Planar Tetracoordinate Fluorine Atoms

Gabriela Castillo-Toraya,¹ Mesías Orozco-Ic,¹ Eugenia Dzib,¹ Ximena Zarate,² Filiberto Ortíz-Chi,³ Jorge Barroso,¹,* Gabriel Merino.¹,*

¹ Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Unidad Mérida, Mérida, Yucatán, México.

² Instituto de Ciencias Químicas Aplicadas, Facultad de Ingeniería, Universidad Autónoma de Chile, Santiago, Chile.

³ CONACYT-Universidad Juárez Autónoma de Tabasco, Centro de Investigación de Ciencia y Tecnología Aplicada de Tabasco, Cunduacán 86690, Tabasco, México.

E-mail: gmerino@cinvestav.mx
jorge.barroso@cinvestav.mx
Abstract

Unlike other atoms, planar tetracoordinate fluorines are elusive. So far, there are no theoretical or experimental reports suggesting their existence. Herein, we introduce the first six combinations, whose global minima contain a planar tetracoordinate fluorine. All of them are surrounded exclusively by atoms of group 13. The bonding scheme shown by these species is entirely different from analogous systems with carbon, nitrogen, or oxygen atoms. The magnetic response characterizes these systems mostly as σ-aromatic. The planar form is somewhat stabilized by subtle ionic interactions of the fluorine with the peripheral atoms, forming an adequately sized cavity.
Planar tetracoordinate carbon (ptC) atoms are oddities, they embody a conflict with one of the most important paradigms in organic chemistry, yet some exist in bottles. The long-standing tetrahedral model of van't Hoff and Lebel was first questioned in 1968 when Monkhorst suggested a transition state (TS) with a ptC in the stereomutation of some tetrahedral carbon compounds. Two years later, Hoffmann, Alder, and Wilcox proposed a few rules for stabilizing such TS based on planar methane's molecular orbital analysis. Schleyer and co-workers adopted this idea to introduce the first structure with a ptC that is energetically more favorable than its tetrahedral counterpart. In 1991, Boldyrev and Schleyer predicted various planar tetracoordinate atom molecules with carbon (cis-Al₂Si₂C and trans-Al₂Si₂C) and other second-row elements as OAl₄ and its isoelectronic congeners NAl₄⁻, NAl₃Si, and BAlSi₃, all of them with 18 valence electrons (18ve).

Later, Boldyrev and Simons established that 18ve are required to stabilize a planar form, in which three C−ligand σ-bonds, one C−ligand π-bond, and one ligand−ligand bond take place. The first neutral pentaatomic ptC molecules with 17 and 18ve experimentally observed in the gas-phase via anion photoelectron spectroscopy and characterized by ab initio computations were CAl₄⁻ and CAl₄²⁻, respectively. Although the 18ve valence rule is not universal (a rule is not a law), it proved useful in predicting new planar hypercoordinate atoms.

So, the theory has played a fundamental role in predicting and understanding these peculiar species. Although the list is long, it does not include a theoretically or experimentally reported planar tetracoordinate fluorine (ptF) atom, which does not make sense since the $D_{4h}$ CAl₄²⁻, NAl₄⁻, and OAl₄ structures are the global minima on their corresponding potential energy surfaces (PESs). Why is the isoelectronic FAI₄⁺ not planar? Is it possible to introduce fluorine into the flat world? Herein, we systematically explored the PESs of all viable pentaatomic clusters containing a fluorine atom combined with main group elements, totaling 18ve and charges from +2 to -2. This
amounts to 440 combinations and around 100,000 optimizations. Gratifyingly, we found six stoichiometries as the global minima containing a ptF atom.

The systematic exploration of the corresponding PESs was carried out through a modified genetic algorithm, as implemented in the GLobal Optimization of MOlecular Systems (GLOMOS). GLOMOS is written in Python and includes stochastic and evolutive methodologies to carry out the global optimization of atomic and molecular clusters, where the local optimizations are solved through an electronic structure code. The initial screening was done at the TPSS/def2-SVP level. All the stationary points were re-minimized and characterized at the TPSS/def2-TZVP level, including Grimme’s D3 dispersion scheme with Becke-Johnson damping. The final energies were refined at the CCSD(T)/def2-TZVP level, including the zero-point energy correction at the TPSS-D3(BJ)/def2-TZVP. Thus, the energetic discussion is based on the CCSD(T)/def2-TZVP//TPSS-D3(BJ)/def2-TZVP results. All of these computations were performed with Gaussian 16.

