

Revisiting Aromaticity and Chemical Bonding of Fluorinated Benzene Derivatives

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The electron delocalization of benzene (C₆H₆) and hexafluorobenzene (C₆F₆) was analyzed in terms of the induced magnetic field, nucleus-independent chemical shift (NICS), and ring current strength (RCS). The computed out-of-plane component of the induced magnetic field at a distance (*r*) greater than or equal to 1.0 Å above the ring center correlates well ($R^2 > 0.99$) with the RCS value. According to these criteria, fluorination has two effects on the C₆ skeleton; concomitantly, the resonant ef-

fects diminish the π electron delocalization and the inductive effects decrease the charge density at the ring center and therefore reduce the magnitude of the paratropic current generated in this region. The equilibrium between both effects decreases aromaticity in the fluorinated benzene derivatives. These results can be extrapolated to determine the aromaticity of any derivative within the series of fluorinated benzene derivatives (C₆H_(6-n)F_n, where $n = 1-5$).

Introduction

The nucleus-independent chemical shift (NICS)^[1] is perhaps one of the most popular criteria to determine aromaticity.^[2] This aromaticity index is defined as the negative of the isotropic magnetic shielding evaluated at the ring center of an (anti)-aromatic system ($\text{NICS}(0) = -\sigma_{\text{iso}}$). Thus, part of its popularity is due to its ease of calculation with any standard quantum chemical program.^[1,2] Despite the success of NICS at describing aromaticity in a plethora of cyclic compounds, several aspects of NICS have been subject to criticism. Some authors have pointed out that the validity of NICS is limited by spurious con-

tributions from the in-plane tensor components, which are not necessarily related to aromaticity.^[3-5] To avoid these issues, some variants of NICS have been proposed, such as dissected NICS^[6] (where the σ and π components are separated), the NICS(1)^[7] (where the NICS is evaluated at 1.0 Å above the ring center), and the zz component of the NICS tensor (NICS_{zz}),^[8] which has been proven to be particularly sensitive to π -electron delocalization patterns. In several cases, NICS has shown inconsistencies, but suitable conclusions have been obtained when this magnetic response has been analyzed in deeper detail.^[4,9]

One particular example where magnetic-based descriptors of aromaticity are inconsistent is in the case of aromaticity assessment of fluorinated benzene derivatives. In 1997, Fowler et al. compared both the total and the π current densities of benzene and hexafluorobenzene, concluding that these systems show almost a similar magnetic response and, therefore, the same aromatic character.^[10,11] In contrast, NICS(1)_{zz} indicates that aromaticity decreases proportionally to the number of fluorine atoms.^[12] The computed NICS_{zz} by Wu et al. revealed that fluorine induces only a local paratropic contribution at the hexafluorobenzene ring center, which according to the authors is not related to aromaticity.^[13] Recently, Stainmann et al. evaluated the changes in NICS_{zz} and NICS at the ring center of benzene and hexafluorobenzene by localizing the π electrons using the block-localized wave (BLW) function method.^[14] While in benzene NICS(0) is -8.7 ppm and NICS(0)_{BLW} is 1.9 ppm, the values in hexafluorobenzene are -18.0 ppm and -9.4 ppm, respectively. Similar trends are obtained using NICS(0)_{zz} and NICS(0)_{zz}(BLW). Hence, both indexes suggest a bigger change upon blocking in benzene than in hexafluorobenzene, supporting that benzene is more aromatic than its fluorinated derivatives. The assumption in this strategy is that aromaticity is turned off after localization (blocking) procedure.

