

Accepted Manuscript

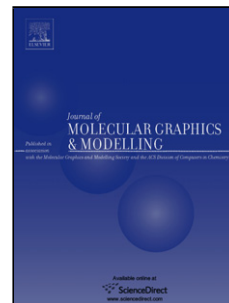
Title: Evaluation of the aromaticity of non-planar and bowl-shaped molecules by NICS criterion

Author: Adel Reisi-Vanani Ali Asghar Rezaei

PII: S1093-3263(15)30005-X
DOI: <http://dx.doi.org/doi:10.1016/j.jmgm.2015.05.015>
Reference: JMG 6567

To appear in: *Journal of Molecular Graphics and Modelling*

Received date: 17-2-2015
Revised date: 21-5-2015
Accepted date: 22-5-2015



Please cite this article as: Adel Reisi-Vanani, Ali Asghar Rezaei, Evaluation of the aromaticity of non-planar and bowl-shaped molecules by NICS criterion, *Journal of Molecular Graphics and Modelling* <http://dx.doi.org/10.1016/j.jmgm.2015.05.015>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Evaluation of the aromaticity of non-planar and bowl-shaped molecules by NICS criterion

Adel Reisi-Vanani^{*,a}, *Ali Asghar Rezaei*^b

^aDepartment of Physical Chemistry, Faculty of Chemistry, University of Kashan, Kashan,
Iran

^bDepartment of Pure Mathematics, Faculty of Mathematical Sciences, University of Kashan,
Kashan, Iran

Corresponding author: areisi@kashanu.ac.ir; Fax: +98 3155552397.

Graphical abstract:

Highlights

- We evaluated aromaticity of corannulene and sumanene by NICS_{zz}-scan method.
- Pentagon and hexagon rings of corannulene have antiaromatic and aromatic character.
- Pentagon and outer hexagon of sumanene have antiaromatic and aromatic character.
- Paratropic and diatropic induced ring currents are in concave more than convex face.
- Confirmation of more aromaticity of corannulene than sumanene by NICS_{zz} criterion.

Abstract

Nucleus independent chemical shift (NICS) criterion was used to gauge the amount of aromaticity in a lot of publications in two last decades. Non-planar molecules with many polygons in different sheets that make angle together have not been studied by this criterion.

Perhaps, one ascribes this deficiency to NICS index, but we think it is concern to depauperation in evaluation methods. Therefore, in this work, we try to evaluate aromaticity of two fullerene substructures bowl-shaped molecules, namely corannulene and sumanene as typical non-planar molecules by using of the NICS_{zz}-scan method. The gauge-independent atomic orbital (GIAO) NMR calculations were done at B3LYP/6-311+G(d) level of theory. Energetic criterion as another tool for evaluation of the aromaticity of compounds was used and discussed. Results show that pentagon and hexagon rings in corannulene have antiaromatic and aromatic character, respectively and in sumanene, pentagon and outer hexagon rings have antiaromatic and aromatic character, respectively. However, the picture obtained based on the NICS computations did not provide any insight towards the real nature of current density in the corannulene and sumanene.

Keywords: Nucleus independent chemical shift; Induced ring current; Aromaticity; Fullerene substructure; Non-planar polycyclic molecule.

1. Introduction

Nucleus independent chemical shift is a criterion for determination of aromaticity and antiaromaticity of compounds and was introduced in 1996 for the first time [1] that was an extension of the already existed probe in previous paper by Buhl and van Wullen [2]. They simulated the chemical shift of helium in the helium encapsulated fullerenes.

Since its introduction, the "NICS" index has been used frequently to characterize aromaticity and antiaromaticity of the rings [3-8], clusters [9, 10], transition states [11, 12], transition metal complexes [4, 13-15], etc. with cyclically delocalized or localized electrons. Like other indices in science and engineering, NICS index has some advantages and disadvantages that have been discussed in literatures [4, 6-8, 12, 15-27]. Lazzeretti and coworkers have mentioned that in general NICS is an unreliable descriptor of aromaticity (non-physical nature of NICS) and merely a local descriptor of aromaticity which can not provide a clear picture of the current density [28, 29]. Foroutan-Nejad and his colleagues offered reasons for failure of NICS and its derivatives for assessing the aromaticity in particular of transition-metal clusters/molecules and there is danger of contamination from local currents on the NICS values [30, 31].

