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A Computational Study on the Electronic and Optical Properties of Boron-Nitride Circumacenes [†]

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Additional Material

Total Energies of the clusters

In this section we report some additional details of our results, concerning both the electronic and the optical properties of the systems analyzed. Firstly, Tabs. 1 and 2 show the calculated values for the ground-state total energies on which the stability criterion has been based, for all the molecules under study and its corresponding anion (all the values are expressed in atomic units AU).

To clarify the sentence previously mentioned (see section 'Electronic Properties'), we verify that all the anions have deeper ground-state energies with respect to their neutral molecules. The only exception concerns the anion of the three first members of the BN-family (highlighted in red in Tab. 2): in fact, $\mathrm{BNC^-}$, $\mathrm{BCO^-}$ and $\mathrm{BNCA^-}$ have lower values (in module) as compared to their corresponding neutral parents and this fact is explained in the negative value assumed by $\mathrm{EA_V}$. For the C-made (BN-made families), in general, both the neutral and the charged species become more stable as their dimension increase. This effect is roughly the same in both the family, either for the neutrals and the anions, considering the percentage deviation as calculated with respect the smallest member (C and BNC): the trend in the increase (in absolute value) of the ground-state total energies are the same.

Table S 1 Ground-state total energies, $\mathrm{E_N^0}$ ($\mathrm{E_A^0}$), for Circumacenes and their corresponding anions.The percentage deviation has been calculated with respect to $\mathrm{C(C^-)}$. The values are given in AU.

Neutral	$\mathrm{E_N^0}$ (AU)	Anion	$\mathrm{E_N^A}$ (AU)
C	-921.92	**$\mathrm{C^-}$**	-921.94
O	-1228.04 (+33.2%)	**$\mathrm{O^-}$**	-1228.08 (+33.2%)
CA	-1534.15 (+66.4%)	**$\mathrm{CA^-}$**	-1534.21 (+66.4%)
CT	-1840.26 (+99.6%)	**$\mathrm{CT^-}$**	-1840.33 (+99.6%)
CP	-2146.36 (+132.8%)	**$\mathrm{CP^-}$**	-2146.37 (+132.8%)

Size Effects on the Electronic and Optical Properties

To make a pictorial comparison about the size effects on the electronic properties, for example, Fig. 1 shows the behavior of the above mentioned observables (EA_V, IE_V and E_{gap}) through a diagrammatic representation, analyzing the smallest and the largest molecule of the two species, and respectively C vs BNC and CP vs BNCP. Going from C (BNC) to CP (BNCP) a rise of the vertical affinity, a decrease of the ionization energy and a consequent lowering of the QP gap takes place.

Table S 2 Ground-state total energies, $\mathrm{E_N^0}$ ($\mathrm{E_A^0}$), for BN-Circumacenes and their corresponding anions.The percentage deviation has been calculated with respect to BNC ($\mathrm{BNC^-}$). The values are given in AU.

Neutral	$\mathrm{E_N^0}$ (AU)	Anion	$\mathrm{E_N^A}$ (AU)
BNC	-963.775	**$\mathrm{BNC^-}$**	-963.766
BNO	-1283.875 (+33.2%)	**$\mathrm{BNO^-}$**	-1283.869 (+33.2%)
BNCA	-1603.974 (+66.4%)	**$\mathrm{BNCA^-}$**	-1603.972 (+66.4%)
BNCT	-1924.073 (+99.6%)	**$\mathrm{BNCT^-}$**	-1924.074 (+99.6%)
BNCP	-2244.172 (+132.8%)	**$\mathrm{BNCP^-}$**	-2244.175 (+132.8%)

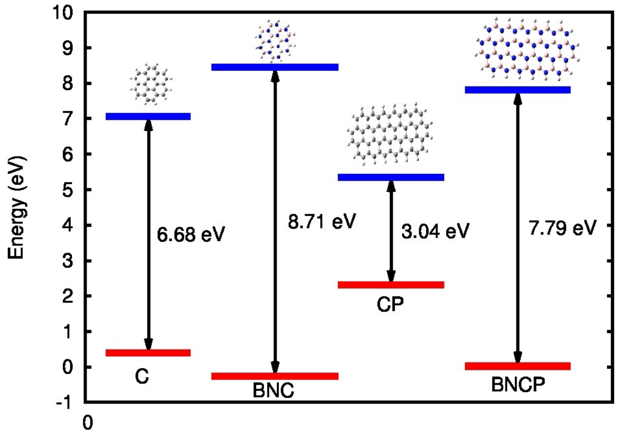

Fig. S 1 Vertical electron affinities (red lines), vertical ionization energies (blue lines) and fundamental gaps (black arrows) for C, BNC, CP and BNCP, from left to right, respectively.

