Replacing of Boron and nitrogen atoms in [8] annulene molecule help us for explaining the details of mentioned magnetic mechanism concerning the ring currents of the carbon disappearing in the isoelectronic azabora-hetero-cycles variants \(B_n N_n C(8-2n) H_8\) \((n=0,1,2,3\) and 4). The \((4n+2)\pi\) systems aromatic on variants of \(BnNnC(8-2n) H_8\) \((n=0,1,2,3\) and 4) via the localized orbital by considering the current density induced have been studied. It has been predicted a four-electron dia-tropic (aromatic) ring current for \((4n+2)\pi\) azabora-hetero-cycles variants of \(BnNnC(8-2n) H_8(n=0,1,2,3,4)\) and a two-electron paratropic (anti-aromatic) current for \((4n)\pi\). HOMO and LUMO energies and also HOMO/LUMO overlapping in whole space have been calculated. Two forms can be considered, first the HOMO–LUMO transition leads to a para-tropic contribution, and second HOMO–LUMO\(+1\) transitions to the dia-tropic contributions. In addition, the NICS and SNICS values confirm the amounts of aromaticity and anti-aromaticity in those rings.

KEYWORDS: Aromaticity, LOL, ELF, Annulene, current density induced, azabora-hetero-cycles.

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Recibido: 09/01/2020

Aceptado: 12/02/2020
(4n +2) π Regla de Huckel de Bn NnC (8-2n) H8 como sistema heterocíclico contra el cáncer

RESUMEN

El reemplazo de los átomos de boro y nitrógeno en la molécula de anuleno [8] nos ayuda a explicar los detalles del mecanismo magnético con respecto a las corrientes anulares del carbono que desaparecen en las variantes isoelectrónicas de azabora-heterociclos (Bn Nn C (8-2n) H82−, n = 0,1,2,3 y 4). Los sistemas (4n + 2) π aromáticos en variantes de BnNnC (8-2n) H8 (n = 0, 1, 2,3 y 4) se ha estudiado la densidad de corriente inducida a través del orbital localizado. Se ha predicho una corriente de anillo dia-trópico (aromático) de cuatro electrones para (4n + 2) π aza-bora-heterociclos variantes de BnNnC (8-2n) H8 (n = 0, 1, 2,4) y una corriente para-trópica (antiaromática) de dos electrones para (4n) π. las energías HOMO y LUMO y también la superposición de HOMO / LUMO en todo el espacio. Se han calculado dos formas, primero, la transición HOMO-LUMO conduce a una contribución para-trópica, y la segunda transición HOMO-LUMO + 1 a las contribuciones dia-trópicas. Además, los valores NICS y SNICS confirman las cantidades de aromaticidad y anti-aromaticidad en esos anillos.

PALABRAS CLAVE: Aromaticidad, LOL, ELF, Annulene, inducida por densidad de corriente, azabora-heterociclos.

Introduction

1,3,5,7-Cyclooctatetraene (COT) is known as “Annulene” and in contrast of benzene structure, COT follows a nonplanar conformation with alternating double and single bonds via \( D_2d \) symmetry (Willstätter and Waser, 1911; Willstätter and Heidelberger, 1913). \( \text{C}_8\text{H}_8^2^- \), is an aromatic ring with high resonance energy in the aromatic reactions. This molecule is both planar and octagonal in the shape and aromatic with the Huckel electron count of \((4\times2)+2=10\). Huckel’s long-standing “4n+2” rule indicates mono aromatic rings from anti-aromatics, and correlates the electronic structures of those systems with their magnetic properties (Gellini and Salvi, 2010). Through the interaction between alternating bonds it has been confirmed that the structure of COT involves a planar transition state of \( D_{4h} \) symmetry (Wu et al., 2012). Moreover the NMR experimental data indicate that COT\(^2^-\) also adopts a \( D_{8h} \) symmetry structure (Naor and
Luz, 1982). Although the planar D_{4h} structure for the ring inversion of COT has a transition state (TS) with around 12 kcal/mol barrier energy (Nishinaga et al., 2010), the D_{8h} bond switching TS lays a few kilocalories per mole higher. Actually, COT has three fundamental structural changing including 1- ring inversion, 2- bond shifting and 3- valence isomerization (Schild and Paulus, 2013).