Interestingly, structures with a ptF only arise in clusters formed by substituents exclusively of group 13 (Figure 1). Let us start with those systems with a single element as ligands, i.e., FE₄⁺ (E = Al, Ga, In, Tl). The planar D₄ᵥ form of FAl₄⁺, with F-Al bond lengths (r_F-Al) of 2.214 Å, has two imaginary frequencies. Apparently, the cavity formed by four aluminum atoms is not large enough to accommodate a fluorine atom. The putative global minimum, 18.7 kcal/mol lower in energy, is a C₂ᵥ aluminum tetrahedron with fluorine at the edge (see Figure S1). For the FGa₄⁺ case, the D₄ᵥ arrangement (r_F-Ga = 2.238 Å) is a transition state (ν_min = -70 cm⁻¹), 4.5 kcal/mol higher in energy than the most stable structure formed by a gallium triangle and F-Ga fragment. Gratifyingly, the global minimum structures for FIn₄⁺ (r_F-In = 2.415 Å) and FTl₄⁺ (r_F-Tl = 2.533 Å) have the perfect cavity to stabilize a ptF. In other words, the cavity size is critical.
Figure 1. TPSS-D3/def2-TZVP structures of the FE$_4^+$ (E = Al, Ga, In, Tl) series. Bond lengths are in Å.

With this in mind, we explored the possibility of combining two elements of group 13 (except boron because it creates a small cavity) as ligands to produce more clusters with a ptF. Notably, there is no ptF as the global minimum if the structure contains aluminum. The only ptFs, but as local minima, are FIn$_3$Al$^+$ and FTL$_3$Al$^+$. It might be assumed that replacing a Ga atom in FGa$_4^+$ with a heavier element should create a cavity large enough to stabilize a ptF, but it is not so obvious (this only occurs for FGaIn$_3^+$). Interestingly, while the putative global minimum of FGaIn$_3^+$ ($r_{F-Ga} = 2.180$ Å) is a ptF, the ptF isomer for FGaTl$_3^+$ ($r_{F-Ga} = 2.110$ Å) is 0.6 kcal/mol higher in energy than the structure with the tricoordinate fluorine atom. In fact, the F-Ga bond lengths are shortened in clusters containing Tl, reducing the cavity space. So, using larger atoms does not necessarily lead to larger cavities. In contrast, the three combinations that include In and Tl (FIn$_2$Tl$_2^+$, FIn$_3$Tl$^+$, and FInTl$_3^+$) yield cavities with the perfect size for stabilizing a true ptF.

Why are ptFs so elusive compared to their isoelectric analogues CAl$_4^{2-}$, NAl$_4^-$, and OAl$_4$? Table 1 reveals particular trends among planar tetracoordinate atoms surrounded by Al. First, our
computations show that going from CAl$_4^{2-}$ to FAl$_4^+$, there is a natural charge\textsuperscript{30} decrease on the central atom (from -2.62 |e| to -0.88 |e|) with a charge increment on the peripheral atoms (from +0.16 |e| to +0.47 |e|). So, the charge transfer from the Al$_4$ skeleton to the central atom is more effective in the fluorine case. In other words, the ionic character between the hypercoordinate center and the metal fragment increases from C to F. This is also supported by the significant reduction in the total values of the Wiberg Bond Index (WBI)\textsuperscript{31} of the central atom from 2.29 in CAl$_4^{2-}$ to only 0.24 in FAl$_4^+$, which, of course, is a consequence of the electronegativity difference between the peripheral atoms and the corresponding planar tetracoordinate atom. The electron transfer mechanism is less obvious, while carbon acts as $\sigma$-acceptor, and this is compensated by the back-donation from its 2$p_c$ electrons to the $\pi$-bonding ($2s^{1.60}$ $2p_x^{1.76}$ $2p_y^{1.76}$ $2p_z^{1.46}$), the back-donation is null in the fluorine compounds. This is the main reason why these species are so rare.

