

# On the high aromaticity of B<sub>20</sub> and neighbouring boron toroids

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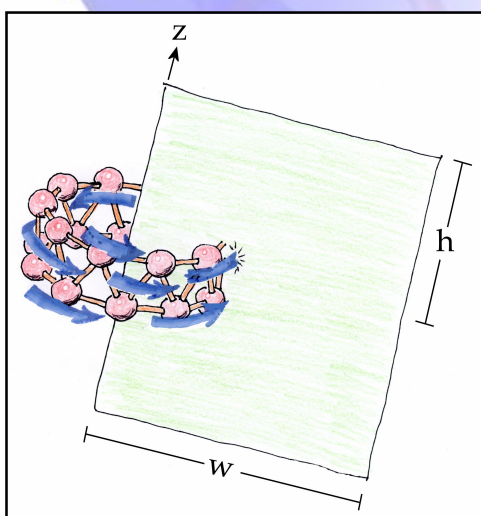
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## Introduction

- The neutral form of B<sub>20</sub> was recently suggested to be a highly symmetric, beautiful double ring, marking the onset of true three-dimensionality for small, neutral boron clusters [1]
- Suggested to be **highly aromatic**
- Here, the **magnetically induced ring currents** in B<sub>20</sub> and its nearest neighbours are investigated

## Methodology

- B3LYP / TZVPP level
- The **ring currents** obtained with the Gauge Including Magnetically Induced Currents (GIMIC) methodology [2]
- GIMIC can provide a **quantitative measure** of the induced **current strength**
- By integrating the current passing defined **cut planes**, the net current, including di- and paramagnetic contributions, is obtained:



- Cut plane in **green**
- Blue arrows** depict the current flow
- Turbomole** used for all QC calculations
- gOpenMol** and **gnuplot** for figures

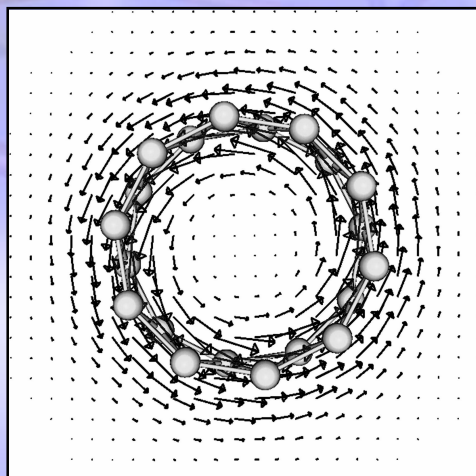
## Molecular structure

- Highest possible symmetry for B<sub>2n</sub> is D<sub>nh</sub>
- B<sub>16</sub>, B<sub>20</sub> and B<sub>24</sub> stable closed shell molecules in the highest symmetry group
- B<sub>18</sub> and B<sub>22</sub> of lower symmetry, C<sub>2h</sub> and C<sub>i</sub>

TABLE 1: Calculated Structural Parameters for the Boron Clusters Studied: Symmetry, Spin-State (S), Lowest Vibration Frequency ( $\nu_1$ , cm<sup>-1</sup>), Binding Energy Per Atom ( $E_b$ , kJ/mol), HOMO-LUMO Gap (gap, eV), and HOMO and LUMO Orbital Symmetries (Occupation for HOMO<sup>a</sup>)

	sym	S	$\nu_1$	$E_b$	gap	HOMO	LUMO
B <sub>16</sub>	D <sub>6d</sub>	0	176	458.2	2.36	e <sub>1</sub> (4)	e <sub>2</sub>
B <sub>20</sub>	D <sub>10d</sub>	0	115	473.9	2.47	e <sub>2</sub> (4)	e <sub>2</sub>
B <sub>24</sub>	D <sub>12d</sub>	0	79	478.9	1.96	e <sub>3</sub> (4)	e <sub>3</sub>
B <sub>18</sub>	D <sub>6d</sub>	1	143	464.6	1.41	$\alpha$ -e <sub>1g</sub> (2)	$\beta$ -e <sub>1g</sub>
	C <sub>2h</sub>	0	17	464.3	1.30	$\beta_g$ (2)	$\beta_g$ (2)
B <sub>22</sub>	D <sub>14d</sub>	1	92	474.3	1.10	$\alpha$ -e <sub>2g</sub> (2)	$\beta$ -e <sub>2g</sub>
	C <sub>i</sub>	0	17	474.5	1.18	a <sub>g</sub> (2)	a <sub>g</sub>

## Ring currents



- Highly uniform, diamagnetic ring currents are indeed induced!**
- The **degree** of aromaticity cannot be deduced from just the picture, however
- For a quantitative measure, let's integrate:

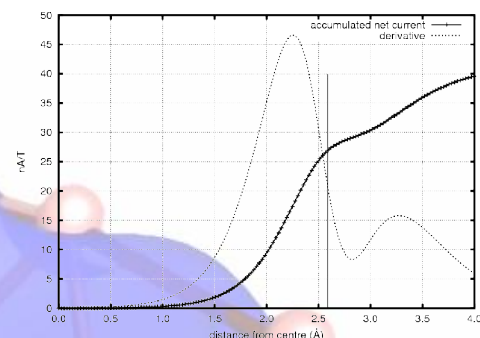
TABLE 2: Integrated Induced Currents for Selected Molecules in nA/T

	sym	total current	diamagnetic	paramagnetic	NICS
B <sub>16</sub>	D <sub>6d</sub>	31	33	-1	-33
B <sub>20</sub>	D <sub>10d</sub>	42	43	-1	-40
B <sub>24</sub>	D <sub>12d</sub>	50	51	-1	-35
B <sub>18</sub>	C <sub>2h</sub>	-117	11	-128	+62
B <sub>22</sub>	C <sub>i</sub>	-121	8	-130	+90
B <sub>12</sub>	C <sub>3v</sub>	25	25	0	-30
C <sub>60</sub> <sup>0/+2</sup>	I <sub>h</sub>	60	81	-21	-82
C <sub>4H<sub>4</sub></sub>	D <sub>6h</sub>	12	17	-5	-8

- B<sub>16</sub>, B<sub>20</sub> and B<sub>22</sub> possess **very strong currents**
- Almost no paramagnetic contribution, in contrast to, e.g., benzene, **highly aromatic**
- B<sub>18</sub> and B<sub>22</sub> have very strong paramagnetic currents – **antiaromatic**
- NICS agrees qualitatively with GIMIC

## Where is the current?

- To **spatially pinpoint** the regions of strong current, integrations over **partial planes** were performed



- Accumulated current for increasing width, going out from the centre of B<sub>20</sub>
- Derivative as dotted line
- Vertical line at 2.59 Å marks the radius
- 2/3 of the current from the inside region**
- The in-plane current not concentrated to the location of the B<sub>10</sub> rings, strongest contribution from the middle plane of the ring

## Conclusions

- The experimentally known B<sub>20</sub> shown to possess **very strong ring currents**, 3.5 times higher than in benzene – **Superaromatic!**
- Also B<sub>16</sub> and B<sub>24</sub> sustain strong diamagnetic currents
- B<sub>18</sub> and B<sub>22</sub> appear strongly anti-aromatic, and should be destabilised.

## Acknowledgements

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## References

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