

On the Aromaticity of the Planar Hydrogen-Bonded (HF)₃ Trimer

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Abstract: The nuclear magnetic shieldings and magnetically induced ring currents have been calculated for the planar ring-shaped hydrogen fluoride trimer (HF)₃ at correlated ab initio and density functional theory levels. Calculations of the magnetically induced current densities using the gauge-including magnetically induced current (GIMIC) method show that, contrary to a recent suggestion, (HF)₃ has, at the MP2/TZVPP level, 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. An external magnetic field perpendicular to the ring plane induces strong edge currents circling around each HF molecule giving rise to a nonvanishing magnetic shielding at the center of the ring. The GIMIC results are supported by calculations of the long-range magnetic shielding function; the long-range magnetic shielding is very small, indicating that the magnetically induced ring-current is very weak. The surprisingly large nucleus-independent chemical shift (NICS) value for (HF)₃ was recently taken as an indication of “H-bonded aromaticity”. The NICS value calculated at the CCSD/QZ2P level is 2.77 ppm. The present GIMIC and aromatic ring-current shielding study shows that some care has to be taken when using NICS values as aromaticity indices.

I. Introduction

Aromatic molecules were originally defined as planar organic molecules fulfilling the $4n + 2$ rule for the electron count, with benzene as the archetypal example.¹ Aromatic molecules were also found to sustain diamagnetic currents when exposed to external magnetic fields, whereas antiaromaticity was coined to describe molecules sustaining paramagnetic ring currents; that is, the current circles in the opposite direction as compared to the aromatic ones.^{2–4} The aromaticity concept has lately been extended to comprise many kinds of molecules with electron delocalization.⁵ Nowadays, it is used not only in organic chemistry but also to describe inorganic systems.^{6,7} Metal clusters are found to be both aromatic and antiaromatic.^{8–10} Molecules sustaining ring currents in the σ orbitals are denoted σ aromatic. Homo-

aromatic molecules are bent organic species that sustain strong ring currents even though they have aliphatic bonds in the ring, which at first sight seem to interrupt the electron delocalization of the ring.^{11–13} Spherical aromatic molecules consist of approximately spherical (e.g., icosahedral) molecules fulfilling a $2(N + 1)^2$ rule for the number of valence electrons.^{14–18} These are the magic numbers of electrons for closed-shell model systems with an indefinitely thin spherically symmetric shell potential. Simpler three-dimensional cage-shaped molecules are found to possess 3D aromaticity.¹⁹

Chemists are very fond of the aromaticity concept, even though, or because, it is not very well defined. Computational chemists have invented new computational tools to predict and define molecular aromaticity and the degree of aromaticity. As a result, regularly, new aromaticity concepts are born, some more successful than others. Recently, Datta et al.^{20,21} proposed the term *H-bonded aromaticity* as a new

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kind of aromaticity. Computationally, they found a significant diamagnetic shielding at the center of cyclic HX (X = F, Cl, and Br) trimers and interpreted it as a result of ring currents passing the hydrogen bonds between the monomers. They have also reported similar results for water clusters (H₂O)_n.²¹ In their studies, nucleus-independent chemical shifts (NICSs) were used to determine the degree of aromaticity.²² The NICS value is an often-engaged tool to assess molecular aromaticity.²³

The discovery of “H-bonded aromaticity” involving strong ring currents across hydrogen bonds would indeed be very intriguing. In principle, the NICS index is supposed to be linearly related to the strength of the induced ring current. In practice, however, the magnetic shielding at the center of the molecule can be strongly affected by the local electronic structure. Thus, care must be taken in the interpretation of calculated NICS values.^{13,24–27} In this work, we use the aromatic ring-current shielding (ARCS) index²⁸ and the newly developed gauge-including magnetically induced current (GIMIC) method²⁹ to study the nature of the induced currents and to assess the degree of aromaticity of the (HF)₃ ring.

II. Computational Methods

The molecular structure was optimized at the second-order Møller–Plesset perturbation level (MP2) using the TURBOMOLE program package.³⁰ In the structure optimization, we employed the Karlsruhe standard triple- ζ valence basis sets augmented with double polarization functions (TZVPP) as well as Dunning’s correlation consistent quadruple- ζ (cc-pVQZ) and quintuple- ζ (cc-pV5Z) basis sets.³¹ The molecular structure was also optimized at the density functional theory level (DFT) employing Becke’s three-parameter functional in combination with the Lee–Yang–Parr correlation functional (B3LYP)^{32,33} using the TZVPP basis sets.