These effects are slightly stronger in the C-made family, since the percentage variation going from C to CP are ∼ +500%, −24% and −54% for the vertical electron affinity, the vertical ionization energy and the fundamental gap, respectively. For the same quantities in the case of BN compounds we found (going to BNC to BNCP) percentage deviations of the order of ∼ +135%, −7% and −11%.

As for the electronic observables, we propose a comparative

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analysis for the size effects of the optical properties through a graphical representation, presenting data for C to CP on one side and BNC and BNCP on the other (see Fig. 2). Passing from the smallest molecule C (BNC) to the largest one CP (BNCP) there is a lowering of the fundamental gap, a redshift of the optical onset and a reduction of the exciton-binding energy. The effect is slightly stronger in the C-made family, since the percentage decrease going from C to CP are $\sim -54\%$, -71% and -28% for the fundamental gap, the optical onset and the exciton binding-energy, respectively. For the same observables we find a deviation in the case of the BN-made counterparts, going from BNC to BNCP, of the order of $\sim -11\%$, $+6\%$ and -24%, for the fundamental gap, the optical onset and the exciton binding-energy, respectively.

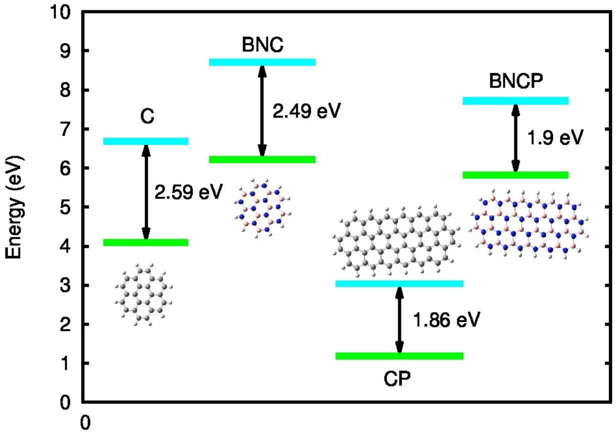

Fig. S 2 Fundamental gaps (light-blue lines), optical onsets (green lines) and exciton binding energies (black arrows) for C, BNC, CP and BNCP, from left to right, respectively.

Aromaticity

As noted by authors in previous publications, one can consider also the aromaticity of the molecules as parameter to study in a systematic way their electronic and optical properties[1–3]. Considering different state of the art parameters associated to aromaticity, one should demonstrate that the BN counterparts with respect to the Circumacenes are less aromatic[3]. However, since there is no single definition of the concept of aromaticity, one should, in principle, consider some/many different criteria/parameters of aromaticity and apply them to each member of the family under study[4]. This systematic study is out of the scope of the present work. On the other hand, we report a bond analysis based on the Wiberg bond index and a comparison of the HOMO-LUMO gap (which could be considered related to aromaticity criteria[1,4]) in two different approximations for each cluster under study. All these points support the concept of the less aromatic nature of the BN-Circumacenes with respect to their Carbon-based original counterparts.

Criteria of Aromaticity

As more advanced parameters of aromaticity, one can consider the NICS (nucleus independent chemical shifts), the HOMA (harmonic oscillator model of aromaticity), the PDI (para-delolalization index) and the fluctuation index FLU. FLU is typically close to zero for aromatic species and increases as the molecule depart from aromatic nature, while PDI is proportional to the delocalization of the electrons, HOMA which is related to parameters functions of the bond lengths is zero for non aromatic systems while equals 1 for aromatic ones[4]. But also the energy gap between HOMO and LUMO can be considered a parameter related to the aromaticity (see the dedicated lines in the main text). One can consider as prototype structure, the $B_6N_6H_6$ to be compared with the benzene PAH. One can discuss the different aromaticity character of these systems through the above mentioned parameters and extend the results of this in comparison to the whole family of BN made PAH considered in the present work. After Tab.2 of Ref.[4] the NICS(0) and NICS(1) going from $B_6N_6H_6$ to C_6H_6 show respectively increase in modulus (decrease as negative values) by around 75% and 83%, while NICS(1)zz shows an increase in modulus (decrease as negative values) by around 82%. NICS(0)zz parameter shows a decrease from $B_6N_6H_6$ to C_6H_6 by around 182% , switching from positive to negative value. The HOMA and the PDI parameters increase respectively of about 3% and 90% going from BN-benzene to benzene, stressing again the more aromatic character of the latter compound. It is not clear on the other hand the tendency from the FLU parameter (Tab.2 of Ref.[4]). Along the previous discussion, we therefore expect the same trend for the larger (i.e. number of rings larger than 1) members of the Circumacenes and BN families: demonstrating therefore the less aromatic nature of the BN-Circumacenes with respect to their Carbon counterparts. Consider that in studies on the aromaticity also the energy (HOMO-LUMO) gap of the molecules can be considered as a criterium of aromaticity (see e.g. Tab.2 in Ref .[4]) . For this particular observable we reported two kind of calculations for each member of pure and BN-substituted Circumacenes: namely the DFT-gap and the QP-gap. We demonstrated and commented extensively that each member of the pure carbon Circumacenes present a DFT-gap/QP-gap smaller, even in a consistent way, with respect with that for the corresponding BN-substituted counterpart (see Tab. **??** in our text). The important reduction of the gap comparing Benzene and BN-Benzene is confirmed in Ref.[4] with a decrease of $\sim$ 18%. This can be considered as a manifest demonstration of the less aromatic nature of the BN-substituted Circumacenes. Moreover, studies could be performed on the effects of the substitutions of single or multiple B-N to C-C bonds in PAHs. In general, the B-N substitution determines a decrease in the aromaticity of the host cluster (Ref.[3]).