Schleyer and other authors somewhat modified NICS index in the next years that it was proposed. We think that there are certain deficiencies in using of this index in evaluation of aromaticity and antiaromaticity. These kinds of studies mostly have been done in the planar compounds, however in some studies, cages and fullerenes with high symmetry were investigated. For fullerenes with high symmetry, NICS values in specific points were calculated. But, non-planar molecules with many polygons in different sheets that make angle together (bowl-shaped molecules) such as corannulene, sumanene, other fragments of the fullerene and carbon nano structure, nanocone, etc. have not been studied. We think that this shortcoming is not related to NICS index, but, it is concern to depauperation in evaluation methods, therefore in this work, we try to evaluate aromaticity of non-planar molecules such as corannulene [32] and sumanene [33]. However, there are some certain deficiencies in NICS index, but, it has some advantages, for example, quantitative information is retrieved from NICS easily, while it is difficult (and sometimes impossible) to get it from current density approach. Unfortunately, NICS values and NICS_{zz}-scan can not give an exact picture of aromaticity and antiaromaticity in bowl-shaped molecules, therefore, a current density approach can help to ones for better understanding of them.

There are many previous studies based on the current density analysis on corannulene and other polycyclic aromatic hydrocarbons [34-38]. Fowler demonstrated that corannulene sustain a strong paramagnetic current in the central pentagon and a diatropic current around the periphery of the system. In fact, detailed analysis does not show any local current around the individual 6-membered rings of the system. Accordingly, NICS in the vicinity of the periphery that is the 6-membered ring does not measure strength of the local current but a glimpse of the diamagnetic current, flowing around the periphery of the system [34].

2. Computational details

The geometry optimizations were performed at b3lyp/6-311+g(d) level of theory and then analytical frequency calculations were done to ensure real minima. NICS_{zz} values (in ppm) were computed from the magnetic shielding tensor that was calculated for ghost atoms located above and below the geometric centers of the systems at distances ranging from -4.0 to 4.0 Å (i.e., under to over the center of the molecular plane) at a step size of 0.2 Å along the line perpendicular to the molecular plane. The GIAO-NMR calculations were done at B3LYP/6-311+G(d) level of theory. All calculations were done by Gaussian 03 package [39].

3. Results and discussion

Corannulene is a polycyclic aromatic hydrocarbon with one central five-membered ring and five peripheral six-membered rings (Fig. 1 (a)) that synthesized for the first time by Barth and Lawton in 1966 [32]. Sumanene is a polycyclic aromatic hydrocarbon with one central six-membered ring and three peripheral six-membered and three peripheral five-membered rings, alternately (Fig. 1 (b)) that was synthesized for the first time by Sakurai et al. in 2003 [33].

The values of the NICS_{zz} for concave and convex faces of the corannulene and sumanene were calculated (scan in -4 to 4 Å from center of the ring in 0.2 Å intervals) at the GIAO-B3LYP/6-311+G(d) level of theory by using NICS-scan method [26]. The NICS_{zz}-scan curve of the pentagon and hexagon rings of the corannulene and sumanene depicted in Fig. 2. Negative, positive and almost zero values of NICS_{zz} show aromaticity, antiaromaticity and nonaromaticity, respectively. Because of the non-planarity of these molecules, the size of the regions with paratropic and diatropic current ring is different on the convex and the concave sides.

