Analysis of the Nucleus Independent Chemical Shifts of [10]Cyclophenacene: Is It an Aromatic or Antiaromatic Molecule?

Guglielmo Monaco*, and Riccardo Zanasi*

Department of Chemistry and Biology "A. Zambelli", University of Salerno, via Giovanni Paolo II 132,

Fisciano (SA), Italy

Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937 Corresponding Author

Guglielmo Monaco, e-mail: gmonaco@unisa.it; fax: +39 089 969603.

Riccardo Zanasi, e-mail: <u>rzanasi@unisa.it;</u> fax: +39 089 969603.

ABSTRACT: [10]cyclophenacene is an important synthetic target that shows a pair of NICS values for the center of mass and six-membered rings typical of an aromatic species. This is found in contrast with the global paratropic current density induced by a magnetic field parallel to the main symmetry axis. This apparent contradiction has been analyzed studying the tensor character of the magnetic response. It turns out that the molecule displays two characters: one paratropic (antiaromatic) and another one diatropic (aromatic), depending on the orientation of the inducing magnetic field. The paratropic response, which cannot be recognized from the NICS values, is associated to a well-defined destabilization of the belt closure, as witnessed by homodesmotic reactions. A scalar measure of magnetic aromaticity, the Field-Independent Current Strength (FICS) has been introduced, which allows reaching the conclusion that [10]cyclophenacene is indeed an aromatic molecule, although significantly affected by the paratropic response.

Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937 TOC GRAPHICS



KEYWORDS: current density; current strength; homodesmotic reaction; aromatic belt; carbon nanobelt.

The 40 π -electrons cyclic benzenoid [10]cyclophenacene **1** can be thought as a rolled polyphenantherene-type graphite ribbon,¹ comprising ten fused benzene rings, see Figure 1-left. According to a common definition, **1** is an "aromatic belt",² or carbon nanobelt (CNB),³ a very short armchair (5,5) carbon nanotube (CNT).⁴



Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b0193' Figure 1. Left: structure of the D_{34} ($C_{40}H_{30}$) [10]cyclophenacene (1), symmetry distinct C-C bonds are shown. Right: structure of the C_{2h} ($C_{60}H_{12}$) carbon-capped derivative of 1 (2), where the contained 1 belt has been evidenced, symmetry distinct carbon rings are enumerated. In both cases the main symmetry axis coincides with the *z* Cartesian direction shown in blue, whilst *x* and *y* axes are shown in red and green.

Owing to its bent π -conjugation, **1** is a challenging, and not yet accomplished synthetic target, which is expected to exhibit a number of special properties, e.g., like those of the [*n*]cycloparaphenilenes,⁵⁶ also reported as carbon nanorings (CNRs),³ which have a similar π distorted system. Particular appealing is the possibility of using both CNRs⁷⁹ and CNBs,¹⁰⁴² as well as short CNT end-cap,¹³⁴⁵ as templates for growing single-walled, single-chirality carbon nanotubes.¹⁶⁻¹⁷ The first bottom-up synthesis of a pure benzenoid CNB, a (6,6)CNT portion that is an isomer of [12]cyclophenacene, has been reported only very recently by Povie et al..¹⁸

The experiment which came closest to the isolation of **1** was reported by the Iyoda group in their observation of the mass peak of **1** upon laser irradiation of a stable precursor.¹⁹⁻²⁰ On the other hand, carbon-capped derivatives of **1** have been obtained by rationally designed chemical modification of [60]fullerene.²¹⁻²³ Actually, the spherical π -conjugated [60]fullerene contains **1**, which can be isolated by targeted addition to double bonds at both poles of the cage, as in the case of the model compound **2**, see Figure 1-right and Refs. 21-23 for details.

