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Not All That Has a Negative NICS Is Aromatic: The Case of the H-Bonded Cyclic Trimer of HF

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Abstract: In this work, we used the induced magnetic field ($\mathbf{B}^{ind}$) to study the degree of aromaticity of the planar $(HF)_3$ ring. The induced magnetic field analysis shows that the degree of electron delocalization in the hydrogen-bonded cyclic trimer of HF is very low. This result is in agreement with those obtained using GIMIC and is opposite to the Rehaman's suggestion. Our results demonstrate a clear limitation of the NICS index when a strong anisotropy is exhibited and suggest that the NICS values should be used carefully to discuss aromaticity in systems without an important p_z-orbital overlap that produces the π clouds. In view of the fact that the NICS index is extensively used by computationally and theoretically oriented experimental chemists, this is an important warning.

Introduction

The IUPAC defines aromaticity as "*The concept of spatial and electronic structure of cyclic molecular systems displaying the effects of cyclic electron delocalization which provide for their enhanced thermodynamic stability (relative to acyclic structural analogues) and tendency to retain the structural type in the course of chemical transformations*".[1] Nevertheless, it is enough to check the last two *Chem. Rev.* issues dedicated to aromaticity[2] and electron delocalization[3] to realize that this definition is still controversial. In general, a quantitative and/or qualitative assessment of the degree of aromaticity is given by the chemical behavior (lower reactivity), structural features (planarity and equal bond length tendencies),[4,5] energy (stability), and spectroscopic properties (UV, proton chemical shifts, and magnetic susceptibility exaltation). Recently several magnetic indices of aromaticity have been introduced and discussed. They include the famous nucleus-independent chemical shift (NICS) and related indexes,[6,7] aromatic ring-current shielding (ARCS),[8] and plotted ring-current densities.[9,10] Particularly,

the concept of a ring current, introduced by Pople, has been used widely to interpret the magnetic properties of aromatic molecules.[11,12]

Even though that aromaticity is not well-defined and was originally developed within the organic chemistry scheme, this concept has been extended to inorganic systems. Interestingly, all-metal clusters and inorganic compounds[13−17] have not only the conventional π-(anti)aromaticity but also the σ-,[18−22] δ-[23−25] or even φ-(anti)aromaticity,[26] i.e., a multifold aromaticity.[27−30]

In 2005 Rehaman et al. suggested that the planar hydrogen-bonded cyclic $(HF)_3$ (see Scheme 1) is aromatic.[31] They claimed that the existence of aromaticity in such hydrogen-bond complexes is apparent from the NICS values (in ppm) of -2.94, -1.98, and -1.89 for $(HF)_3$, $(HCl)_3$, and $(HBr)_3$, respectively. Similar results were also reported for water clusters $(H_2O)_n$.[32] Recently, one of us has studied the interplay between aromaticity and hydrogen bonding in 1,3-dihydroxyaryl-2-aldehydes.[33,34] In that case, the quasi-ring partially adopts the role of a typical aromatic ring, favoring phenomena like for proton transfer reactions, contrary to the $(HF)_3$ complex.
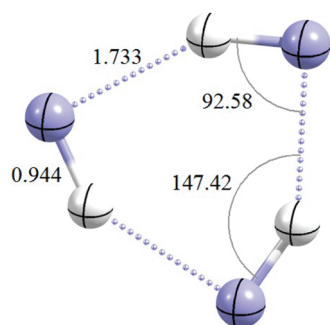
Of course, the existence of "hydrogen-bonded aromaticity" involving strong ring currents across hydrogen bonds is

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Scheme 1

very attractive. However, Lin and Sundholm reported the nuclear magnetic shieldings and magnetically induced ring currents for the planar ring-shaped hydrogen fluoride trimer $(HF)_3$,[35] and using the gauge-including magnetically induced current (GIMIC) method[36] showed that, contrary to the Rehaman et al. suggestion,[31] $(HF)_3$ has a very small ring-current susceptibility of 0.37 nA/T. Thus, only a weak net current is passing across the H···F hydrogen bond.