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Recently, Kaipio et al.^[15] reopened the debate on the effect of fluorination on the aromaticity degree of arenes.^[12,13,15,16] Current susceptibility computations indicate that the degree of aromaticity in the fluorinated benzene derivatives decreases when the number of fluorine atoms increases, contradicting previous findings based on magnetic criteria. The authors also evaluated this effect using the charge density differences between the fluorinated species and benzene, showing that the σ framework is more disturbed than the π skeleton.^[15]

Here, we analyze the distance dependence of the NICS values and the fluorination effect on the chemical bonding of benzene derivatives. Our results support and complement the previous findings of Kaipio et al.^[15] In order to gain insight into the electron delocalization of the title systems, we carried out an analysis using another magnetic descriptor, the induced magnetic field (B^{ind}),^[17] particularly, using the z component of the induced magnetic field (B^{ind}_z), which is equivalent to NICS_{zz}. The results are compared with the magnetically induced current densities as well as with their integrated values (ring current strengths, RCS). The B^{ind}_z analysis shows that fluorination of benzene decreases its aromaticity in agreement with RCS values. The bonding of such systems is studied in terms of the adaptive natural density partitioning (AdNDP) analysis, which supports the inductive and resonant effects into the fluorinated benzene.

Computational Methods

The geometries were fully optimized using the PBE0 functional in conjunction with a 6-311++G(d,p) basis set in Gaussian09.^[18] The shielding tensors were computed at the same level using the GIAO approach, locating the ring center at the origin of the coordinate system making the z -axis identical with the highest symmetry axis. Plots of B^{ind} were generated using the Molekel code 5.4.0.8.^[19]

The magnetically induced current densities were obtained at the PBE0/6-311++G(d,p) level using the four-component

Dirac–Coulomb Hamiltonian as implemented in the DIRAC code.^[20] In DIRAC, the small-component basis set was generated using unrestricted kinetic balance (UKB), which provides a flexible basis set for magnetic properties (simple magnetic balance, sMB).^[21] Even though DIRAC is a relativistic code, the molecules studied here contain light elements of the periodic table, so that the relativistic effects are negligible.

The two-dimensional Gauss–Lobatto algorithm^[22] was used to integrate the magnetically induced current density to obtain the ring-current strengths (RCS), also referred to as ring-current susceptibilities. We chose an integration plane perpendicular to the molecular plane. This integration plane is a perpendicular bisector of a specific bond and starts approximately at the molecular center and extends up to 10 atomic units in all directions.^[21,23] The magnetically induced current density plots were obtained by using the PyNGL package.^[24]

In order to gain further insight into the electron distribution, the AdNDP method was used.^[10] The full-density matrix in the basis of the natural atomic orbitals, as well as the transformation between the atomic orbital and the natural atomic orbital basis sets, were generated at the PBE0/6-311++G** level using the NBO 3.0 code^[25] incorporated into Gaussian 09.

Results and Discussion

Figure 1 depicts the contour lines of the z component of the induced magnetic field (B^{ind}_z) produced by an applied external magnetic field, perpendicular to the molecular planes of benzene and hexafluorobenzene. The external magnetic field induces a current density around the molecular plane. Clearly, at distances ≤ 1.0 Å from the ring center, the nuclear and σ contributions are still present in both systems. At distances ≥ 1.0 Å, a well-defined shielding region (involving the complete ring) emerges. Note that the shielding region of hexafluorobenzene is smaller than that of benzene. The continuous substitution of hydrogen by fluorine in benzene gradually decreases the size