Wiberg Bond Index Calculations

We present here the calculation of the Wiberg-bond indexes (here indicated by the acronym WBI), parameter from which one could estimate the measure of electron population overlap between two atoms. This information connected to the degree of aromatic character of the considered material[5]. Tab. 3 reports the calculated Wiberg bond indexes for some selected bond in the case of C and BNC after the present work. To demonstrate the higher degree of aromaticity of the C-based compounds with respect to the BN-made ones, we focus on the two smallest members of each family, since the same considerations are valid and extensible for all the molecules analyzed, We consider some internal and external bonds, e.g. C-C, B-N, C-H, B-H and N-H (see Fig. 3 in which the selected atoms are labeled by the corresponding numbers).

Table S 3 Wiberg bond indexes as calculated for C-C and B-N peripheral (red circle) and internal (blue and green circles) bonds. The atoms follow the numeration as shown in Fig. 3.

C-C	w	B-N	w
$C_{17}C_{18}$	1.5736	$B_{17}N_{18}$	1.0245
$C_{17}C_{16}$	1.2526	$B_{17}N_{16}$	0.9069
$C_{17}H_{32}$	0.9116	$B_{17}H_{32}$	0.9718
-	-	$N_{18}H_{33}$	0.7842
C_4C_5	1.2327	B_4N_5	0.8942
C_4C_{16}	1.2629	B_4N_{16}	0.8864
C_4C_3	1.2243	B_4N_3	0.8942
C_5C_6	1.2292	N_5B_6	0.8942
C_4C_5	1.2327	N_5B_4	0.8942
C_5C_{19}	1.2666	N_4B_{19}	0.8702

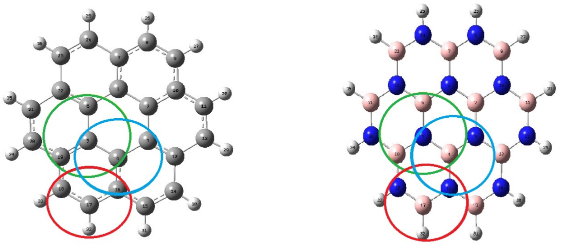

Fig. S 3 Coronene (left) and BN-Coronene (right) in which the region with the selected atoms considered as example for the calculation of WBI has been underlined by circles (the peripheral region by a red circle, the two central ones by blue and green circles). C atoms are in gray, B are in pink, N in blue and the peripheral H in white.

We have found that the average values of WBI for the atoms placed at the peripheral region are for C-C (B-N) 1.2467 (0.9815) with a reduction of ∼-21.3%, as compared to the original C-C bond. Considering the atoms placed in the innermost molecular areas, the average values of WBI are, for C-C (B-N) 1.2399 (0.8916) with a decrease of ∼-28.1%. Finally, we have calculated that the medium value of WBI for the atoms placed at the peripheral region: for C-C (N-B) 1.2428 (0.8862), with a variation of -28.7%. After this Wiberg analysis, BN clusters present less aromatic character with respect to their parent carbonaceous compounds.This is in accordance with other previous results (see e.g. Ref.[3]), which establish that the lower degree of aromaticity of BN-Circumacenes is connected to the larger gaps, the higher delocalization along the structure (observed from the frontier orbitals) and could be an explanation of the fact that these species absorb in the UV and not in the visible part of the spectrum, as their C-made original compounds.

Notes and references

1 I. D. Madura, T. M. Krygowski and M. K. CyraÅĎski, *Tetrahedron*, 1998, **54**, 14913 – 14918.

2 A. Marwitz, M. Matus, L. Zakharov, D. Dixon and S.-Y. Liu, *Angewandte Chemie International Edition*, 2009, **48**, 973–977.

3 F. Feixas, E. Matito, J. Poater and M. SolÃă, *Chem. Soc. Rev.*, 2015, **44**, 6434–6451.

4 D. Ghosh, G. Periyasamy and S. K. Pati, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20627–20636.

5 R. Ghiasi and M. Abdoli, *Journal of the Mexican Chemical Society*, 2014, **58**, 27 – 35.