A magnetic field perpendicular to any plane can induce a current density in and parallel to the selected plane. This current density induces a counter field. In this sense, the induced magnetic fields and induced current densities are complementary to each other. Induced current densities are usually given in one selected plane parallel to the molecular ring, while the induced magnetic field contains information of the overall current density distribution. Having both analyses available is, therefore, advantageous. In other words, the induced magnetic field reveals important information on electron delocalization and, furthermore, of its origin.[37] Recently, we have studied the induced magnetic field of several systems.[38−44] In agreement with current density maps,[10] the response of aromatic, antiaromatic, and nonaromatic examples show different features.

In this work, we used the induced magnetic field $(\mathbf{B}^{ind})$ to study the degree of aromaticity of the planar $(HF)_3$ ring. Similar to the GIMIC results, our calculations show that the mentioned complex is not an aromatic system. Frequently, NICS is related to the strength of the induced ring current. However, in this case, NICS contains contributions from the in-plane components, which can be regarded sometimes as spurious for evaluating aromaticity.

Computational Details

The geometry optimizations were performed with the B3LYP[45,46] functional, as implemented in the Gaussian 03 program,[47] in conjunction with the def2-TZVPP basis set. At variance with the HF dimer,[48,49] the optimized molecular structure of the trimer is not significantly affected by the basis set superposition error (BSSE) and, therefore, we have not considered the BSSE correction in the HF trimer optimization. The induced magnetic field $(\mathbf{B}^{ind})$ calculations were performed by using the PW91 density functional[50] in conjunction with the IGLO-III basis set. The shielding tensors were computed using the IGLO method.[51] The deMon program was used to compute the molecular orbitals[52] and the deMon-NMR package for the shielding tensors.[53] Induced

magnetic fields of the external field applied perpendicularly to the molecular plane were computed in ppm. Assuming an external magnetic field of $|\mathbf{B}^{ext}| = 1.0$ T, the unit of $\mathbf{B}^{ind}$ is 1.0 μT, which is equivalent to 1.0 ppm of the shielding tensor. In order to render the induced magnetic fields, the molecules were oriented so that the center of mass was located at the origin of the coordinate system; the z-axis is parallel to the highest order symmetry axis of the molecule. The external field was applied perpendicular to the $(HF)_3$ plane. VU was employed for the visualization of molecular fields.[54]

Results and Discussion

Figure 1 depicts the contour lines and isosurfaces of both the z-component of the induced magnetic field, $\mathbf{B}^{ind}_z$ and the NICS for the $(HF)_3$ complex. It is important to remark that the $\mathbf{B}^{ind}_z$ for an external field perpendicular to the ring is equivalent to the $NICS_{zz}$ index. In a typical aromatic molecule, like benzene, no paratropic contributions to the $\mathbf{B}^{ind}$ are observed inside the ring, and only a strong shielding region to the carbons inside the ring is obtained. In contrast, the hydrogen complex shows a strong but short-range paratropic response inside the ring (Figure 1A). Interestingly, the shielding cones above and below the $(HF)_3$ complex are comparable in shape and intensity to those of a nonaromatic system.[37] Note that each HF moiety is diatropic, but the deshielding regions are further outside (given in red), and there is not an effective overlap of the HF diatropic zones close to the plane ring.

NICS, defined as the negative total isotropic shielding (average shielding), can be computed at any point in space. Isolines and the isosurface of NICS, that is, the effect on the isotropic shielding, caused by external magnetic fields from all directions, are depicted in Figure 1B. The average virtual shielding (3.7 ppm) evaluated at the center of mass corresponds to a NICS index of −3.7, according to the definition proposed by Schleyer et al. (cf. with the value of −2.9 as reported by Rehaman et al.).[31] It must be remarked that the large anisotropies of the shielding tensors of the $(HF)_3$ complex lead to a notable change between both $\mathbf{B}^{ind}_z$ and NICS scalar fields: (i) The isotropic shielding is smaller in magnitude than that caused only by an external field in the z-direction and (ii) Close to the ring center, the NICS values are negative showing a low aromatic character. Generally, the NICS tensor is strongly anisotropic, i.e., values of σ_{xx} and σ_{yy} components differ strongly from the σ_{zz} contribution; however, in most cases, like in benzene, the absolute value of the $(\sigma_{xx} + \sigma_{yy})$ term is smaller than that of the σ_{zz} one, therefore, the $\mathbf{B}^{ind}_z$ and NICS have the same sign. In this case, at the ring center the $\sigma_{xx} = \sigma_{yy} = 11.5$ ppm and the $\sigma_{zz} = -13.3$ ppm, giving a big difference between both aromaticity indexes.