Getting insight into the aromaticity of systems like **1** and **2** is particularly problematic because their unusual geometry hampers the identification of good reference systems. In similar cases reference-free aromaticity indices, like the nucleus independent chemical shift (NICS),²⁴²⁶ are

often chosen. NICS values for the six-membered rings of 1 and model compound 2, indicate that **Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937** the [10]cyclophenacene belt is aromatic; moreover, its center of mass²⁷ (CM) is predicted to be subject to an aromatic shielding effect.^{21,23}

These results, rather expectable for benzenoid ribbons, can be surprising instead if one considers **1** as an anti-aromatic [20]annulene distorted by 10 C₂-insertions. Prompted by this observation, we have studied the (first-order) current density (J^{μ}) induced by a magnetic field in the electronic cloud of **1**. Figure 2 shows maps of J^{μ} induced in **1** by a magnetic field parallel to the main symmetry axis. Maps have been calculated using the continuous transformation of the origin of the current density (CTOCD-DZ2) method²⁸ at the B3LYP level,^{29,20} for the optimized geometry reported in Ref. 21. Remarkably, the current density maps reveal a global ring current that is largely paratropic inside the macrocycle, where the magnitude of **J**⁴ is comparable to that of the benzene ring current, and only moderately diatropic outside it. Actually, the dominant

contribution to J^{a} arises from the HOMO-LUMO virtual transition that gives a paramagnetic contribution: the product of the HOMO and LUMO symmetries, i.e., $A_{1a} \times A_{2a} = A_{2g}$, matches exactly the symmetry of the rotation around $z.^{31.32}$ This behavior is typical of antiaromatic species.^{31.33}



Figure 2. CTOCD-DZ2//B3LYP/6-31G* maps of J^{*} induced in **1** by a magnetic field **B**=**k***B*_a. On the left, over the *xy* plane passing through the center of mass; on the right, over a surface inside the belt parallel to the nuclear scaffold at 0.8 Å from it. The magnetic field is represented by a vertical long black arrow in the right map and points towards the viewer in the left map. Diatropic/paratropic circulations are clockwise/anticlockwise. Red/blue color implies that **J**^{*} has a component parallel/antiparallel to **B** not smaller than the 30% of the vector modulus. The black arrow in the upper left corner represents the maximum magnitude of the benzene ring current.

Since this finding contrasts with the NICS-based prediction previously reported,²¹⁻²³ it is clear that there is a problem about the aromaticity of **1** that calls for attention.

The indiscriminate use of the NICS as a magnetic indicator of aromaticity has been often criticized,^{34,42} mostly because it induces to neglect the tensor character of the magnetic response.³⁴ Therefore, we start our analysis discussing the calculated, symmetry unique components of the magnetic shielding tensor in the CM of **1** and **2**, reported in Table 1.

As can be observed, the induced magnetic field in the CM, i.e., $\mathbf{B}_{\text{IND}}^{\text{CM}} = -\boldsymbol{\sigma}^{\text{CM}}\mathbf{B}_0$, is predicted to be parallel/antiparallel to the external magnetic field when the latter is parallel/perpendicular to the axis of **1**. In other words, as it concerns the NICS^{CM} = $-1/3\text{Tr}\boldsymbol{\sigma}^{\text{CM}}$, when the external magnetic field is parallel to the belt axis both molecules manifest a paramagnetic (antiaromatic) character; conversely, when the magnetic field is perpendicular to the belt axis the response is diamagnetic (aromatic). In particular, for **1** the two responses have an almost identical magnitude and they cancel each other.

 Table 1. GIAO//B3LYP/6-31G* magnetic shielding tensors in the center of mass (CM) of 1 and

 Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937

 2 and in a six-membered ring center (RC) of 1.

	$\sigma^{\text{CM}}(1)$		
xx = 16.14	yy = 16.08	zz = -16.34	
		NICS = -5.29	
$\sigma^{ ext{CM}}(2)$			
xx = 16.17	yx = -2.10	zz = 16.10	
xy = -2.62	yy = -2.19	NICS = -10.03	
$\sigma^{\text{RC}}(1)$			
xx = 11.23	yy = 5.62	yz = 5.49	
NICS = -6.63	zy = 3.33	zz = 3.05	

⁴In ppm. Optimized molecular geometries have been taken from Ref. 21; the orientation of the principal axes can be seen in Figure 1. Symmetry vanishing tensor components are not reported.

