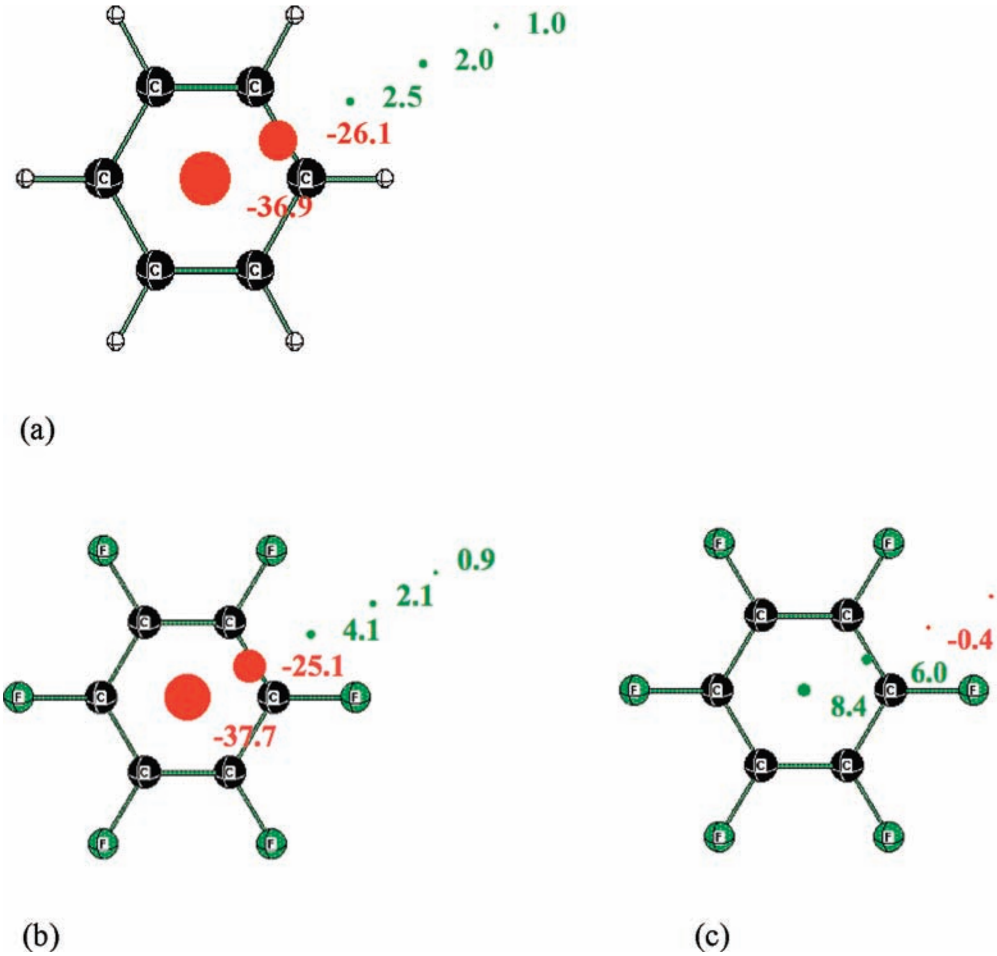


Figure 1. In-plane LMO-NICS$_{\pi zz}$ grid of C_6H_6 and C_6F_6 (NICS data computed at the PW91/IGLOIII level). (a) LMO-NICS$_{\pi zz}$ grid of benzene. (b) "Ring"-LMO-NICS$_{\pi zz}$ grid of C_6F_6. (c) "F"-IGLO-LMO-NICS$_{\pi zz}$ grid of C_6F_6. The insignificant shielding outside of the ring suggests that there are no induced paratropic ring currents coming from the F's, but the F's induce only local paramagnetic deshieldings.

ropic contributions in the ring (+8.4 ppm) and close to the C−C bonds (+6.0 ppm) but negligible diatropic contributions outside of the ring (less than −0.5 ppm).

LMO-NICS$_{\pi zz}$ computations confirm, in agreement with Fowler's ring current density plots of C_6H_6 and C_6F_6,[30] that perfluorination does not change the π ring current of benzene. The aromaticities of C_6H_6 and C_6F_6 are essentially the same, while the F's induce only local paramagnetic deshieldings not related to aromaticity.