Formally, the pure p_z lone pairs of the fluorine atoms become three π orbitals of the planar $(HF)_3$ complex, so the system could be considered a Hückel aromatic complex. However, there is not a remarkable overlap of p_z orbitals that produces the π clouds and, thus, there is not an important electron delocalization in that complex. As our method allows the separation into core σ and π orbitals, we can discuss the
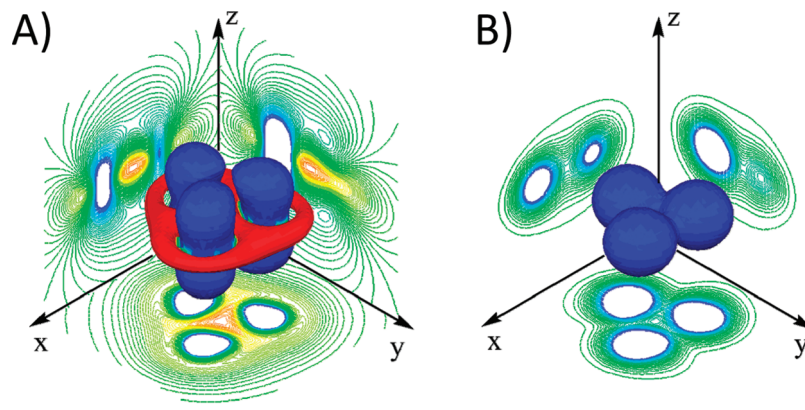
Figure 1. (A) Isosurfaces of the *z*-component of the induced magnetic field $\mathbf{B}^{ind}_z$ and (B) NICS. $|\mathbf{B}^{ind}_z|$ and $|NICS(\mathbf{r})| = 4.0\ \mu T$, and $\mathbf{B}^{ext} = 1.0$ T perpendicular to the molecular plane. Blue and red colors indicate shielding and deshielding areas, respectively.
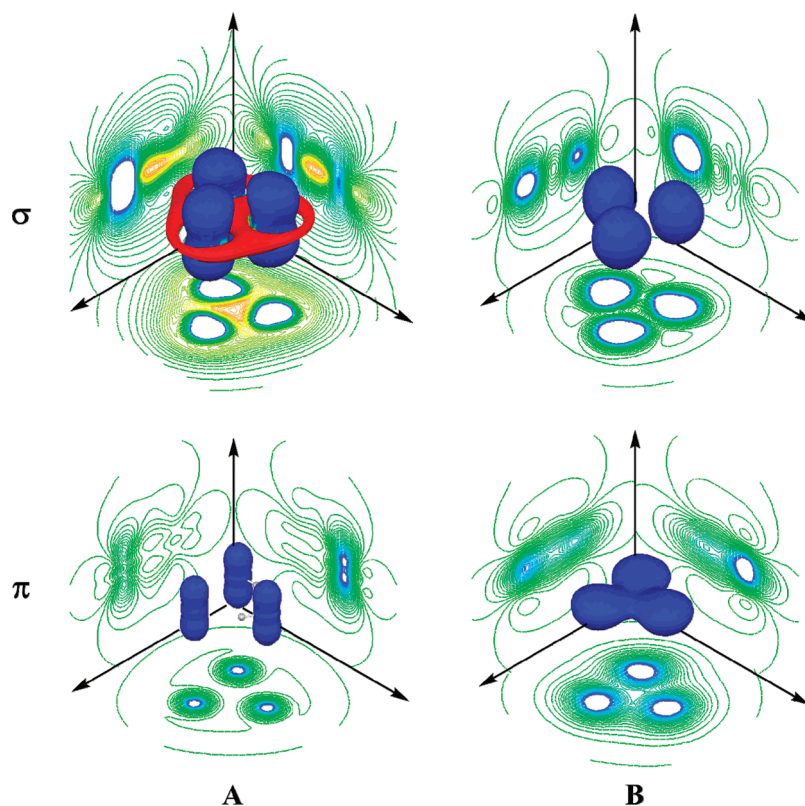

Figure 2. Induced magnetic field and NICS of the $(HF)_3$ complex. (A) The $\mathbf{B}^{ind}_z$, shielding (diatropic, blue) or enforcing (paratropic, red) the external field, shown in the same planes as for the field lines. (B) Contour lines of NICS(**r**) (equivalent to the negative shielding density) are shown in the same planes as the field lines.