Then, the negative NICS value just comes because the perpendicular component appears twice computing the mean. In the case of **2**, the diamagnetic response in the direction perpendicular to the belt axis is very close to that of **1**, whilst the parallel paratropic response is much weaker. Accordingly, looking at the NICS values in the CM, **2** would seem twice as aromatic as **1**. In order to understand such a different paratropic character, as estimated from the magnetic shielding in the CM, we have calculated the parallel component of the linear magnetic shielding density function in the CM along the belt axis

$$\Sigma_{\parallel}^{\mathrm{CM}} = \Sigma_{zz}^{\mathrm{CM}}(z) = -\frac{\mu_0}{4\pi} \int dx \int dy \left[\frac{x - x^{\mathrm{CM}}}{|\mathbf{r} - \mathbf{r}^{\mathrm{CM}}|^3} J_{yz}^{\mathbf{B}}(\mathbf{r}) - \frac{y - y^{\mathrm{CM}}}{|\mathbf{r} - \mathbf{r}^{\mathrm{CM}}|^3} J_{xz}^{\mathbf{B}}(\mathbf{r}) \right],$$

where J_{xz}^{B} and J_{yz}^{B} are current density tensor components (a further integration of Σ_{\parallel}^{CM} gives σ_{\parallel}^{CM} ; for a definition of the volume magnetic shielding density function see Refs. 43-44). The results are shown in Figure 3, where Σ_{\parallel}^{CM} is plotted onto 1 and 2 respectively. As can be observed, for **Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937** both 1 and 2 the function is similarly negative inside the belt; outside the belt, two very small positive shoulders can be seen in 1, whilst the two end-caps of 2 provide a remarkable diamagnetic effect on the center of mass, a result not conceivable *a priori*. Consequently, the large negative NICS in the CM of 2 deceptively leads to an overestimation of the belt aromatic character of the belt in 2.



Figure 3. Left: the Σ_{\parallel}^{CM} function is plotted in blue onto **1**. Right: the Σ_{\parallel}^{CM} function is plotted in green onto **2**.

Now, consider the current density induced in 1 by a perturbing magnetic field **B**=j*B*. Maps of **Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937** such a current are shown in Figure 4. As can be observed, ring currents local to a six-membered ring are not discernable. Instead, a semi-global circulation can be seen on both the outside and the inside of the belt, where the current follows the belt edges in opposite directions. This current is semi-global since the same pattern is present on the rear of the belt by symmetry. Therefore, the two edge circulations form two disconnected semi-global diatropic (aromatic) current loops: one on the front and another one on the rear of the belt. Some diatropic loops local to C-C bonds can also be seen that connect the two edge circulations.



Figure 4. CTOCD-DZ2//B3LYP/6-31G* maps of **J** induced in **1** by a magnetic field $\mathbf{B}=\mathbf{j}B_{j}$. On the left/right over a surface parallel to the nuclear scaffold at 0.8 Å outside/inside the belt. The magnetic field is perpendicular to the figure plane and points towards the viewer. See Figure 1 caption for other details.

Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937 The current density maps of Figures 2 and 4 nicely reflect the tensor values of the shielding discussed above: a strong delocalized paratropic/diatropic current is induced by a magnetic field parallel/perpendicular to the belt axis.

It is nowadays possible to overcome the qualitative character of the current density maps using bond current strengths, or current susceptibilities,⁴⁵⁴⁷ which do not depend explicitly on molecular geometry⁴¹⁴² and can be obtained by integrating the current density crossing a suitably chosen planar domain bisecting a selected C-C bond. This has been done and results are shown in Figure 5. When the inducing magnetic field is perpendicular to the belt axis, see Figure 5 on the left, the superposition of three diatropic circuits can be seen, at least. They correspond to the rim of a phenanthrene unit, the strongest, a picene unit, the intermediate one, a six-membered ring in the phenanthrene center, the weakest. All together these three circuits form a simpler representation

of the semi-global current described above, whose strength does not exceed the 88% of the benzene ring current.



Figure 5. Net bond current strengths in 1. On the left/right, B is perpendicular/parallel to the main symmetry axis of the molecule, pointing toward the viewer (left) and from bottom to top (right). Percentage ratios with respect to net bond current strength in benzene, which amounts to
Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b0193' II nA/T at the same level of theory and integration domain extension, are shown next to each

bond. The apparent current non-conservation depends on the approximate level of the calculation and on the occurrence of through-space flow, which is not intercepted by the integration domains.