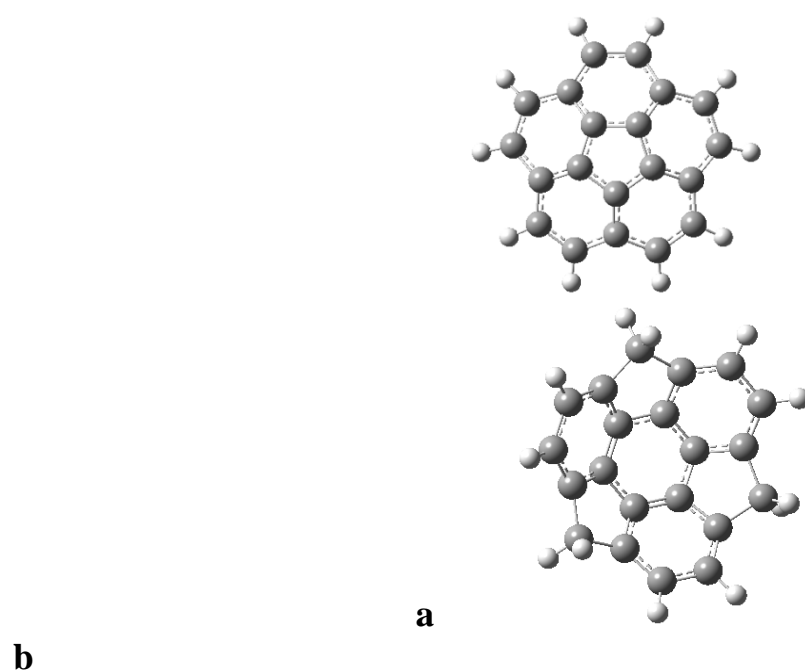


Fig. 1. Structure of: (a) Corannulene and (b) Sumanene molecules.

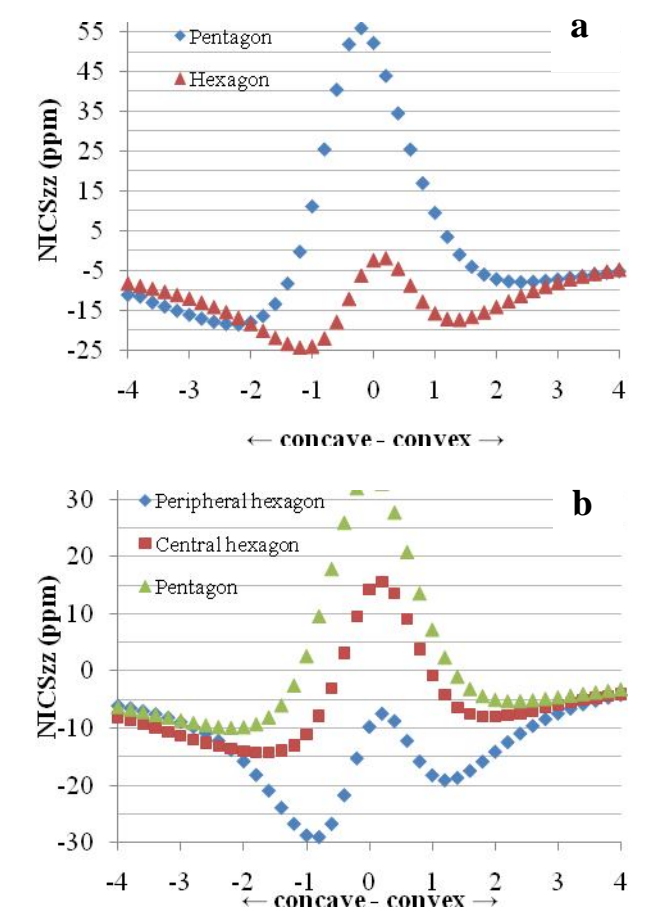


Fig. 2. NICS_{zz} -scan vs distance from center of polygons for (a) corannulene and (b) sumanene.

Computed values of the NICS_{zz} along the perpendicular axis to the pentagon rings of corannulene and sumanene indicate that the region with paratropic current ring spreads to a much greater distance on the convex side than the concave side of the bowl (ca. 1.4 Å on the convex vs ca. 1.2 Å on the concave side in corannulene and ca. 1.35 Å on the convex vs ca. 1.1 Å on the concave side in sumanene). Also in sumanene, region with induced paratropic current ring associated with the central six-membered ring is ca. 1.0 Å on the convex vs 0.5 Å on the concave side. For peripheral hexagon rings in sumanene and hexagon rings in corannulene there are induced diatropic currents in scanned distances. The NICS_{zz} -scan curves of the hexagon ring of corannulene exhibit two minima at a certain distance above and below the ring and have $\text{NICS}_{zz}(0)$ values near to zero clearly exhibit diatropic current of the hub in corannulene. Also, hub diatropic induced ring current is strongly increased inside the bowl but decreased on the outside.