Planar conjugated COT\(^2\) exhibit a strong link between p-electrons. Coupling between COT\(^2\) charge state and its mechanical conformation creates new opportunities for COT\(^2\) as an aromatic molecule including electromechanical converter treatment (Wenthold et al., 1996).

Replacing of Boron and nitrogen atoms in COT help us for explaining the details of mentioned magnetic mechanism concerning the ring currents of the carbon disappearing in the isoelectronic azabora-hetero-cycles variants (B\(_n\)N\(_n\)C\(_{8-2n}\)H\(_8\), n=0,2,4) scheme (Wu et al., 2012) and (Stevenson et al., 1998). Steiner and coworkers investigated a model via frontier-orbital contributions which yields an accurate account of p ring currents in benzene, COT\(^2\) and suchlike planar rings (Schild and Paulus, 2013). London, Pauling and Pople investigated the concept of aromaticity and anti-aromaticity in view point of magnetic criterion, diatropic (Planar of 4n+2 systems) and paratropic currents (planar of 4n systems) (Yoshida et al., 2015). Recently, it has been shown that the ring currents are a consequence of the HOMO–LUMO transition depends on symmetry properties (Andrés et al., 1998). For the 4n+2 hetero-cycles, B\(_n\)N\(_n\)C\(_{8-2n}\)H\(_8\)\(^2\) (n=0,2,4 ), densities maps, exhibit the “p” electrons with the localized circulations around the electronegative nucleus (Hrovat and Borden, 1992).

In this work we exhibited that an extension of the figurative orbital model is able to account for both the currents in carbocyclic aromatic rings and their B-N analogues such as B\(_4\)N\(_4\)H\(_8\)\(^2\). Although it is generally agreed that B\(_3\)N\(_3\)H\(_6\) is not aromatic (due to localized of p electrons on the more negative nitrogen atoms), they have suitable resonance energies for aromatic reactions. Although a few derivatives of the homologues rings of B\(_n\)N\(_n\)C\(_x\)H\(_y\) such as diazadiboretane and borazoin have been synthesized, some compounds
of \( B_nN_nC_{(8-2n)}H_{8n} \) (n=0,2,4) have not been prepared yet. Therefore any theoretical calculation and detailed discussion might be useful for understanding in the area of aromaticity and also physical chemistry mechanism of these kind compounds.

Scheme 1: \( B_nN_nC_{(8-2n)}H_{8n} \), including n=0, 1, 2, 3 and 4

1. Theoretical background
1-1. Aromaticity & ring current

Current-density's map can be estimated through theoretical methods without any gauge-dependence problem by vector potential generating of the magnetic field. Meanwhile from occupied to unoccupied orbitals, the total current densities are evaluated which are modulated and governed by energy denominators and symmetry rules respectively. Aromaticity can be also defined through magnetic criteria (Longuet, 1967) and is a trustworthy account of the currents induced by an external magnetic field capability. In addition chemical shift, isotropy, anisotropy, span, asymmetry and other properties are all integrals of these current densities. For the magnetic criterion, the
resultant of all such components explains the aromaticity or anti-aromaticity which is related to the net dia-tropicity and para-tropicity of the ring current respectively.

1.2. Anticancer properties, heterocyclic rings and Aromaticity

Cancer is one of the important causes of death in the new century. This work is done for developing of modern anticancer drugs. Many of heterocyclic compounds are known as anticancer drugs such as alkylating agents which have targeted cell DNA causing cell death. Heterocyclic structures are composed by atoms other than carbon, where the most times substituents are sulfur, oxygen, Boron and nitrogen. The model size of heterocyclic ring such as $B_nN_nC_{(8-2n)}H_8$, with the substituent group of the core scaffold impact tightly on the chemical and physical properties while among the clinical applications, heterocyclic compound has an active role as anti-bacterial, anti-viral, anti-fungal, anti-inflammatory and anti-tumor drugs. Traditional drugs for anticancer such as alkylating agent has targeted cell DNA causing cell death. Generally, chemical-physics and biochemical properties like donor-acceptor capability, hydrogen bond, $\pi-\pi$ stacking interactions, van der Waals, co-ordination bonds with metals and in total hydrophobic forces have caused the increasing interest in anticancer studies for such compounds $B_nN_nC_{(8-2n)}H_8$. These properties are important of understanding for their reactivity enable derivatives to readily bind with various nucleic acids, enzymes and biological structures.