$C_6F_nH_{(6-n)}$ ($n = 1-6$). Since perfluorination has no significant effect on the aromaticity of benzene, the ring-LMO-NICS(0)$_{\pi zz}$ values of the sequentially fluorinated benzene derivatives ($C_6F_nH_{(6-n)}$, $n = 1-6$) also give similar values (ranging from −34.6 to −37.7 ppm; see Table 1) compared to benzene (−36.9 ppm). However, the F-LMO-NICS(0)$_{\pi zz}$ values are more positive for species with more F's (see Table 1) as they induce greater local paramagnetic deshielding. For this reason, both the CMO-NICS(0)$_{\pi zz}$ and total-LMO-NICS(0)$_{\pi zz}$ values become less negative for the more fluorinated benzene derivatives (see Table 1).

Note that both **2b** and **3c** have the lowest total energies among the di- and trifluorobenzenes, but they also have the *least negative* diatropic ring-LMO-NICS(0)$_{\pi zz}$ values (see Table 1) and thus are less aromatic than their isomers. Interestingly, the ordering for aromaticity (e.g., **2a** > **2c** > **2b**, **3a** > **3b** > **3c**) and that for thermochemical stability (e.g., **2b** > **2c** > **2a**, **3c** > **3b** > **3a**), both for the di- and tri- fluorobenzenes, are completely opposite! The weakened aromaticity of **2b** and **3c** is due to their greater charge alternation in the C_6 ring, which arises from the highly electronegative F's pulling electrons away from the substituted C atoms. Thus, all of the fluorinated carbons have partial positive charges, while the unsubstituted carbons have partial negative charges. As an extreme example, borazine has significant ring charge alternation due to the electronegativity difference between the ring atoms, and it is not very aromatic (NICS(0)$_{\pi zz}$ = −9.2 ppm, compared to −36.9 for benzene). Hence, charge alternation can be thermodynamically favorable for cyclic conjugated systems but is unfavorable in terms of aromaticity. Although fluorination does not perturb the aromaticity of C_6H_6, partially fluorinated benzene derivatives can have weakened aromaticity due to the partial localization induced by alternating charges in the C_6 ring.

Heterocyclic Six-Membered Rings (C_5H_5Y and C_5F_5Y). The ring-LMO-NICS(0)$_{\pi zz}$ values of the heterocyclic C_5H_5Y (ranging from −31.4 to −36.4 ppm) and C_5F_5Y (−28.9 to −35.9 ppm) compounds (X = H, F; Y = BH^-, N, NH^+, O^+) do not differ much from those of benzene (−36.9 ppm) and pentafluorobenzene **5** (−37.1 ppm) (see Table 2); those of $C_5H_5O^+$ (−31.4 ppm) and $C_5F_5O^+$ (−28.9 ppm) are slightly less negative due to the greater electronegativity difference between the ring carbons and O (which is even more electronegative with the positive charge is present). At the extreme, both $C_5H_5F^{2+}$ (−15.7 ppm) and $C_5F_6^{2+}$ (−12.9 ppm) have significantly less negative ring-LMO-NICS(0)$_{\pi zz}$ values. Note that the ring-LMO-NICS(0)$_{\pi zz}$ values of each of the C_5H_5Y species are almost the same as their fluorinated C_5F_5Y counterparts (see Table 2). Thus, perfluorination has no significant effect on the aromaticities of the heterocyclic six-membered rings containing only one first-row element. Aromaticity is not easily perturbed,

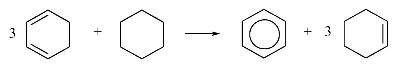
TABLE 2: Ring-LMO-NICS(0)$_{\pi zz}$ Values for C_5X_5Y Compounds (X = H or F; Y = BH^-, CH, N, NH^+, O^+) (NICS Data Computed at the PW91/IGLOIII Level)

	ring-LMO-NICS(0)$_{\pi zz}$	
Y	X = H	X = F
BH^-	−32.1	−35.0
CH	−36.9	−37.1
N	−36.4	−35.9
NH^+	−34.8	−33.0

and for benzene, it is weakened only when unrealistic highly electronegative/electropositive heteroatoms (like F^{2+}), which we have omitted from this study, are incorporated into the ring.