role of each orbital contribution as shown in Figure 2. The core electrons do not contribute to $\mathbf{B}^{ind}$, except in the very close vicinity of nuclei. The σ orbital contributions to $\mathbf{B}^{ind}_z$ have quite a similar shape and magnitude to the total $\mathbf{B}^{ind}_z$. As σ electrons are strongly localized, their local diamagnetic contributions generate a short-range response and a paratropic (deshielding) region at the ring center (Figure 2A). In the same way, the π electrons are quite localized at the fluorine atoms, and only a short-range diamagnetic response is observed. In contrast, the $NICS_\sigma$ still includes the current effects induced by magnetic fields parallel to the ring, which are not negligible and have an impact in the shape of the

shielding cones. The σ component is responsible for the negative value observed at the ring center. Lazzeretti pointed out that serious interpretation errors can be done by confusing the averaged trace and the out-of-plane component.[10] Our results are in agreement with that comment.

Finally, let us estimate the contribution of each H−F fragment to both the induced magnetic field and NICS. Of course, this approximation is only valid for weak interactions. For instance, Poater and co-workers showed that the apparent increase of local aromaticity in superimposed aromatic rings indicated by NICS is not real, but rather the result of the magnetic field generated in one ring due to the electron
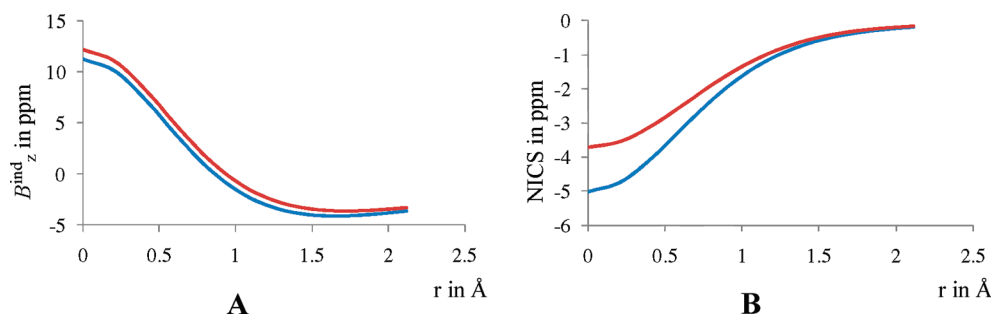
Figure 3. (A) B^{ind}_z and (B) NICS profiles along the *z*-axis of the planar $(HF)_3$ trimer. The blue and red lines show the profiles of the noninteracting and bonded complexes, respectively.

current density of the other ring placed above it.[55] In our case, Figure 3 shows the profiles along the *z*-axis for both scalar fields (B^{ind}_z and NICS); $r = 0$ corresponds to the ring center. Interestingly, at $r = 0$ the contribution of each fragment to B^{ind}_z is 3.75 ppm, i.e., the sum of three fragments is 1.0 ppm lower than in the complex (12.2 ppm). In this sense, our results provide evidence that the noninteracting trimer is more diatropic (aromatic) than the planar bonded $(HF)_3$ complex. A similar conclusion can be emerged from the NICS analysis.

Conclusion

We have shown that the electron delocalization degree in the planar hydrogen-bonded HF cyclic trimer is very low. This result is in agreement with that obtained using GIMIC[36] and is opposite to the Rehaman et al. suggestion.[31] Our results show a clear limitation of the NICS index when a strong anisotropy is exhibited and suggest that the NICS values should be used carefully to discuss aromaticity in systems without an important overlap of p_z orbitals that produces the π clouds. In view of the fact that the NICS index is extensively used by computationally and theoretically oriented experimental chemists, this is an important warning. Our results are also in line with the Lazzeretti comments,[10] who mentioned that the analyses based on average values imply a loss of information, and thus criteria for diatropicity and aromaticity should be established in terms of the out-of-plane component of magnetic tensors. Our conclusion to be cautious regarding an interpretation of the NICS index is also supported by the work of Pierrefixe et al.[5] They showed that the symmetric geometry in benzene-type aromatic species (which is originating the small highest-occupied and lowest-unoccupied molecular orbitals, HOMO−LUMO, gap of the π system and thus contributes to the ring current) is caused by the tendency of the σ system, not the π system, which is still often (erroneously) held responsible.

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