When **B** is parallel to the belt axis, see Figure 5 on the right, a paratropic global circuits can be seen bifurcating from one edge of the belt to the other one. In this case, a large cancellation between two opposing global currents occurs, i.e., the paratropic inside the belt and the diatropic outside the belt, see Fig. 2, resulting in a net paratropic current whose strength reaches only the 45% of the benzene ring current magnitude.

In order to appreciate the physical correctness of the results shown above, we have tested the current conservation integrating the current density cross section over a very large plane cutting the whole molecule in two non-symmetrical pieces, as, for example, extending up to neglecting density the plane bisecting the C-C bond indicated with the letter "b" in Fig.1. For an exact calculation, the integral would be exactly vanishing since $\nabla \cdot J^{\mathbf{B}}(\mathbf{r}) = 0$, for a proof see Ref. 47. For the current computed at the level of approximation adopted here, the integral turns out to be 0.23 nA/T when **B** is parallel to the main symmetry axis, resulting from the difference of a total current of 25.05 nA/T crossing the plane in one direction and 25.28 nA/T in the opposite direction, and 0.87 nA/T when **B** is perpendicular the main symmetry axis, as the difference between 43.91 and 43.04 nA/T for the two opposite crossing currents. These results indicate that the non-conservation of the current affects the current strengths reported in Fig. 5 by only 0.9% and 2%, at least, for parallel and perpendicular magnetic field respectively.

A double faced magnetic response is thus quantitatively assessed. According to common practice, the diatropic and paratropic responses are considered indications of aromaticity and **Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937** antiaromaticity, respectively.^s In such an ambiguous application of the magnetic criterion of aromaticity, the question arises of whether the previously overlooked paratropic current parallels some kind of energetic destabilization. To this end we devised the homodesmotic reactions

 $10 [m+1] \text{phenacene} \rightarrow 10 [m] \text{phenacene} + 1 \tag{1}$

The energy of reactions (1) is the excess energy of **1** over 10 central units C_4H_2 of a linear phenacene: negative/positive values indicate a stabilization/de-stabilization due to belt closure. A de-stabilization is clearly expected because of the bent structure of **1**. To take into account the effect of curvature, the two phenacenes in reactions (1) can be built cutting pieces of appropriate length form **1**, adding H atoms and optimizing only the lengths of the newly formed C-H bonds. The results of this approach, at the B3LYP/6-31G* level, are given in Table 2. The reaction energies smoothly approach a limit for the curved phenacenes, while they show some oscillation

for the planar ones. This notwithstanding, the last value obtained for the planar phenacenes is close to 138.3 kcal mol⁴, the value obtainable using the limit energy per repeat unit reported in Ref. 49. Table 1 shows that the strong penalty to belt-closure, roughly 140 kcal mol⁴, is essentially due to the bent geometry. However, correction for the geometry penalty, still leaves a small energetic disadvantage upon belt-closure (roughly a single kcal mol⁴). Thus, from an energetic point of view, the belt in **1** (defined in terms of a super-ring), is a slightly super-antiaromatic topological feature, in full qualitative agreement with a paper by Aihara.⁸

The previous results could indicate a vector character for the aromaticity. Although this could be possibly linked with different choices of reference acyclic systems for different directions of the field, it is certainly at odds with the vast literature on aromaticity as a scalar quantity. It is thus desirable to end up with a single indication on aromaticity from the analysis of the three-

dimensional magnetic response. This has been done signing the current strength of bond AB as Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937 positive/negative if it is paratropic/diatropic, averaging over all possible directions of the field, and normalizing in a percent scale by the averaged signed current strength of benzene. The result, to be called Field-Independent Current Strength (FICS), is

$$\text{FICS}_{\text{AB}} = \frac{\overline{I_{\text{AB}}^{B_{x}} + I_{\text{AB}}^{B_{z}}}}{\overline{I_{\text{CC, benzene}}^{B_{z}}}} \times 100,$$