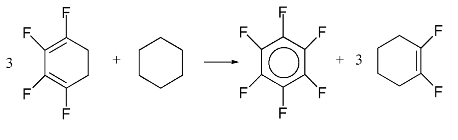
2. Extra Cyclic Resonance Energy (ECRE). ***C_6H_6 and C_6F_6.*** The aromatic stabilization energies of C_6H_6 and C_6F_6 were estimated based on their extra cyclic resonance energies (ECREs),[41] which measures the extra stabilization associated with the aromaticity of the cyclic conjugated systems. ECREs can be derived from the BLW-computed REs of the cyclic conjugated aromatic compound minus that of its appropriate acyclic references, which represent the same number and type of conjugation present in the aromatic system and thus cancel out all energetic effects other than aromaticity.[41] For example, the ECRE of benzene (29.3 kcal/mol) is derived from the RE of benzene (61.4 kcal/mol) minus that of three *syn*-butadienes (−10.7 kcal/mol each). Similarly, the ECRE of C_6F_6 (28.5 kcal/mol) can be derived from the RE of C_6F_6 (61.8 kcal/mol) minus the BLW RE sum of three *syn*-1,2,3,4-tetrafluorobutadienes (worth 11.1 kcal/mol each). Remarkably, the ECRE values for C_6H_6 and C_6F_6 are almost the same! Hence, C_6F_6 is energetically as aromatic as C_6H_6.

The aromatic stabilization energy (ASE) of C_6F_6 can also be evaluated based on the recommended hyperhomodesmotic equation[43] (eq 1) adopted for benzene.[44] Thus, eq 1 has equal numbers of C−C bond types and equal numbers of each type of carbon atom (sp^3, sp^2, sp) with zero, one, two, or three hydrogens attached on both sides and is balanced also for the number of conjugations and hyerconjugations.[43] For C_6F_6, eqs 2 and 3 are derived from eq 1 and also retain balanced C−C and C−F bond types and carbon hybridizations. On the basis of eqs 1−3, the estimated ASE for C_6F_6 (−35.0 kcal/mol, eq 2; −36.1 kcal/mol, eq 3) also is close to that of benzene (−32.6 kcal/mol, eq 1)[45].



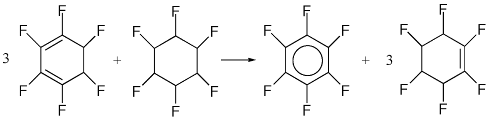
(1)

–32.6 kcal/mol (B3LYP/6-311+G** ZPE corrected; –28.8 kcal/mol expt.[45])



(2)

–35.0 kcal/mol (B3LYP/6-311+G** ZPE corrected)



(3)

–36.1 kcal/mol (B3LYP/6-311+G** ZPE corrected)

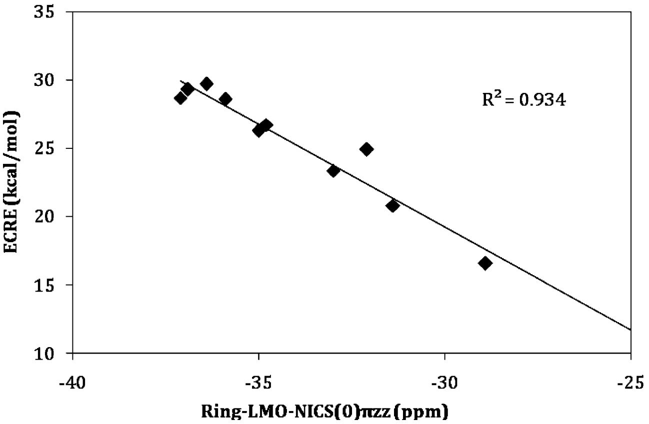
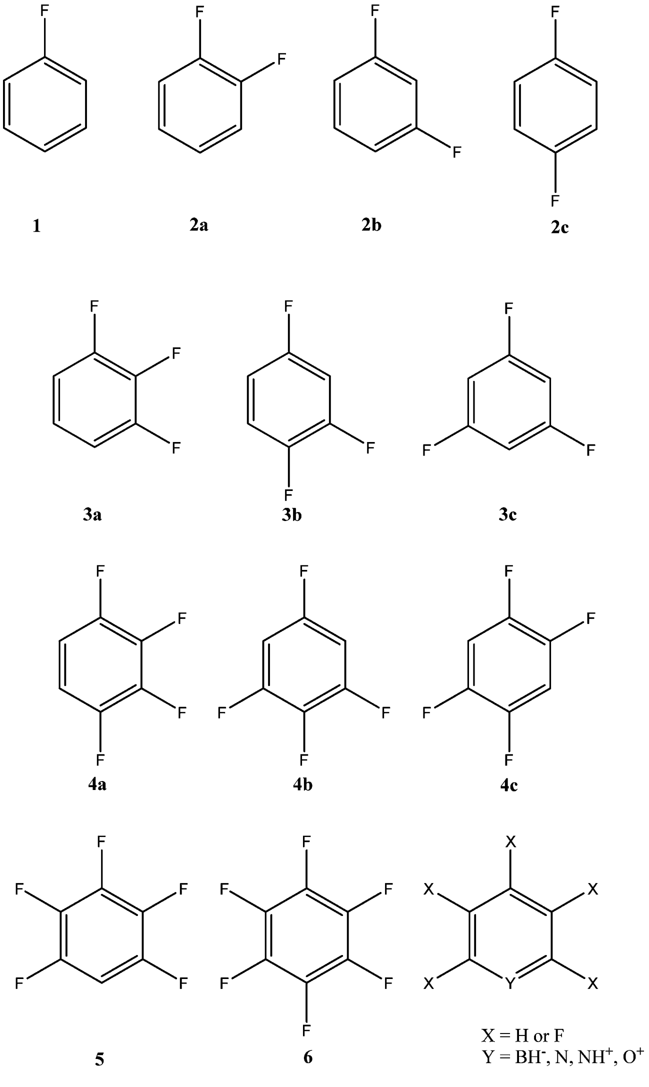