While several ptCs have been predicted and even detected experimentally, only six from 440 compositions contain a planar fluorine atom within the established parameters. For all ptFs, global minimum or not, there is a negligible variation of the fluorine charges and orbital occupancies. The only distinction is a subtle increase in the total WBI values of the gallium clusters due to their relatively short Ga-F bonds.
Table 1. NPA charges (q, |e|), valence population, and the total Wiberg bond index of the planar hypercoordinate atom. HOMO-LUMO gap (Δ_H-L, eV) and the lowest vibrational frequency, ν_{min}.

| Configuration | q   | Configuration | WBI_{total} | Δ_H-L (eV) | ν_{min} |
|---------------|-----|---------------|-------------|------------|---------|
| FAl_4^+       | -0.88 | 2s^{1.97} 2p_x^{1.97} 2p_y^{1.97} 2p_z^{1.97} | 0.24 | 1.15 | -47 |
| FGa_4^+       | -0.86 | 2s^{1.97} 2p_x^{1.96} 2p_y^{1.96} 2p_z^{1.97} | 0.28 | 1.13 | -71 |
| FIn_4^+       | -0.88 | 2s^{1.98} 2p_x^{1.97} 2p_y^{1.96} 2p_z^{1.97} | 0.24 | 0.95 | 33 |
| FTl_4^+       | -0.87 | 2s^{1.98} 2p_x^{1.96} 2p_y^{1.96} 2p_z^{1.97} | 0.25 | 0.86 | 28 |
| FGaIn_3^+     | -0.85 | 2s^{1.97} 2p_x^{1.96} 2p_y^{1.95} 2p_z^{1.97} | 0.30 | 0.84 | 26 |
| FGaTl_3^+     | -0.84 | 2s^{1.97} 2p_x^{1.95} 2p_y^{1.95} 2p_z^{1.96} | 0.32 | 0.79 | 24 |
| FGaIn_2^+     | -0.84 | 2s^{1.97} 2p_x^{1.96} 2p_y^{1.95} 2p_z^{1.96} | 0.31 | 0.80 | 30 |
| FGaTl_2^+     | -0.83 | 2s^{1.97} 2p_x^{1.96} 2p_y^{1.95} 2p_z^{1.96} | 0.33 | 0.79 | 25 |
| FGaIn_3^+     | -0.87 | 2s^{1.97} 2p_x^{1.96} 2p_y^{1.97} 2p_z^{1.97} | 0.26 | 0.97 | 42 |
| FGaTl_3^+     | -0.86 | 2s^{1.97} 2p_x^{1.96} 2p_y^{1.97} 2p_z^{1.97} | 0.27 | 0.89 | 33 |
| FIn_2Tl_2^+   | -0.88 | 2s^{1.98} 2p_x^{1.96} 2p_y^{1.96} 2p_z^{1.97} | 0.25 | 0.89 | 10 |
| FIn_3Tl_3^+   | -0.88 | 2s^{1.98} 2p_x^{1.96} 2p_y^{1.96} 2p_z^{1.97} | 0.25 | 0.92 | 25 |
| FInTl_3^+     | -0.87 | 2s^{1.98} 2p_x^{1.96} 2p_y^{1.96} 2p_z^{1.97} | 0.25 | 0.87 | 31 |
| CAI_4^2       | -2.62 | 2s^{1.60} 2p_x^{1.76} 2p_y^{1.76} 2p_z^{1.46} | 2.29 | 1.55 | 86 |
| NAI_4^-       | -2.27 | 2s^{1.79} 2p_x^{1.88} 2p_y^{1.88} 2p_z^{1.71} | 1.33 | 1.79 | 95 |
| OAI_4         | -1.68 | 2s^{1.91} 2p_x^{1.94} 2p_y^{1.94} 2p_z^{1.88} | 0.63 | 1.64 | 94 |

The AdNDP analysis\textsuperscript{32} also identifies the back-donation absence from fluorine to the peripheral atoms. According to the AdNDP analysis of FTl_4\textsuperscript{+} (Figure 2), the bonding scheme can be described by a delocalized 4c-2e σ-bond involving the external ring, one lone-pair on each peripheral atom, and four lone pairs on the central fluorine, i.e., no overlap between the central atom and the E_4 skeleton. This is entirely consistent with the charge analysis and WBI values and
opposite to CAI₄²⁻, in which the 5c-2e π- and 3c-2e σ-bonds are involved with the central carbon. The AdNDP analysis of the remaining ptFs show similar behavior and are included in Figures S16-S18.