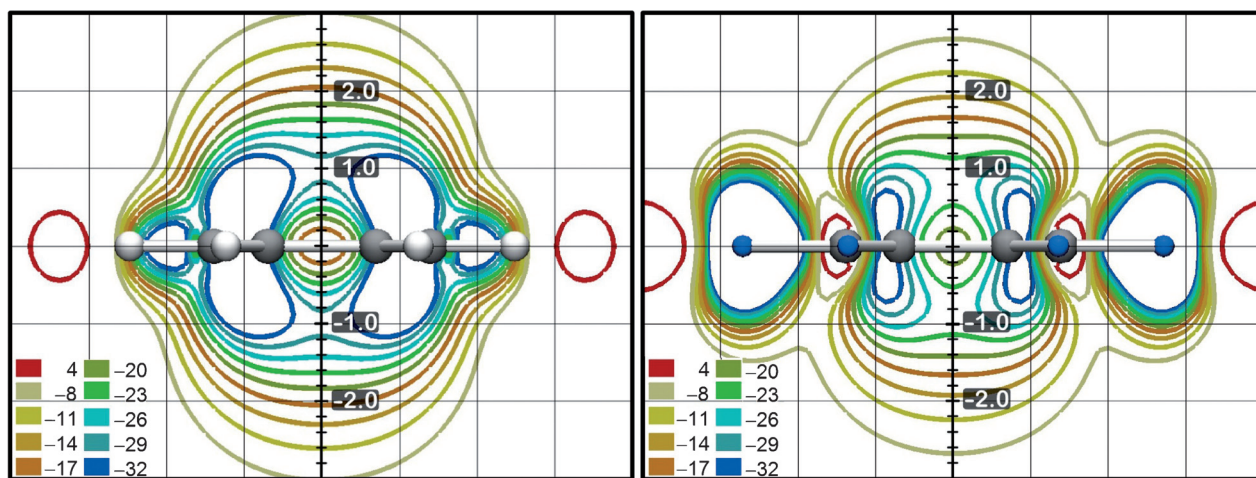


Figure 1. Contour lines of the z -component of the induced magnetic field (B^{ind}_z), in a plane perpendicular to the molecule, for benzene (left) and hexafluorobenzene (right). The scale is given in ppm and the spatial scale in Å.

of the shielding region (see Figures S1.1–S1.2 in the Supporting Information).

When induced current densities are computed, there is a paratropic ring current at the center of the benzene ring. This phenomenon has been attributed, using a naive hydrodynamic analogy, to the superposition of diatropic currents of the σ bonds.^[26] The magnitude of this paratropic current density diminishes after fluorination (Figure 2). Thus, it is clear that at the ring center, the shielding tensor should be affected by this paratropic contribution, avoiding an appropriate comparison of the magnetic descriptors among benzene and its fluorinated derivatives (Scheme 1).

The integrated induced ring current susceptibilities, as well as different NICS and B^{ind}_z computations, are summarized in Table 1. The largest RCS value is obtained for benzene. The RCS value for monofluorobenzene is slightly smaller and decreases as the number of fluorine atoms increases. The RCS value (in nA/T) for benzene is 12.0 whereas for hexafluorobenzene is 9.9. These results show the same trends as those reported by Kaipo et al.^[15] (see Figure S2 in the Supporting Information), which is not surprising because the computed property is the same; however, we calculated the RCS values with the aim of comparing them with NICS and B^{ind}_z at the same theoretical level. Notice that in this work, RCS is considered as the reference among the magnetic descriptors of aromaticity.

Four points at different distances with respect to the ring center were considered in order to evaluate the shielding tensor ($r=0.00, 1.00, 1.180$ and 1.96 \AA). The third and fourth points correspond to the distance where the in-plane component of NICS ($1/3(\sigma_{yy} + \sigma_{xx})$) becomes zero (free-of-in-plane component (FiPC) NICS) in benzene and hexafluorobenzene (FiPC_{max}), respectively. This is shown in the scatter diagrams of $1/3\sigma_{zz}$ versus $1/3(\sigma_{yy} + \sigma_{xx})$ (Figure 3), which provides information about the changes in the shielding tensor components (anisotropy) within the complete series of $C_6H_{6-n}F_n$ molecules. This strategy was recently proposed in order to minimize the risks of reporting false (anti)aromaticity data in inorganic heterocycles using