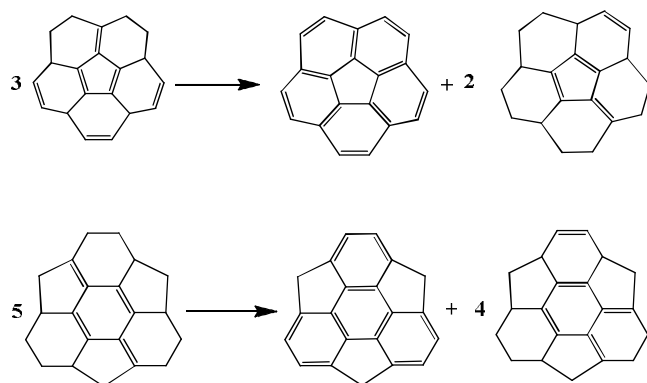
The NICS_{zz} -scan curve of the central six-membered ring of sumanene, as shown in Fig. 2 (b), indicates antiaromatic character (paratropic ring current) at the ring center with a maximum $\text{NICS}_{zz}(0.2)$ value of 15.6 ppm and a range diatropicity with minimum $\text{NICS}_{zz}(2)$ and $\text{NICS}_{zz}(-1.6)$ values of -8.0 and -14.3 ppm respectively. Therefore the inner six-membered ring of sumanene can be considered practically as antiaromatic. The NICS_{zz} -scan curve of the outer five-membered ring of sumanene clearly illustrates the antiaromatic character of the ring (paratropic ring current), while the NICS_{zz} -scan curve of the outer six-membered ring of sumanene exhibiting two minima at a certain distance above and below the molecular plane ($\text{NICS}_{zz}(-0.8)$ and $\text{NICS}_{zz}(1.2)$ values of -29.1 and -19.1 ppm, respectively) and a maximum ($\text{NICS}_{zz}(0.2)$ value close to -7.4 ppm) that shows aromatic character of the ring (diatropic ring current). It is important to mention that one can conclude that both paratropic

and diatropic induced ring currents are enhanced in concave face but reduced on the convex face as a result of ring currents superposition.

Our obtained results by NICS_{zz}-scan are generally in agreement with Fowler and Soncini study about aromaticity of bowl-shaped molecules [40]. By current density analysis, they showed that in corannulene there is a global diatropic ring current at the rim (aromaticity in outer hexagons) and local paratropic ring current at the hub (antiaromaticity in pentagon). Albeit, the aromatic properties may be very different from those expected if each of the six-membered rings would have its own localized ring current. Unfortunately, NICS_{zz}-scan can not give this picture, exactly. Recently, Gershoni-Poranne and Stanger presented a NICS-based method for the determination of local and global ring currents in conjugated multi-ring systems [23]. They claimed that its method, namely the NICS-XY-scan, gives information equivalent to that obtained through current density analysis methods, and in some cases, provides even more details.

Energetic criterion is another tool for evaluation of the aromaticity of compounds and estimation of the aromatic stabilization energy (ASE) due to cyclic π -electron delocalization of corannulene and sumanene that was estimated on the basis of the isodesmic reaction formalism (Scheme 1). Results show that resonance energy (RE) of corannulene and sumanene are 143.59 and 101.66 kcal mol⁻¹ and resonance energy per electron (REPE) of them are 7.18 and 5.65 kcal mol⁻¹, respectively. Therefore, corannulene shows more aromaticity than sumanene according to energetic criterion that is in concurrence with NICS_{zz} criterion (Fig. 3). We calculated average of the NICS_{zz} vs distance that depicted in Fig. 3 to compare overall aromaticity of corannulene and sumanene in concave and convex faces. To determine of the average of NICS_{zz}, a summation over NICS_{zz} in the center of all hexagons and pentagons was done and then was divided by number of the rings. In all distances of the

inside and outside of the bowl, average of the NICS_{zz} of corannulene is less than it for sumanene that shows corannulene has more aromatic character than sumanene.