where $\overline{I_{AB}^{B_{\alpha}}}$ is the signed current strength of bond AB coming from the B_{α} component of the magnetic field. The FICS is positive/negative for a dominating diatropic/paratropic response and equals +100 for the CC bond of benzene. The computation of FICS requires two calculations of current strength for two directions (x and z) of the field perpendicular to the bond AB (parallel to the y axis). The results for symmetry-unique bonds "a" and "c", see Fig.1, which can be obtained by inspection of Fig. 5, are FICS_a = 88 - 45=43 and FICS_a = 82 - 10=72. Both values indicate

a substantial diatropic response, though lower than the reference benzene value. In particular, the values 82 and 88 for bonds "a" and "c" respectively, can be interpreted as a reduced aromaticity with respect to benzene due to the belt curvature, whilst the values -45 and -10 arise from the paratropic response of the [20]annulene along the middle of the belt, and the belt edges formed by the C_i-insertions, respectively.

т	planar	curved
1	138.7	5.1
2	150.3	1.6
3	134.3	1.0
4	139.1	1.1

Table 2. Energies of homodesmotic reactions.

^a In kcal/mol.

Accepted Version of Investigated whether the paratropic response leads to a low kinetic stability,

defined as the HOMO-LUMO gap times the number of conjugated carbon atoms.^{31,32} This seems not the case: the B3LYP/6-31G* kinetic stability is as high as 124 eV in **1**, i.e., well above that of the antiaromatic corannulene² (6.2 eV), of the aromatic corannulene⁴ (32.8 eV),³³ and of the antiaromatic [20]annulene (38.4 eV).⁵⁴

In conclusion, the NICS values of [10]cyclophenacene 1 have been interpreted in terms of current density maps, and bond current strengths. 1 is endowed with a diatropic/paratropic current when exposed to a magnetic field perpendicular/parallel to its main symmetry axis, thus showing a double-faced magnetic response, which cannot be recognized by the NICS values. Although the paratropic response is not associated to a low kinetic stability, homodesmotic calculations indicate that the belt closure reaction is disfavored not only by strain, but also by electronic reasons. Therefore, the paratropic current can be associated with a super-

antiaromaticity, i.e., a disfavored belt closure reaction, just as the paratropic response in planar systems is associated with standard antiaromaticity, i.e., a disfavored ring closure reaction. The introduction of a scalar measure of magnetic aromaticity, i.e., the FICS, allows reaching the conclusion that **1** is indeed an aromatic molecule, although significantly affected by a paratropic response.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Calculation details; sketches of the HOMO and LUMO; current density map arising from the

HOMO; current density animations; current strengths integration domains; derivation of the **Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937** equation of the FICS. (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: gmonaco@unisa.it; Fax: +39 089 969603, Tel: +39 089 969570.

*E-mail: <u>rzanasi@unisa.it;</u> Fax: +39 089 969603, Tel: +39 089 969590.

ORCID

Guglielmo Monaco: orcid.org/0000-0001-5268-940X

Riccardo Zanasi: orcid.org/0000-0002-8374-6080

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Financial support from the MIUR and University of Salerno is gratefully acknowledged.

REFERENCES

- Mallory, F. B.; Butler, K. E.; Evans, A. C.; Brondyke, E. J.; Mallory, C. W.; Yang, C.; Ellestein, A. Phenacenes: A Family of Graphite Ribbons. 2. Syntheses of Some
 [7]Phenacenes and an [11]Phenacene by Stilbene-like Photocyclizations. *J. Am. Chem. Soc.* 1997, *119*, 2119-2124.
- (2) Yao, T.; Yu, H.; Vermeij, R. J.; Bodwell, G. J. Nonplanar Aromatic Compounds. Part 10:
 a Strategy for the Synthesis of Aromatic Belts-All Wrapped Up or Down the Tubes?

Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937

- (3) Segawa, Y.; Yagi, A.; Ito, H.; Itami, K. A Theoretical Study on the Strain Energy of Carbon Nanobelts. Org. Lett. 2016, 18, 1430-1433.
- (4) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, Ph., Editors, *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications;* Topics in Applied Physics, v. 80; Springer: Berlin, 2001.
- (5) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, R. Synthesis, Characterization, and Theory of [9]-, [12]-, and [18]Cycloparaphenylene: Carbon Nanohoop Structures. J. Am. Chem. Soc. 2008, 130, 17646-17647.