The back-donation absence also has consequences on the magnetic response. Let us compare the induced magnetic field (B\text{ind}) \text{33,34} of FLn₄⁺ and CAI₄²⁻. In both cases, the magnetic response of the σ- and π-electrons is diatropic, but the first one much stronger compared to that caused by the π-cloud (almost negligible), as Figure 3 shows. Note that the σ-electrons response

**Figure 2.** AdNDP analysis of FTl₄⁺ and CAI₄²⁻. ON stands for occupation number.
at the molecular plane of FIn₄⁺ is stronger than in the carbon structure. So, both clusters could be classified as aromatic, predominantly σ-aromatic. More details about the magnetic response are provided by the induced current density \( (J^{\text{ind}}) \). For CAI₄²⁺, there is a strong diatropic ring current around the Al₄ skeleton (in deep blue) and a paratropic (counterclockwise) current around the carbon vicinity (in red, see Figure 3). In contrast, in FIn₄⁺, a local diatropic current is entirely localized at the fluorine atom (light blue). In order to quantify the ring-current strength, the \( J^{\text{ind}} \) is integrated into a specific area. For the typical reference system, benzene, the integration plane starts in the center of the ring, intersects the C-C bond ending about 4 Å away. This results in a ring-current strength of 12 nA/T. A ring-current strength of 20.5 (FIn₄⁺) and 13.7 (CAI₄²⁺) nA/T are obtained using the same integration domain. However, these values include the currents located at the central atoms. So, it is mandatory to avoid these local ring-current effects to quantify only the peripheral ring current. An integration plane starting at 1.2 (FIn₄⁺) and 0.7 Å (CAI₄²⁺) from the central atom was selected, which are inflection points from the local pathway to a ring current pathway. This selection provides a ring-current strength of 17.1 nA/T for FIn₄⁺, which is smaller than the corresponding one for CAI₄²⁺ (22.6 nA/T).
Figure 3. The isolines of the orbital contributions to $B^{\text{ind}}_{z}$ calculated in the transverse plane and in the molecular plane of FIn$_4^+$ and CAI$_4^+$ shown in the left panel. The $J^{\text{ind}}$ vector maps of FIn$_4^+$, and CAI$_4^{2-}$ in the right panel. The diatropic and paratropic currents are shown in blue and red, respectively. All the computations were performed at PW91/TZP-DKH level.

In summary, the exhaustive exploration of the PESs of pentaatomic systems with a fluorine atom and main group elements revealed that only atoms of group 13 as ligands could stabilize a ptF. Among the 440 examined combinations, only six clusters with a ptF are the energy global minimum, two of them with the same element as the ligand, FIn$_4^+$ and FTl$_4^+$, and the four composite species FGaIn$_3^+$, FIn$_2$Tl$_2^+$, FIn$_3$Tl$^+$, and FInTl$_3^+$. All analyses indicate ionic interactions between the center and the peripheral atoms with lone pairs localized on each atom, affecting the
electronic delocalization. In other words, as opposed to planar tetracoordinate systems with carbon, nitrogen, or oxygen atoms, the fluorine in the ptFs does not act as a $\sigma$-acceptor, restraining any back-donation. This is reflected in the magnetic response. Although ptFs could be characterized as $\sigma$-aromatic and with a diatropic external current on the E$_4$ ring, they also show a diatropic current entirely localized on the central F, as opposed to systems with a ptC. The above implies that the stabilization of these species is through subtle ionic interactions and an adequate cavity to accommodate the central atom, hence its scarcity.

**Acknowledgments**

G.C.-T., E. D., M.O.-I. and J. B. thank Conacyt for their PhD fellowships.

**References**

(1) Monkhorst, H. J. Activation Energy for Interconversion of Enantiomers Containing an Asymmetric Carbon Atom without Breaking Bonds. *Chem. Commun.* **1968**, 1111–1112.