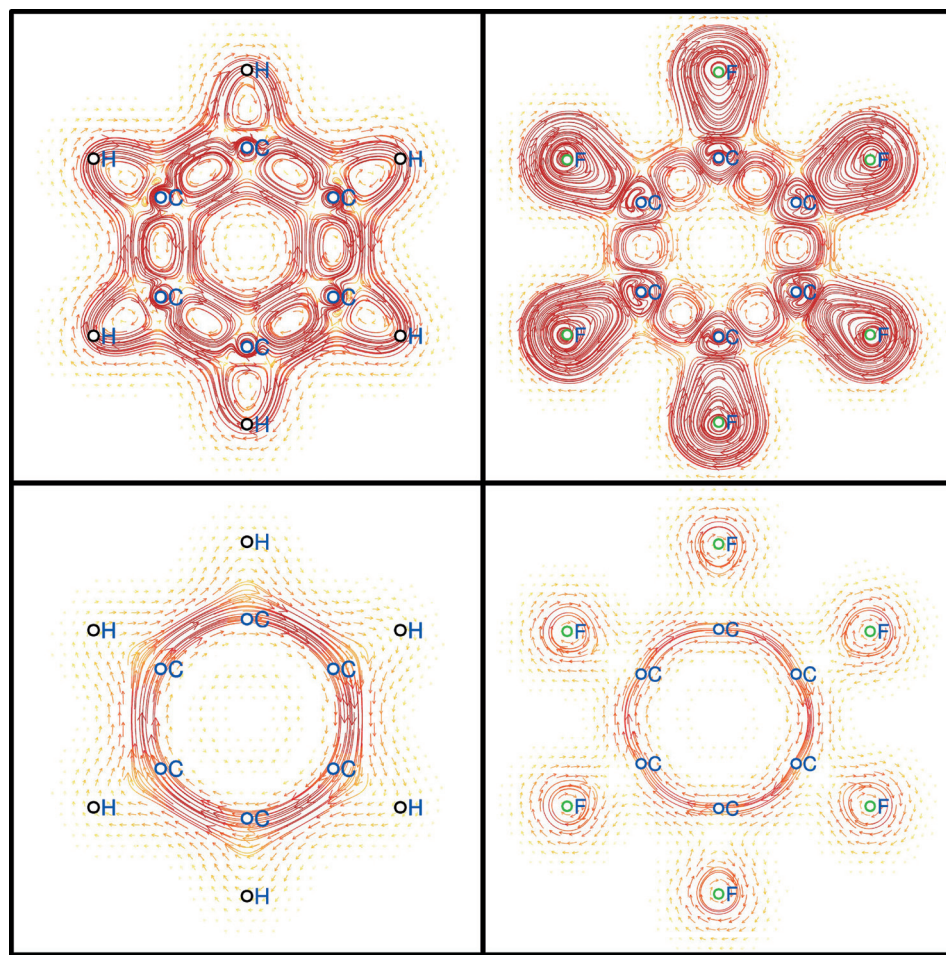
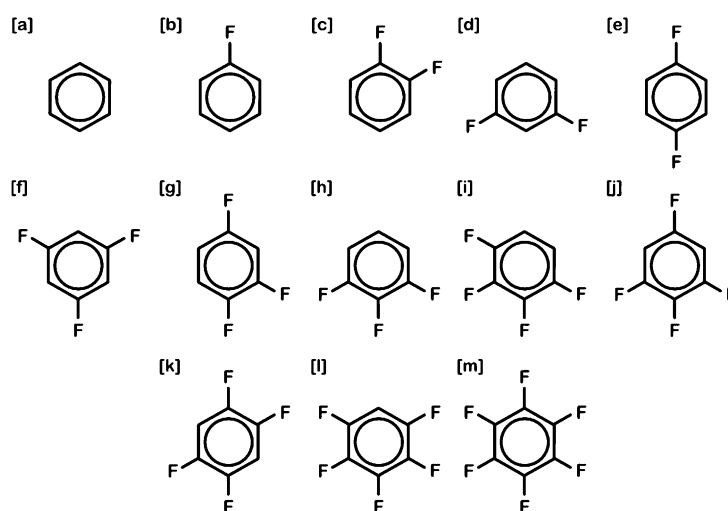


Figure 2. The magnetically induced current density of benzene and hexafluorobenzene. The plots on the molecular plane and 0.52 \AA above the molecular plane for benzene (left) and perfluorobenzene (right) are shown at the top and bottom of the figure, respectively. The magnetic field vector points towards the reader.



Scheme 1. Benzene and its fluorinated derivatives. Labels are the same as those used in Ref. [15].