- (6) Darzi, E. R.; Jasti, R. The Dynamic, Size-Dependent Properties of [5]–
 [12]Cycloparaphenylenes. *Chem. Soc. Rev.* 2015, 44, 6401-6410.
- (7) Tian, X.; Jasti, R. Cycloparaphenylenes: the Shortest Possible Segments of Armchair Carbon Nanotubes. In *Fragments of Fullerenes and Carbon Nanotubes: Designed Synthesis, Unusual Reactions, and Coordination Chemistry*, Chap. 11, p. 291-309; Petrukhina, M. A.; Scott, L. T., Editors, John Wiley & Sons: Hoboken, New Jersey, 2012.
- (8) Omachi, H.; Nakayama, T.; Takahashi, E.; Segawa, Y.; Itami, K. Initiation of Carbon Nanotube Growth by Well-Defined Carbon Nanorings. *Nature Chem.* 2013, 5, 572-576.
- (9) Sisto, T. J.; Zakharov, L. N.; White, B. M.; Jasti, R. Towards Pi-Extended Cycloparaphenylenes as Seeds for CNT Growth: Investigating Strain Relieving Ring-

Accepted Penings and Rearrangements ICham 28917,2816,7, 2681-3688. 10.1021/acs.jpclett.7b01937

- (10) Tahara, K.; Tobe, Y. Molecular Loops and Belts. Chem. Rev. 2006, 106, 5274-5290.
- (11) Eisenberg, D.; Shenhar, R.; Rabinovitz, M. Synthetic Approaches to Aromatic Belts:
 Building Up Strain in Macrocyclic Polyarenes. *Chem. Soc. Rev.* 2010, *39*, 2879-2890.
- (12) Schaller, G. R.; Herges, R. Aromatic Belts as Sections of Nanotubes. In *Fragments of Fullerenes and Carbon Nanotubes: Designed Synthesis, Unusual Reactions, and Coordination Chemistry*, Chap. 10, p. 259-289; Petrukhina, M. A.; Scott, L. T., Editors, John Wiley & Sons: Hoboken, New Jersey, 2012.

- (13) Rim, K. T.; Siaj, M.; Xiao, S.; Myers, M.; Carpentier, V. D.; Liu, L.; Su, C.; Steigerwald, M. L.; Hybertsen, M. S.; McBreen, P. H.; *et al.* Forming Aromatic Hemispheres on Transition-Metal Surfaces. *Angew. Chem.* 2007, *119*, 8037-8041.
- (14) Scott, L. T.; Jackson, E. A.; Zhang, Q.; Steinberg, B. D.; Bancu, M.; Li, B. A Short,
 Rigid, Structurally Pure Carbon Nanotube by Stepwise Chemical Synthesis. *J. Am. Chem. Soc.* 2012, *134*, 107-110.
- (15) Belanger, A. P.; Mirica, K. A.; Mack, J.; Scott, L. T. Hemispherical Geodesic Polyarenes: Attractive Templates for the Chemical Synthesis of Uniform-Diameter Armchair Nanotubes. In *Fragments of Fullerenes and Carbon Nanotubes: Designed Synthesis, Unusual Reactions, and Coordination Chemistry*, Chap. 9, p. 235-258; Petrukhina, M. A.; Scott, L. T., Editors, John Wiley & Sons: Hoboken, New Jersey, 2012.
 Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937
 - (16) Bodwell, G. J. Growth Potential: Could Carbon nanotubes of a Single Chirality BeGrown from the Bottom Up Using a Common Organic Reaction? *Nature Nano*. 2010, *5*, 103-104.
 - (17) Bunz, U. H. F.; Menning, S.; Martín, N. Para-Connected Cyclophenylenes and Hemispherical Polyarenes: Building Blocks for Single-Walled Carbon Nanotubes? Angew. Chem. Int. Ed. 2012, 51, 7094-7101.
 - (18) Povie, G.; Segawa, Y.; Nishihara, T.; Miyauchi, Y.; Itami, K. Synthesis of a Carbon Nanobelt. *Science* 2017, 356, 172-175.
 - (19) Iyoda, M.; Yamakawa, J.; Rahman, M. J. Conjugated Macrocycles: Concepts and Applications. *Angew. Chem. Int. Ed.* **2011**, *50*, 10522-10553.