Scheme 1. Isodesmic reactions for calculation of resonance energies (RE) and resonance energies per electron (REPE).

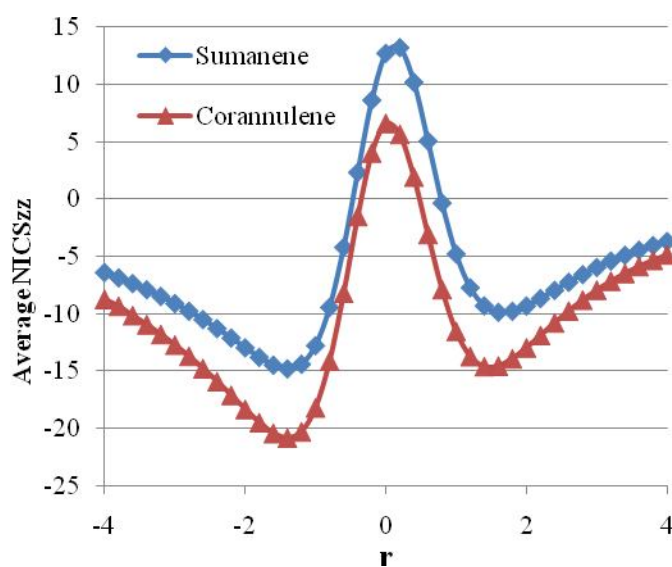


Fig. 3. Average of the NICS_{zz} vs distance.

4. Conclusions

The NICS_{zz} -scan curves of the pentagon and hexagon rings of corannulene and sumanene were obtained at the GIAO-B3LYP/6-311+G(d) level of theory. Results indicate that NICS_{zz} values along the perpendicular axis to the pentagon and hexagon rings of corannulene are

positive (antiaromaticity) and negative (aromaticity), respectively. Also, in sumanene, these values for pentagon and outer hexagon rings are positive (antiaromaticity) and negative (aromaticity), respectively. Energetic criterion as another gauge shows corannulene has more aromatic character than sumanene that is in concurrence with NICS_{zz} criterion. It was seen that both paratropic and diatropic induced ring currents are enhanced in concave face but reduced on the convex face. In general, NICS index and current density approach as two methods for determining aromaticity and antiaromaticity character of the compounds have their advantages and disadvantages. For example, quantitative information is retrieved from NICS easily, while it is difficult (and sometimes impossible) to get it from current density approach. As a matter of fact, the best is to use both methods for obtaining a comprehensive picture.

Acknowledgment

The authors are grateful to the University of Kashan for supporting this work by Grant No. 363026/1.

References

- [1] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. v. E. Hommes, Nucleus-independent chemical shifts: a simple and efficient aromaticity probe, *J. Am. Chem. Soc.* 118 (1996) 6317-6318.
- [2] M. Bühl, C. v. Wüllen, Computational evidence for a new C₈₄ isomer, *Chem. Phys. Lett.* 247 (1995) 63-68.
- [3] A. A. Fokin, H. Jiao, P. v. R. Schleyer, From Dodecahedrapentaene to the “[n]Trannulenes”. A New In-Plane Aromatic Family, *J. Am. Chem. Soc.* 120 (1998) 9364-9365.