Figure 2. ECRE versus ring-LMO-NICS(0)$_{\pi zz}$ values for heterocyclic six-membered rings C_5X_5Y (X = H, F; Y = BH^-, CH, N, NH^+, O^+). All ECRE data were computed with the BLW method at the B3LYP/6-31G* level, and all NICS(0)$_{\pi zz}$ values were computed with the LMO-NICS method at the PW91/IGLOIII level.

CHART 1



Heterocyclic Six-Membered Rings (C_5H_5Y and C_5F_5Y). The ECREs[41] of the heterocyclic C_5H_5Y (20.8 to 29.7 kcal/mol) and C_5F_5Y (16.6 to 28.6 kcal/mol) (Y = BH^-, N, NH^+, O^+) species also do not deviate very much from those of benzene (29.3 kcal/mol) and **5** (28.7 kcal/mol). The ECREs of $C_5H_5O^+$ (20.8 kcal/mol) and $C_5F_5O^+$ (16.6 kcal/mol) are particularly smaller due to the electronegativity difference between the ring atoms, as discussed earlier. The ECREs of C_5H_5Y also do not differ much from their fluorinated C_5F_5Y derivatives; thus, perfluorination does not change the aromatic stabilization energies of the heterocyclic six-membered rings. Notably, the $\mathrm{NICS}_{\pi zz}$ and ECRE results correlate remarkably well for the C_5X_5Y species ($R^2 = 0.934$; see Figure 2). Hence, for benzene, the substitution of a single-ring carbon by other first-row ring heteroatoms has only little effect on the aromatic stabilization energy, except in extreme cases when highly electronegative heteroatoms are incorporated.

Conclusion

Perfluorination has no significant effect on the aromaticity of benzene, either energetically or magnetically. The computed ring-LMO-$\mathrm{NICS}_{\pi zz}$ and ECRE values for C_6H_6 and C_6F_6 are essentially the same. For these reasons, the aromatic solvent induced shift (ASIS)[2−5] effect for C_6H_6 and C_6F_6 cannot be due to the absence of ring currents in C_6F_6, but other causes, for example, the different solute−substituent interactions for C_6F_6, could be responsible.

Although CMO- and LMO-NICS are complementary and are generally in very good agreement with each other, LMO-NICS are superior for evaluating substituent effects for aromatic systems as they distinguish the ring and substituent contributions separately. The F-LMO-NICS grid of C_6F_6 reveals that F's induce only local paratropic contributions in the ring center but are not related to aromaticity. Thus, Laali's conclusion suggesting diminished ring currents for the sequentially fluorinated benzenes[31] is not substantiated. All of the fluorinated benzenes **1**−**6** have very similar ring-LMO-$\mathrm{NICS}(0)_{\pi zz}$ values (−34.6 to −37.7 ppm), but **2b** and **3c** are slightly less aromatic (less negative ring-LMO-$\mathrm{NICS}(0)_{\pi zz}$ values) than the other di- and trifluorobenzenes as they have a greater degree of alternating ring charges. For comparison, borazine is only very weakly aromatic ($\mathrm{NICS}(0)_{\pi zz} = -9.2$ ppm). The aromaticities of heterocyclic six-membered rings (containing only one first-row heteroatom), isoelectronic to benzene, are weakened only when strongly electronegative heteroatoms (e.g., O^+) are involved. Remarkably, the aromaticity of benzene is quite persistent and is not easily perturbed by substituents[46] or heteroatoms[47] in the ring.

Acknowledgment. We dedicate this paper to Prof. Timothy Clark on the occasion of his 60th birthday. We gratefully acknowledge financial support from the National Science Foundation Grant CHE-0716718 (P.v.R.S.).

References and Notes

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