- (20) Iyoda, M.; Kuwatani, Y.; Nishinaga, T.; Takase, M.; Nishiuchi, T. Conjugated Molecular Belts Based on 3D Benzannulene Systems. In *Fragments of Fullerenes and Carbon Nanotubes: Designed Synthesis, Unusual Reactions, and Coordination Chemistry*, Chap.
 12, p. 311-342; Petrukhina, M. A.; Scott, L. T., Editors, John Wiley & Sons: Hoboken, New Jersey, 2012.
- (21) Nakamura, E.; Tahara, K.; Matsuo, Y.; Sawamura, M. Synthesis, Structure, and Aromaticity of a Hoop-Shaped Cyclic Benzenoid [10]Cyclophenacene. J. Am. Chem. Soc.
 2003, 125, 2834-2835.
- (22) Matsuo, Y.; Nakamura, E. in *Functional Organic Materials: Synthesis, Strategies and Applications*, Chap. 2, p. 59-80; Editors: Müller, T. J. J.; Bunz, U. H. F.; Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2006.
 Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937
 - (23) Matsuo, Y.; Tahara, K.; Nakamura, E. Theoretical Studies on Structures and Aromaticity of Finite-Length Armchair Carbon Nanotubes. *Org. Lett.* **2003**, *5*, 3181-3184.
 - (24) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. van E.
 Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe. *J. Am. Chem. Soc.* 1996, *118*, 6317-6318.
 - (25) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion. *Chem. Rev.* 2005, *105*, 3842-3888.

- (26) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v.
 R. Which NICS Aromaticity Index for Planar π Rings is Best? Org. Letters 2006, 8, 863-866.
- (27) We refer to the center of mass rather than the center of gravity used in Ref. 12a, both for continuity with the vast literature on NICS and for the different meaning assigned to the expression center of gravity in the field of monodimensional NMR, see Benshafrut, R.; Shabtai, E.; Rabinovitz, M.; Scott, L. T. π-Conjugated Anions: From Carbon-Rich Anions to Charged Carbon Allotropes. *Eur. J. Org. Chem.* **2000**, 1091-1106.
- (28) Lazzeretti, P. Ring Currents. *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1-88 and references therein.
- Accept (29) Havenitle, R. W. Fowfel, P.W. Isocentric Ring Cutrents in Density Fluctional Theory 01937 Chem. Phys. Lett. 2007, 449, 347-353.
 - (30) Soncini, A.; Teale, A. M.; Helgaker, T.; De Proft, F.; Tozer, D. J. Maps of Current Density Using Density-Functional Methods. J. Chem. Phys. 2008, 129, 074101-1-15.
 - (31) Steiner, E.; Fowler, P. W. Four- and Two-Electron Rules for Diatropic and Paratropic Ring Currents in Monocyclic π Systems. *Chem. Commun.* 2001, 2220-2221.
 - (32) Steiner, E.; Fowler, P. W. Patterns of Ring Currents in Conjugated Molecules: A Few-Electron Model Based on Orbital Contributions. *J. Phys. Chem. A* **2001**, *105*, 9553-9562.
 - (33) Monaco, G.; Fowler, P. W.; Lillington, M.; Zanasi, R. Designing Paramagnetic Circulenes. Angew. Chem. Int. Ed. 2007, 46, 1889-1892.