(2) Hoffmann, R.; Alder, R. W.; Wilcox, C. F. Planar Tetracoordinate Carbon. *J. Am. Chem. Soc.*, **1970**, 92, 4992–4993.

(3) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. Stabilization of Planar Tetracoordinate Carbon. *J. Am. Chem. Soc.*, **1976**, 98, 5419–5427.

(4) Schleyer, P. v. R.; Boldyrev, A. I. A New, General Strategy for Achieving Planar Tetracoordinate Geometries for Carbon and Other Second Row Periodic Elements. *J. Chem. Soc., Chem. Commun.*, **1991**, 1536–1538.

(5) Boldyrev, A. I.; Simons, J. Tetracoordinated Planar Carbon in Pentaatomic Molecules. *J. Am.*
(6) Li, X.; Wang, L.-S.; Boldyrev, A. I.; Simons, J. Tetracoordinated Planar Carbon in the Al₄C⁻ Anion. A Combined Photoelectron Spectroscopy and Ab Initio Study. *J. Am. Chem. Soc.*, 1999, 121, 6033–6038.

(7) Wang, L.-S.; Boldyrev, A. I.; Li, X.; Simons, J. Experimental Observation of Pentaatomic Tetracoordinate Planar Carbon-Containing Molecules. *J. Am. Chem. Soc.*, 2000, 122, 7681–7687.

(8) Cui, Z.-H.; Ding, Y.-H.; Cabellos, J. L.; Osorio, E.; Islas, R.; Restrepo, A.; Merino, G. Planar Tetracoordinate Carbons with a Double Bond in CAI₃E Clusters. *Phys. Chem. Chem. Phys.*, 2015, 17, 8769–8775.

(9) Jimenez-Halla, J. O. C.; Wu, Y.-B.; Wang, Z.-X.; Islas, R.; Heine, T.; Merino, G. CAI₄Be and CAI₃Be₂⁻: Global Minima with a Planar Pentacoordinate Carbon Atom. *Chem. Commun.*, 2010, 46, 8776-8778.

(10) Grande-Aztatzi, R.; Cabellos, J. L.; Islas, R.; Infante, I.; Mercero, J. M.; Restrepo, A.; Merino, G. Planar Pentacoordinate Carbons in CBe₅⁺ Derivatives. *Phys. Chem. Chem. Phys.*, 2015, 17, 4620–4624.

(11) Cui, Z.-H.; Vassilev-Galindo, V.; Cabellos, J. L.; Osorio, E.; Orozco, M.; Pan, S.; Ding, Y.-H.; Merino, G. Planar Pentacoordinate Carbon Atoms Embedded in a Metallocene Framework. *Chem. Commun.*, 2017, 53, 138–141.

(12) Pan, S.; Cabellos, J. L.; Orozco-Ic, M.; Chattaraj, P. K.; Zhao, L.; Merino, G. Planar Pentacoordinate Carbon in CGa₅⁺ Derivatives. *Phys. Chem. Chem. Phys.*, 2018, 20, 12350–12355.

(13) Wang, M.-H.; Dong, X.; Cui, Z.-H.; Orozco-Ic, M.; Ding, Y.-H.; Barroso, J.; Merino, G.
Planar Pentacoordinate Silicon and Germanium Atoms. *Chem. Commun.* **2020**, *56*, 13772–13775.

(14) Castro, A. C.; Martínez-Guajardo, G.; Johnson, T.; Ugalde, J. M.; Wu, Y.-B.; Mercero, J. M.; Heine, T.; Donald, K. J.; Merino, G. CBe$_5$E$^-$ (E = Al, Ga, In, Tl): Planar Pentacoordinate Carbon in Heptaatomic Clusters. *Phys. Chem. Chem. Phys.*, **2012**, *14*, 14764.

(15) Guo, J.-C.; Feng, L.-Y.; Barroso, J.; Merino, G.; Zhai, H.-J. Planar or Tetrahedral? A Ternary 17-Electron CBe$_5$H$_4^+$ Cluster with Planar Pentacoordinate Carbon. *Chem. Commun.*, **2020**, *56*, 8305–8308.