NICS.^[5] The shapes of all curves are in the negative region of both in-plane and out-of-plane components, which is characteristic of aromatic rings.^[5]

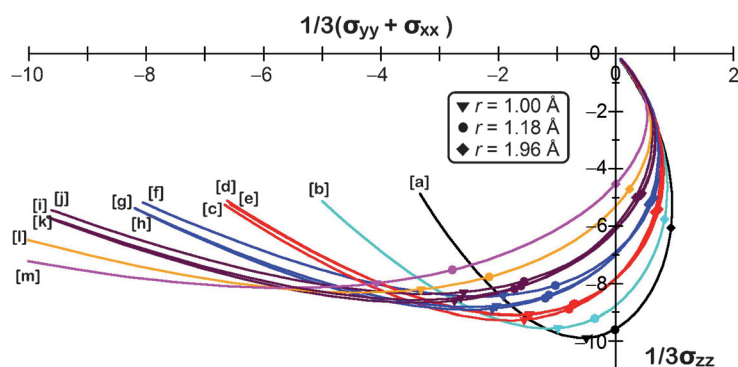


Figure 3. Plots of $1/3\sigma_{zz}$ versus $1/3(\sigma_{yy} + \sigma_{xx})$ (in ppm) for the aromatic series $C_6H_{6-n}F_n$ ($n=0-6$). The dots represent the distance (r in Å) where the in-plane component ($1/3(\sigma_{yy} + \sigma_{xx})$) becomes zero.

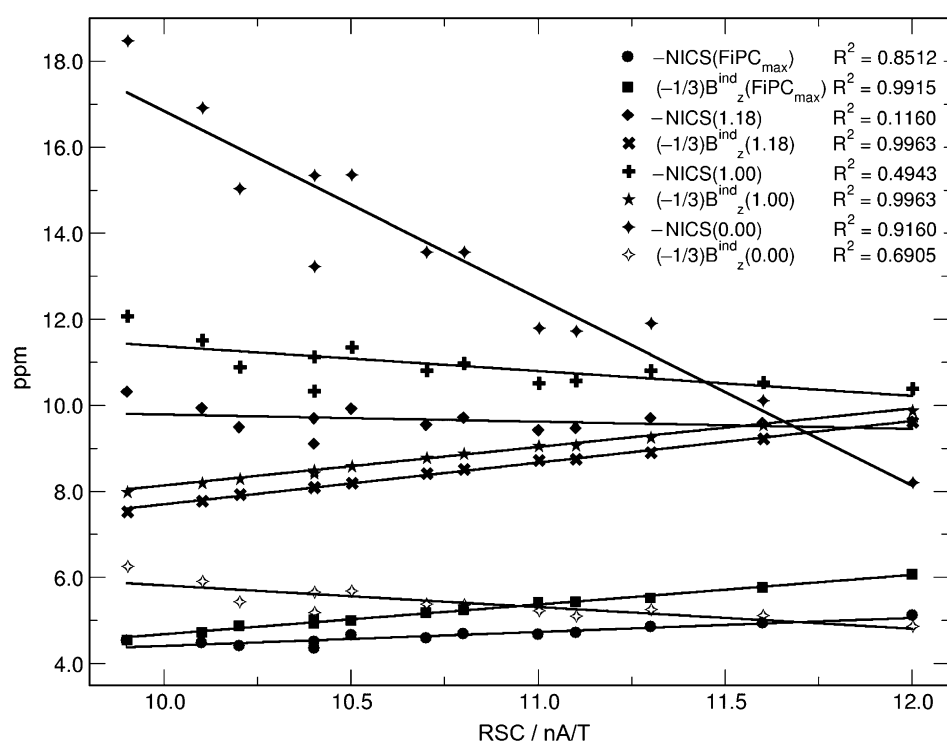


Figure 4. Correlation between NICS or the induced magnetic field and the ring current strength (RCS) values for the series $C_6H_{6-n}F_n$ ($n=0-6$). Negative values of NICS are given in the y -axis to allow direct correlation as the aromaticity increases.

In Figure 4, the different magnetic criteria reported in Table 1 are compared to the RCS for the series $C_6H_{6-n}F_n$. Clearly, out of all the isotropic descriptors, only $NICS(FiPC_{max})$ has a good linear correlation ($R^2=0.8512$) with the RCS values. In contrast, B_z^{ind} (which is equal to $NICS_{zz}$) has a good linear correlation with RCS, except for the value computed at the ring center, $B_z^{ind}(0)$. So, the suitable distances to compute NICS or B_z^{ind} as indicators of ring current intensities, are those where the $NICS_{in-plane}$ versus $NICS_{out-of-plane}$ curves show the same trend, which indicates that both magnetic criteria are mainly influenced by the same phenomena. The linear correlation of B_z^{ind} versus RCS suggests that B_z^{ind} values at distances ≥ 1.0 Å

above the center of the molecular rings are more sensitive to both π - and σ -ring currents.