- [4] C. Foroutan-Nejad, Z. Badri, S. Shahbazian, P. Rashidi-Ranjbar, The Laplacian of electron density versus NICS_{zz} scan: measuring magnetic aromaticity among molecules with different atom types, *J. Phy.Chem. A* 115 (2011) 12708-12714.
- [5] C. Foroutan-Nejad, S. Shahbazian, P. Rashidi-Ranjbar, The electron density vs. NICS scan: a new approach to assess aromaticity in molecules with different ring sizes, *Phys. Chem. Chem. Phys.*, 12 (2010) 12630-12637.
- [6] R. Gershoni-Poranne, C. M. Gibson, P. W. Fowler, A. Stanger, Concurrence between Current Density, Nucleus-Independent Chemical Shifts, and Aromatic Stabilization Energy: The Case of Isomeric [4]-and [5] Phenylenes, *J. Org. Chem.* 78 (2013) 7544-7553.
- [7] A. Stanger, Obtaining relative induced ring currents quantitatively from NICS, *J. Org. Chem.* 75 (2010) 2281-2288.
- [8] C. Corminboeuf, T. Heine, G. Seifert, P. v. R. Schleyer, J. Weber, Induced magnetic fields in aromatic [n]-annulenes?interpretation of NICS tensor components, *Phys. Chem. Chem. Phys.* 6 (2004) 273-276.
- [9] M. L. McKee, Z. -X. Wang, P. v. R. Schleyer, Ab Initio Study of the Hypercloso Boron Hydrides B_nH_n and B_nH_n⁻. Exceptional Stability of Neutral B₁₃H₁₃, *J. Am. Chem. Soc.* 122 (2000) 4781-4793.
- [10] A. Hirsch, Z. Chen, H. Jiao, Spherical Aromaticity in I_h Symmetrical Fullerenes: The 2(N+1)² Rule, *Angew. Chem. Int. Ed.* 39 (2000) 3915-3917.
- [11] D. Sawicka, S. Wilsey, K. N. Houk, The 16 kcal/mol Anomaly: Alteration of [2 + 2 + 2] Cycloaddition Rates by Through-Bond Interactions, *J. Am. Chem. Soc.* 121 (1999) 864-865.
- [12] P. v. R. Schleyer, J. I. Wu, F. P. Cossio, I. Fernandez, Aromaticity in transition structures, *Chem. Soc. Rev.* 43 (2014) 4909-4921.

- [13] P. v. R. Schleyer, B. Kiran, D. V. Simion, T. S. Sorensen, Does Cr(CO)₃ Complexation Reduce the Aromaticity of Benzene?, *J. Am. Chem. Soc.* 122 (2000) 510-513.
- [14] B. T. Psciuk, R. L. Lord, C. H. Winter, H. B. Schlegel, Can Metallapyrimidines Be Aromatic? A Computational Study into a New Class of Metallacycles, *J. Chem. Theory Comput.* 8 (2012) 4950-4959.
- [15] C. Corminboeuf, T. Heine, J. Weber, Evaluation of aromaticity: A new dissected NICS model based on canonical orbitals, *Phys. Chem. Chem. Phys.* 5 (2003) 246-251.
- [16] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, Nucleus-independent chemical shifts (NICS) as an aromaticity criterion, *Chem. Rev. Columbus* 105 (2005) 3842-3888.
- [17] H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, Which NICS aromaticity index for planar π rings is best?, *Org. Lett.* 8 (2006) 863-866.
- [18] G. V. Baryshnikov, B. F. Minaev, M. Pittelkow, C. B. Nielsen, R. Salcedo, Nucleus-independent chemical shift criterion for aromaticity in pi-extended tetraoxa[8]circulenes, *J. Mol. Model.* 19 (2013) 847-850.
- [19] W. Collier, S. Saebø, C. U. Pittman Jr, Nucleus independent chemical shift evaluation of the aromaticity of pentafulvene and its exocyclic Si, Ge, and Sn derivatives, *J. Mol. Struct. THEOCHEM*, 549 (2001) 1-8.
- [20] F. Feixas, E. Matito, J. Poater, M. Solà, Aromaticity of distorted benzene rings: Exploring the validity of different indicators of aromaticity, *J. Phys. Chem. A*, 111 (2007) 4513-4521.
- [21] I. Fernández, J. I. Wu, P. v. R. Schleyer, Substituent effects on “hyperconjugative” aromaticity and antiaromaticity in planar cyclopolyenes, *Org. Lett.* 15 (2013) 2990-2993.