1.3. Isotropic and anisotropic parameter

Spherical tensors can be noted as $\sigma_{iso}^{(2)} = \sqrt{\frac{3}{2}} \zeta_{zz}$ and $\sigma_{\pm 2}^{sym} = \frac{1}{2} \zeta_{zz}$ (1)

Where, $\zeta_{zz}$ is the reduced anisotropy and can be calculated through $[\zeta_{zz} = (\sigma_{zz} - \sigma_{iso}) = (\sigma_{33} - \sigma_{iso})]$(2). Haeberlen and Mehring (Haeberlen, 1967) have investigated fundamental tensors as $\sigma = \sigma_{iso}^{(0)} + \sigma_{anti}^{(1)} + \sigma_{sym}^{(2)}$ (3). This parameter is related to the anisotropy ($\Delta \sigma$) with $\Delta \sigma = \frac{3}{2} \zeta_{zz}$ (4) and ($\eta$) shielding which can be estimated via
\[
\Delta \sigma = \sigma_{zz} - \frac{1}{2} (\sigma_{xx} + \sigma_{yy}) \quad (5) \quad \text{and} \quad \eta = \left( \frac{\sigma_{yy} - \sigma_{xx}}{\zeta_{(zx)}} \right) = \frac{3(\sigma_{yy} - \sigma_{xx})}{2\Delta \sigma} \quad (6) \quad \text{(Anet and O'Leary, 1992)}.
\]

Since the magnetic resonance of a spin is seldom isotropic, therefore they have to represent by new tensors by Herzfeld-Berger notation. These tensors are known as Span (\( \Omega \)) \( \Omega \geq 0 \), which describes the maximum width of the model and the skew (\( \kappa \)) of the tensor which is a magnitude of the values \( \Omega = \sigma_{33} - \sigma_{11} \) \( (7) \) and \( \kappa = \frac{3(\sigma_{iso} - \sigma_{22})}{\Omega} \) \( (8) \). Moreover the orientation of asymmetry tensor is given by \( \kappa = \frac{-3\gamma_{(yy)}}{\Omega} \) or \( \kappa = \frac{3(\sigma_{iso} - \sigma_{22})}{\Omega} \) \( (-1 \leq \kappa \leq +1) \), and \( \gamma_{(yy)} = \sigma_{22} - \sigma_{iso} \). Asymmetry (\( \eta \)) indicates that how much deviation can be appeared from an axially symmetric tensor, therefore the region of \( \eta \) is between zero and one \( (0 \leq \eta \leq +1) \) and in some cases \( \eta = 0 \).

1.4. ELF and LOL functions
Electron density can be written as \( \rho(r) = \eta_i \left| \varphi_i(r) \right|^2 = \sum_i \eta_i \left| \sum_l C_{li} \chi_l(r) \right|^2 \) \( (10) \).

Where “\( \chi \)” is the basis function of orbitals and \( \eta_i \) is occupation number. \( C \) is also a coefficient matrix. The unit of electron density in atomic scale is e/Bohr\(^3\). Bader exhibited that the regions with having large electron localization must have a large magnitude of Fermi-hole integration. Becke and Edgecombe cleared that spherically averaged like-spin pair has direct correlation to the Fermi hole. Consequently, they introduced a new function as “electron localization function” (ELF) \( (Lu and Chen, 2012) \).