Let us compare the bonding in benzene and hexafluorobenzene using AdNDP. In benzene, the σ electrons are localized in two sets of two-center two-electron ($2c-2e$) bonds (Figure 5a), and the π electrons are distributed in three completely delocalized $6c-2e$ bonds (Figure 5b), as expected.^[11] In the case of hexafluorobenzene, 24 electrons are localized in twelve in-plane σ lone pairs (σ -LPs). The σ skeleton is comprised by six $2c-2e$ C–F bonds and six $2c-2e$ C–C bonds (Figure 6a). Remarkably, AdNDP provides two solutions to localize the π bonding in hexafluorobenzene. The first solution includes six p_z -LPs ($ON=1.92|e|$) on the fluorine atoms and three $6c-2e$ bonds ($ON=2.00|e|$) distributed on the C_6 fragment (Figure 6b). The second solution involves six $2c-2e$ C–F π bonds ($ON=2.00|e|$) and three $12c-2e$ π bonds ($ON=2.00|e|$) (Figure 6c). While both solutions are viable, given that the second option completely localizes the π electrons, we consider this to be the most appropriate localization scheme.

The inductive effect can be clearly understood when the $2c-2e$ C–F bonds in hexafluorobenzene are compared with the $2c-2e$ C–H bonds in benzene using the same isosurface (see Figures 5a and 6a). The charge density inside the C_6 ring is depleted in the case of the hexafluorobenzene. On the other hand, the resonant effect is also exhibited because the C–F bonds have a π -bonding character (Figure 6c). A gradual substitution of H by F shows also a gradual increment of both effects (see Figure S3.1–S3.2 in the Supporting Information). Therefore, the inductive and resonant effects on the fluorinated benzene are apparent from the AdNDP analysis. So, decreased aromaticity upon fluorination of benzene is consistent with the fact that the fluorine atoms attract electron density through C–F σ bonds (inductive effect), deshielding the nuclear charge on carbon atoms. At the same time, the carbon atoms try to compensate this effect by withdrawing electron density from F through $p_z-\pi$ conjugation. Therefore, such perturbation on the π cloud induces a loss of aromaticity, which is also supported by the analysis of the induced magnetic field (see above). It has been also reported that fluorination decreases aromaticity in polycyclic aromatic hydrocarbons (PAHs).^[15] In contrast, the effect of fluorination

Table 1. Comparison of RCS with NICS(*r*) and $B_z^{\text{ind}}(r)$ values calculated for benzene and fluorinated benzene derivatives.

Atomic system ^[a]	RCS [nA/T]	$-(1/3) B_z^{\text{ind}}(r)^{[b]}$ [ppm]				$-NICS(r)^{[b]}$ [ppm]			
		(1.96 Å)	(1.18 Å)	(1.00 Å)	(0.00 Å)	(1.96 Å)	(1.18 Å)	(1.00 Å)	(0.00 Å)
a	12.00	6.07	9.62	9.90	4.88	5.12	9.62	10.40	8.21
b	11.60	5.77	9.24	9.57	5.13	4.94	9.59	10.55	10.13
c	11.30	5.52	8.92	9.27	5.26	4.86	9.71	10.83	11.92
d	11.00	5.42	8.73	9.07	5.25	4.68	9.42	10.53	11.81
e	11.10	5.43	8.76	9.10	5.12	4.72	9.48	10.58	11.74
f	10.40	5.02	8.09	8.43	5.19	4.36	9.11	10.34	13.24
g	10.70	5.18	8.42	8.80	5.39	4.59	9.55	10.82	13.57
h	10.80	5.25	8.52	8.90	5.38	4.69	9.71	10.99	13.57
i	10.50	5.01	8.20	8.61	5.69	4.66	9.92	11.36	15.38
j	10.20	4.87	7.94	8.32	5.45	4.42	9.49	10.90	15.05
k	10.40	4.94	8.10	8.51	5.68	4.51	9.70	11.14	15.36
l	10.10	4.73	7.79	8.22	5.92	4.49	9.94	11.54	16.93
m	9.90	4.54	7.54	8.01	6.27	4.54	10.32	12.08	18.49

[a] For system structures, see Scheme 1; [b] The negative value of both (1/3) $B_z^{\text{ind}}(r)$ and NICS was used to facilitate comparison with RCS.