- (34) Lazzeretti, P. Assessment of Aromaticity Via Molecular Response Properties. *Phys. Chem. Chem. Phys.* **2004**, *6*, 217-223.
- (35) Steiner, E.; Fowler, P. W. On the Orbital Analysis of Magnetic Properties. *Phys. Chem. Chem. Phys.* 2004, 6, 261-272.
- (36) Bultinck, P.; Fias, S.; Ponec, R. Local Aromaticity in Polycyclic Aromatic Hydrocarbons: Electron Delocalization versus Magnetic Indices. *Chem. Eur. J.* 2006, *12*, 8813-8818.
- (37) Seal, P.; Chakrabarti, S. Is Nucleus-Independent Chemical Shift Scan a Reliable Aromaticity Index for Planar Heteroatomic Ring Systems? J. Phys. Chem. A 2007, 111, 9988-9994.
- (38) Carion, R.; Champagne, B.; Monaco, G.; Zanasi, R.; Pelloni, S.; Lazzeretti, P. Ring
 Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937 Current Model and Anisotropic Magnetic Response of Cyclopropane. J. Chem. Theory
 Comput. 2010, 6, 2002-2018.
 - (39) Radenković, S.; Bultinck, P. Ring Currents in Polycyclic Sodium Clusters. J. Phys. Chem. A 2011, 115, 12493-12502.
 - (40) Badri, Z.; Pathak, S.; Fliegl, H.; Rashidi-Ranjbar, P.; Bast, R.; Marek, R.; Foroutan-Nejad, C.; Ruud, K. All-Metal Aromaticity: Revisiting the Ring Current Model among Transition Metal Clusters. *J. Chem. Theory Comput.* **2013**, *9*, 4789-4796.
 - (41) Pelloni, S.; Monaco, G.; Lazzeretti, P.; Zanasi, R. Beyond NICS: Estimation of the Magnetotropicity of Inorganic Unsaturated Planar Rings. *Phys. Chem. Chem. Phys.* 2011, 13, 20666-20672.

- (42) Monaco, G.; Zanasi, R. Assessment of Ring Current Models for Monocycles. J. Phys. Chem. A 2014, 118, 1673-1683.
- (43) Jameson, C. J.; Buckingham, A. D. Molecular Electronic Property Density Functions: The Nuclear Magnetic Shielding Density. J. Chem. Phys. 1980, 73, 5684-5692.
- (44) Soncini, A.; Fowler, P. W.; Lazzeretti, P.; Zanasi, R. Ring-Current Signatures in Shielding-Density Maps. Chem. Phys. Lett. 2005, 401, 164-169.
- (45) Jusélius, J.; Sundholm, D.; Gauss, J. Calculation of Current Densities Using Gauge-Including Atomic Orbitals. J. Chem. Phys. 2004, 121, 3952-3963.
- (46) Fliegl, H.; Sundholm, D.; Taubert, S.; Jusélius, J.; Klopper, W. Magnetically Induced Current Densities in Aromatic, Antiaromatic, Homoaromatic, and Nonaromatic
 Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937 Hydrocarbons. J. Phys. Chem. A 2009, 113, 8668-8676.
 - (47) Monaco, G.; Zanasi, R.; Pelloni, S.; Lazzeretti, P. Relative Weights of σ and π Ring Currents in a Few Simple Monocycles. *J. Chem. Theory Comput.* **2010**, *6*, 3343-3351.
 - (48) Fowler, P. W.; Steiner, E.; Havenith, R. W. A.; Jenneskens, L. W. Current Density, Chemical Shifts and Aromaticity. *Magn. Reson. Chem.* **2004**, *42*, S68-S78.
 - (49) Schulman, J. M.; Disch, R. L. Aromatic Character of [n]Helicenes and [n]Phenacenes. J. Phys. Chem A 1999, 103, 6669-6672.
 - (50) Aihara, J. Aromaticity and Superaromaticty in Cyclopolyacenes. J. Chem. Soc. Perkin Trans. 2 **1994**, 971-974.

- (51) Aihara, J. Weighted HOMO-LUMO Energy Separation as an Index of Kinetic Stability for Fullerenes. *Theor. Chem. Acc.* **1999**, *102*, 134-138.
- (52) Mills, N. S.; Levy, A.; Plummer, B. F. Antiaromaticity in Fluorenylidene Dications.
 Experimental and Theoretical Evidence for the Relationship between the HOMO/LUMO
 Gap and Antiaromaticity. J. Org. Chem. 2004, 69, 6623-6633.
- (53) Monaco, G.; Zanasi, R. Anionic Derivatives of Altan-Corannulene. J. Phys. Org. Chem.2013, 26, 730-736.
- (54) Choi, C. H.; Kersetz, M. Bond Length Alternation and Aromaticity in Large Annulenes. J. Chem. Phys. 1998, 108, 6681-6688.

Accepted Version of J. Phys. Chem. Lett. 2017, 8, 19, 4673 doi: 10.1021/acs.jpclett.7b01937