\[ \text{ELF}(r) = \frac{1}{1 + [D(r)/D_0(r)]^2} \quad (11) \]

where

\[ D(r) = \frac{1}{2} \sum_i \eta_i \left| \nabla \varphi_i \right|^2 - \frac{1}{8} \left[ \frac{|\nabla \rho_\alpha|^2}{\rho_\alpha(r)} + \frac{|\nabla \rho_\beta|^2}{\beta(r)} \right] \quad (12) \quad \text{and} \quad D_0(r) = \frac{3}{10} \left( 6\pi^2 \right)^2 \left[ \rho_\alpha (r) \right]^5 + \left[ \rho_\beta (r) \right]^5 \quad (13) \]

for close-shell system, since \( \rho_\alpha (r) = \rho_\beta (r) = \frac{1}{2} \rho \), \( D \) and \( D_0 \) terms can be simplified as

\[ D(r) = \frac{1}{2} \sum_i \eta_i \left| \nabla \varphi_i \right|^2 - \frac{1}{8} \left[ \frac{|\nabla \rho|^2}{\rho(r)} \right] \quad (14) \quad \text{and} \quad D_0(r) = \frac{3}{10} \left( 3\pi^2 \right)^2 \rho(r) \quad (15) \]
SamieiSoofi and Monajjemi /// (4n +2)π Hückel’s rule of BnNnC(8-2n)H8 ...

Savin et al., indicated which D(r) reveals the excess kinetic energies densities caused by Pauli repulsion, while \( D_0(r) \) can be noted as Thomas-Fermi kinetic energies densities. In other words they reinterpreted ELF in view point of kinetic energy through Kohn-Sham DFT’s wave-function. Therefore ELF would be in the range of [0, 1] and a large ELF value indicates that electrons are strongly localized. ELF has been widely used for a wide variety of systems, such as organic and inorganic small molecules, atomic crystals, coordination compounds, clusters.

LOL or Localized orbital locator is another function for locating high localization regions likewise ELF, invistegated by Schmider and Becke. \( LOL(r) = \frac{\tau(r)}{1+\tau(r)} \), where \( \tau(r) = \frac{D_0(r)}{2\sum_{\eta_i} \nabla \varphi_{\eta_i}^2} \). \( D_0(r) \) for spin-polarized system and close-shell system are defined in the same way as in ELF. LOL has similar expression compared to ELF. Actually, the chemically significant regions that highlighted by LOL and ELF are generally qualitative comparable, while Jacobsen pointed out that LOL conveys more decisive and clearer picture than ELF. Obviously LOL can be interpreted in kinetic energy way as for ELF; however LOL can also be interpreted in view of localized orbital. Small (large) LOL value usually appears in boundary (inner) region of localized orbitals because the gradient of orbital wave-function is large (small) in this area. The value range of LOL is identical to ELF, namely [0, 1].

2. Computational details

Geometry & electronics structures have been accomplished using the m06 groups in (DFT) functional. This methods are based on an iterative solution of Kohn-Sham equation (Kohn and Sham, 1965) of DFT in the plane-waves with the projector-augmented wave pseudo-potentials. The Perdew-Burke-Ernzerhof (PBE) (Perdew et al, 1996) exchange-correlation functional of the generalized gradient approximation (GGA) is adopted. The geometry of each part of ions was optimized at the various methods including M062x/cc-pvdz, M062x/cc-pvtz and CASSCF methods. For obtaining ab-initio amounts on the currents in BN analogues of the 4n and 4n+2 carbo-cycles, calculations
were performed for $C_8H_8^2$, BNC6H8, $B_2N_2C_4H_8$ and $B_4N_4H_8$ and currents were calculated by using the ipso-centric approach. At this level of theory, $C_8H_8$ and $B_4N_4H_8$ have planar structures with $D_{4h}$ symmetry. To draw the contour line maps of Current-density for both the constrained planar and the fully optimized structures Multiwfn software have been used. We have plotted the contour line corresponding to electron densities-0.001 a.u., which are defined by R. F. W Bader (Bader, 1990). This is useful for analyzing distribution of the electrostatic potential on potential surfaces. Such contour lines have also been plotted in gradient lines and vector field’s maps through the same options.

The relief maps were used for presenting the height data at each point. If these values are too large, they will also be truncated in those graphs. Therefore, it can be chosen for scaling the values with a factor for avoiding truncation. Shaded surfaces maps with and without projection are used in our representation of height values at each situation. For confirmation the data several extra calculation including MP4 (SDQ)/6-31+G(d’), QCISD(T)/6-31+G(d’) and CAM-b3lyp/6-311g have also been done. The charges transfers were also evaluated using the Merz-Kollman-Singh, chelp, or chelpG. Those methods are based on molecular electrostatic potential approaches (MESP) fitting which are suitable for small molecules (in large molecules some of the innermost atoms are located far away from the points at which the MESP is computed). Obviously the representative atomic charges for molecules should be computed as average values over several molecular conformations. A detailed overview of the effects of the basis set and the Hamiltonian on the charge distribution can be found in.