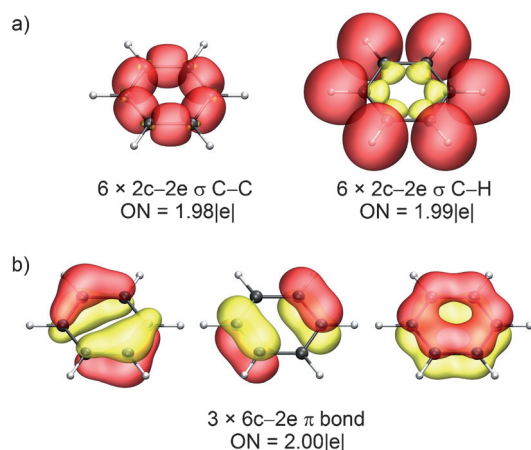


Figure 5. The a) σ -bonding pattern and b) π -bonding pattern of benzene according to AdNDP.

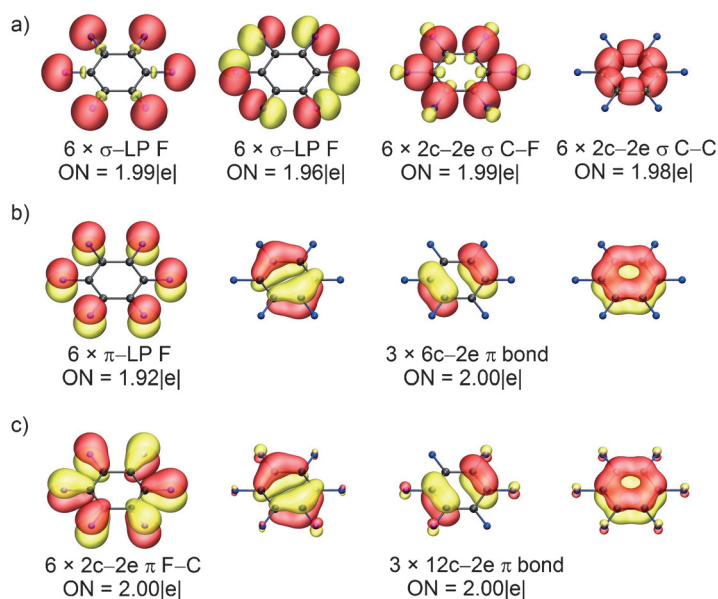


Figure 6. The a) σ -bonding pattern and b,c) two possible π -bonding patterns of hexafluorobenzene according to AdNDP.

on the aromaticity of a series of 1- and 2-indenones and their aza derivatives has been reported to be negligible,^[27] suggesting that these findings cannot be extrapolated to heteroaromatic rings.

Conclusions

A detailed analysis of the magnetic descriptors (RCS, NICS, or B_z^{ind}) leads to the same conclusion, benzene is more aromatic than hexafluorobenzene. The AdNDP analysis supports the presence of inductive and resonant effects in the fluorinated species. The effects on the mag-

netic properties are rationalized as follows: the resonant effect should diminish the π electronic delocalization and, therefore, aromaticity in the fluorinated species. On the other hand, the inductive effect should decrease the charge density at the ring center and thus, decrease the magnitude of the paratropic current generated in this region. So, the evaluation of the magnetic properties at the center of the rings should strongly be influenced by this paratropic current, leading to erroneous interpretations of aromaticity. These findings could be extrapolated to any fluorinated species in the series $C_6H_{6-n}F_n$ ($n=1-5$), therefore our results support the proposal of Kaipio et al.^[15] which states that fluorination should decrease aromaticity, due to the decrease of the π cloud on the ring.

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Keywords: adaptive natural partitioning analysis · aromaticity · induced magnetic fields · magnetically induced current density · fluorinated benzenes

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