The nuclear magnetic shieldings were calculated at the coupled-cluster singles and doubles (CCSD) level using Ahlrichs’ quadruple- ζ (QZ) quality (11s7p/6s4p) basis sets augmented with 2d1f polarization functions for F. For H, Ahlrichs’ QZ basis set (7s/4s) was augmented with 2p1d polarization functions.³⁰ We denote these basis sets QZ2P. Magnetic shielding calculations were also performed at the MP2 and B3LYP levels. The magnetic shielding calculations at the MP2 and CCSD levels were performed with the ACES II program,^{34–37} whereas the B3LYP and some MP2 calculations of the magnetic shieldings were done with TURBOMOLE.^{38,39} The magnetically induced current densities were deduced from the one-particle density matrix and the magnetically perturbed density matrices calculated at the MP2 level using the GIMIC approach.²⁹ The ring-current susceptibility was obtained by numerical integration of the current density passing cut planes perpendicular to the molecular ring. The ring-current susceptibility was also estimated from the long-range magnetic shielding along the symmetry axis perpendicular to the molecular plane using the ARCS approach. The ring-current susceptibility can be obtained by fitting the ARCS function to Biot–Savart’s expression for a circular and infinitely thin conducting wire.

Table 1. Molecular Structure of (HF)₃ Optimized at the MP2 and B3LYP Levels Using Different Sizes of Basis Sets^a

level	R(H–F)	R(H···F)
MP2/TZVPP	93.7	173.9
MP2/cc-pVQZ	93.5	174.2
MP2/cc-pV5Z	93.5	175.5
B3LYP/TZVPP	94.4	173.4
B3LYP/cc-pVQZ	94.3	173.0
B3LYP/6-311G++(d,p) ^b	94	183

^a The HF hydrogen bond is denoted with H···F. The bond lengths are given in pm. ^b Ref 20.

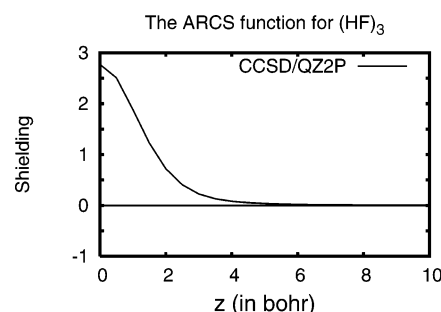


Figure 1. Nuclear magnetic shielding function (in ppm) calculated at the CCSD/QZ2P level. The shielding function is calculated from the ring center along the symmetry axis perpendicular to the ring.

NICS values were obtained as the negative magnetic shielding in the center of the molecular ring.^{22,23}

III. Molecular Structures

The molecular structure optimized at the MP2 and B3LYP levels are given in Table 1. At the MP2 level, the length of the hydrogen bond increases slightly with the size of the basis set, because the basis-set superposition error causes some overbinding, which decreases with increasing basis-set size. The length of the hydrogen bond is found to be slightly longer at the MP2 level than at the B3LYP level. In their recent study, Rehaman et al.²⁰ obtained 10-pm-longer hydrogen bonds at the B3LYP/6-311G++(p,d) level.

IV. Magnetically Induced Currents and Magnetic Shieldings

The calculation of the magnetic shielding function along the symmetry axis (the ARCS function) shows that the long-range magnetic shielding vanishes outside the electron charge density, indicating that the molecular ring does not sustain any strong ring current. The ARCS function calculated at the CCSD/QZ2P level is shown in Figure 1. The ring-current susceptibility deduced from the ARCS function is 0.9 nA/T as compared to the benzene value of 8 ppm.²⁸ The ARCS fit is not very accurate because the long-range magnetic shielding is small as a result of the weak ring current. In the ARCS fit, the angular coefficient is 1.88 and not 1.5 as it should be. For comparison, a ring-current susceptibility of 0.34 nA/T was obtained by performing a numerical integration of the current density passing a cut plane of the molecular ring through the center of the HF bond. The current density was calculated at the MP2/TZVPP level using