(16) Xu, J.; Zhang, X.; Yu, S.; Ding, Y.-H.; Bowen, K. H. Identifying the Hydrogenated Planar Tetracoordinate Carbon: A Combined Experimental and Theoretical Study of CAl$_4$H and CAl$_4$H$.^+$ *J. Phys. Chem. Lett.*, **2017**, *8*, 2263–2267.

(17) Guo, J.-C.; Feng, L.-Y.; Zhang, X.-Y.; Zhai, H.-J. Star-Like CBe$_5$Au$_5$ Cluster: Planar Pentacoordinate Carbon, Superalkali Cation, and Multifold ($\pi$ and $\sigma$) Aromaticity. *J. Physi. Chem. Lett.*, **2018**, *122*, 1138–1145.

(18) Keese, R. Carbon Flatland: Planar Tetracoordinate Carbon and Fenestranes. *Chem. Rev.*, **2006**, *106*, 4787–4808.

(19) Vassilev-Galindo, V.; Pan, S.; Donald, K. J.; Merino, G. Planar Pentacoordinate Carbons. *Nat. Rev. Chem.*, **2018**, *2*.

(20) Yang, L.-M.; Ganz, E.; Chen, Z.; Wang, Z.-X.; von Ragué Schleyer, P. Four Decades of the Chemistry of Planar Hypercoordinate Compounds. *Angew. Chem. Int. Ed.*, **2015**, *54*, 9468–9501.

(21) Merino, G.; Méndez-Rojas, M. A.; Vela, A.; Heine, T. Recent Advances in Planar Tetracoordinate Carbon Chemistry. *J. Comput. Chem.*, **2007**, *28*, 362–372.
(22) F. Ortiz-Chi, G. M. GLOMOS, Cinvestav, Mérida, Mexico, 2020.

(23) Grande-Aztatzi, R.; Martínez-Alanis, P. R.; Cabellos, J. L.; Osorio, E.; Martínez, A.; Merino, G. Structural Evolution of Small Gold Clusters Doped by One and Two Boron Atoms. *J. Comput. Chem.*, **2014**, *35*, 2288–2296.

(24) Ramirez-Manzanares, A.; Peña, J.; Azpiroz, J. M.; Merino, G. A Hierarchical Algorithm for Molecular Similarity (H-FORMS). *J. Comput. Chem.*, **2015**, *36*, 1456–1466.

(25) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta–Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.*, **2003**, *91*.

(26) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297–3305.

(27) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.*, **2011**, *32*, 1456–1465.

(28) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. Quadratic Configuration Interaction. A General Technique for Determining Electron Correlation Energies. *J. Chem. Phys.*, **1987**, *87*, 5968–5975.

(29) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T.
Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox. Gaussian 16, Revision C.01.

(30) Reed, A. E.; Weinstock, R. B.; Weinhold, F. Natural Population Analysis. J. Chem. Phys., 1985, 83, 735–746.

(31) Wiberg, K. B. Application of the Pople-Santry-Segal CNDO Method to the Cyclopropylcarbinyl and Cyclobutyl Cation and to Bicyclobutane. Tetrahedron, 1968, 24, 1083–1096.

(32) Zubarev, D. Y.; Boldyrev, A. I. Developing Paradigms of Chemical Bonding: Adaptive Natural Density Partitioning. Phys. Chem. Chem. Phys. 2008, 10, 5207–5217.

(33) Merino, G.; Heine, T.; Seifert, G. The Induced Magnetic Field in Cyclic Molecules. Chem. Eur. J., 2004, 10, 4367–4371.

(34) Heine, T.; Islas, R.; Merino, G. σ and π Contributions to the Induced Magnetic Field: Indicators for the Mobility of Electrons in Molecules. J. Comput. Chem., 2007, 28, 302–309.

(35) Fias, S.; Boisdenghien, Z.; Stuyver, T.; Audiffred, M.; Merino, G.; Geerlings, P.; de Proft, F. Analysis of Aromaticity in Planar Metal Systems Using the Linear Response Kernel. J. Phys. Chem. A, 2013, 117, 3556–3560.

(36) Sundholm, D.; Fliegl, H.; Berger, R. J. F. Calculations of Magnetically Induced Current Densities: Theory and Applications. Wiley Interdiscip. Rev. Comput. Mol. Sci., 2016, 6, 639–678.