- [22] C. Foroutan-Nejad, Interatomic magnetizability: a QTAIM-based approach toward deciphering magnetic aromaticity, *J. Phys. Chem. A*, 115 (2011) 12555-12560.
- [23] R. Gershoni-Poranne, A. Stanger, The NICS-XY-Scan: Identification of Local and Global Ring Currents in Multi-Ring Systems, *Chemistry*, 20 (2014) 5673-5688.
- [24] J. A. N. F. Gomes, R. B. Mallion, Aromaticity and ring currents, *Chem. Rev.* 101 (2001) 1349-1384.
- [25] K. E. Horner, P.B. Karadakov, Chemical bonding and aromaticity in furan, pyrrole, and thiophene: a magnetic shielding study, *J. Org. Chem.* 78 (2013) 8037-8043.
- [26] A. Stanger, Nucleus-independent chemical shifts (NICS): distance dependence and revised criteria for aromaticity and antiaromaticity, *J. Org. Chem.* 71 (2006) 883-893.
- [27] A. Stanger, The Different Aromatic Characters of Some Localized Benzene Derivatives, *J. Phys. Chem. A*, 112 (2008) 12849-12854.
- [28] P. Lazzeretti, Assessment of aromaticity via molecular response properties, *Phys. Chem. Chem. Phys.* 6 (2004) 217-223.
- [29] S. Pelloni, G. Monaco, P. Lazzeretti, R. Zanasi, Beyond NICS: estimation of the magnetotropy of inorganic unsaturated planar rings, *Phys. Chem. Chem. Phys.* 13 (2011) 20666-20672.
- [30] C. Foroutan-Nejad, Is NICS a reliable aromaticity index for transition metal clusters?, *Theor. Chem. Acc.* 134 (2015) DOI: 10.1007/s00214-015-1617-7.
- [31] Z. Badri, S. Pathak, H. Fliegl, P. Rashidi-Ranjbar, R. Bast, R. Marek, C. Foroutan-Nejad, K. Ruud, All-Metal Aromaticity: Revisiting the Ring Current Model among Transition Metal Clusters, *J. Chem. Theor. Comput.* 9 (2013) 4789-4796.
- [32] W. E. Barth, R. G. Lawton, Dibenzo[ghi,mno]fluoranthene, *J. Am. Chem. Soc.* 88 (1966) 380-381.

- [33] H. Sakurai, T. Daiko, T. Hirao, A synthesis of sumanene, a fullerene fragment, *Science*, 301 (2003) 1878-1878.
- [34] E. Steiner, P. W. Fowler, L. W. Jenneskens, Counter-Rotating Ring Currents in Coronene and Corannulene, *Angew. Chem. Int. Ed.* 40 (2001) 362-366.
- [35] P. W. Fowler, E. Steiner, Pseudo- π currents: rapid and accurate visualisation of ring currents in conjugated hydrocarbons, *Chem. Phys. Lett.* 364 (2002) 259-266.
- [36] P. W. Fowler, E. Steiner, R. Havenith, L. Jenneskens, Current density, chemical shifts and aromaticity, *Magn. Reson. Chem.* 42 (2004) S68-S78.
- [37] E. Steiner, P. W. Fowler, Patterns of ring currents in conjugated molecules: a few-electron model based on orbital contributions, *J. Phys. Chem. A*, 105 (2001) 9553-9562.
- [38] E. Steiner, P. W. Fowler, A. Soncini, L. W. Jenneskens, Current-density maps as probes of aromaticity: global and Clar π ring currents in totally resonant polycyclic aromatic hydrocarbons, *Faraday discuss.* 135 (2007) 309-323.
- [39] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, J. Montgomery Jr, T. Vreven, K. Kudin, J. Burant, J. Millam, S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, Cossi M, G. Scalmani, N. Rega, G. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. Knox, H. Hratchian, J. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. Stratmann, O. Yazyev, A. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Ayala, K. Morokuma, G. Voth, P. Salvador, J. Dannenberg, V. Zakrzewski, S. Dapprich, A. Daniels, M. Strain, O. Farkas, D. Malick, A. Rabuck, K. Raghavachari, J. Foresman, J. Ortiz, Q. Cui, A. Baboul, S. Clifford, J. Cioslowski, B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Martin, D. Fox, T. Keith, M. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P. Gill, B.

Johnson, W. Chen, M. Wong, C. Gonzalez, J. Pople, Gaussian 03, Revision E. 01.

Wallingford CT: Gaussian, Inc. (2004).

- [40] P. W. Fowler, A. Soncini, Visualising aromaticity of bowl-shaped molecules, *Phys. Chem. Chem. Phys.* 13 (2011) 20637-20643.