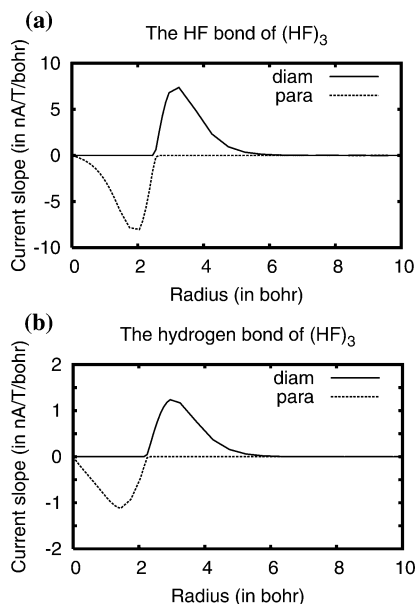


Figure 2. Diamagnetic and paramagnetic currents passing a cut plane (a) through the HF bond and (b) through the hydrogen bond of the $(\text{HF})_3$ trimer. Note that the maximum for the hydrogen bond is about a factor of 6 smaller than that for the HF molecule. The calculation is performed at the MP2/TZVPP level.

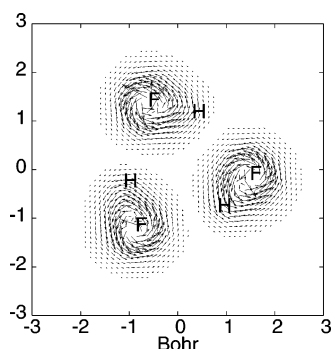


Figure 3. Magnetically induced current density in the molecular plane calculated at the MP2/TZVPP level.

the GIMIC approach. At the B3LYP/TZVPP level, we obtained, in the similar GIMIC calculation, a ring-current susceptibility of 0.44 nA/T. The ring-current susceptibility function calculated at the MP2/TZVPP level is shown in Figure 2. The ring-current susceptibility for benzene calculated at the CCSD/TZP level is 11.8 nA/T.²⁹ For comparison, the ring-current susceptibility for the edge current circling around the HF molecules calculated at the MP2/TZVPP and B3LYP/TZVPP levels are 9.1 and 8.8 nA/T, respectively. The magnetically induced current density in the molecular plane is shown in Figure 3. The current is diamagnetic on the outside of the molecule, whereas the return current on the inside of the HF monomer becomes paramagnetic (negative). At the MP2/TZVPP level, the integration of the current passing the cut plane across the hydrogen bond yields a ring-current susceptibility of 0.37 nA/T (0.46 nA/T at the B3LYP/TZVPP level), which is very close to the sum of the diamagnetic and paramagnetic currents circling the HF molecules, as it should be. The ARCS and GIMIC calcula-

tions of the ring-current susceptibility show that $(\text{HF})_3$ should not be considered aromatic according to the ring-current criterion.

The NICS values obtained at different levels of theory are 2.89 ppm (MP2/QZ2P), 2.77 ppm (CCSD/QZ2P), 2.97 ppm (B3LYP/cc-pVQZ), and 3.24 ppm (B3LYP/TZVPP). Thus, according to the NICS values, the ring current circling the ring should be about one-third of the benzene value. Thus, the NICS calculation is not capable of providing the correct degree of aromaticity for this system, showing that NICS values as aromaticity indices cannot be used as a black-box tool but require careful consideration. Lazzeretti has also recently pointed out that the NICS value is not a very reliable aromaticity index.⁴⁰ This notion is supported by our study.

Conclusion

The magnetically induced current density and magnetic shieldings of the planar $(\text{HF})_3$ trimer have been studied at ab initio and DFT levels using large basis sets. The calculation of the long-range magnetic shieldings and the explicit integration of the magnetically induced ring-current susceptibility yield ring-current susceptibilities of 0.37 nA/T (MP2/TZVPP), showing that $(\text{HF})_3$ cannot be considered to be aromatic, as recently proposed by Rehman et al.²⁰ The obtained NICS values are 2.77–3.24 ppm, depending on the computational level. The surprisingly large NICS value is not due to a magnetically induced ring-current and is, therefore, not an indication of molecular aromaticity but a result of the strong edge currents circling around each HF monomer in the ring. The ARCS and GIMIC calculations clearly show that the $(\text{HF})_3$ ring is nonaromatic and that NICS values as aromaticity indices should be used with care.

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