The electron densities (Both of Gradient and Laplacian), values of orbitals and LUMO, HOMO wave-functions, electrons spin densities, electrostatic potentials from nuclear atomic charges, electrons localization functions (ELF), localized orbital locator (LOL) and total electrostatic potential (ESP), as well as the exchange-correlation densities, correlation holes and correlation factors, and the averages local ionization energies using the Multifunctional Wave-function Analyzer have also been calculated in this work. Among the various methods and basis sets (both large and medium) which have
been used in this study, the cc-pvdz and cc-pvtz basis sets exhibit the most favorable results for electrostatic potential (ESP) fitting. The cc-pvdz is a double-ζ basis set with a single set of polarization functions for B to F and cc-pvtz is a triple-ζ basis set including diffuse functions, double d-polarizations, and a single set of polarization functions. The active space for the CASSCF method was composed of all valence electrons and orbitals of B, N and C atoms. A Quadratic CI calculation including single and double substitutions has been used to evaluate various one-electron properties including NBO, bonding analysis, atoms in molecules (AIM), natural population analysis, multipole moment, electrostatic potentials, and electrostatic potential-derived charge using the Merz-Kollman-Singh, chelp, or chelpG (Besler et al., 1990).

The AIM keyword is also used for computing the atomic charges of atoms in molecules, covalent bonds, localized orbitals, and critical points for any further properties predication of atoms in molecules (Chirlian and Francl, 1987). In addition Polarizabilities and hyper-polarizabilities have been calculated through CISD, QCISD and CASSCF methods. CHELPG charges (Martin and Zipse, 2005) can also be computed using the well-known ab initio quantum chemical packages such as Gaussian or GAMESS-US. In this study, it is indeed difficult and at some points not important to use the large basis sets and demanding methods such as MRCI for CHELPG and ESP calculations due to the large number of calculations in various situations of MESP simulation. Therefore, with medium methods in terms of computational cost, we have found the accurate results for our approach. All the calculations were performed using the Gaussian program package and the optimization were done along with the frequencies calculation for confirming that the geometries were real minimum without any imaginary frequencies.

3. Result and discussion

The compounds of \( B_n N_n C_{(8-2n)} H_8 \), \( n=1,2,3 \) and 4 have not been synthesized, although many derivatives of the homologues such as di-aza-di-boretidine and borazocine have been prepared.
SamieiSoofi and Monajjemi /// (4n +2)π Hückel's rule of $B_nN_nC_{(8-2n)}H_8$...

Although $8\pi$-electron of $B_nN_nC_{(8-2n)}H_8$, ($n=2,4$) were originally called “an inorganic Compounds” and believed to have a resonance energy similar to that of Annulene, they were soon recognized that they took part in few reactions typical of aromatic systems. Geometries and energies of $C_8H_8^{2+}$ in various methods have been listed in Table.1. It has been exhibited (Table.1) that m06x/cc-pVdz method has more accurate results compare to other methods, therefore this method has been considered for investigation and calculation on variant of $B_nN_nC_{(8-2n)}H_8$, ($n=0,1,2,3$ and $4$). It is now generally agreed that homologues rings of $B_nN_nC_xH_y$ such as diazadiboretane and borazoin are not aromatic.

In contrast to benzene or $C_8H_8^{2+}$, the p electrons are localized on the more negative nitrogen atoms, even if a few chemical behaviors are reminiscent of that of aromatic rings. ELF current-density map from ab initio calculations on COT $^2$ and $B_4N_4H_8^{2-}$, are shown in (Fig.1) and the currents are dominated by HOMO contributions Table 2.

Table.1: Geometry and energy of $C_8H_8^{2+}$ in various methods

| Methods                      | Energy (Hartree) | C-C & C-H in resonated ring (Å) |
|------------------------------|------------------|---------------------------------|
| MP4(SDQ)/6-31+G(d')          | -308.46562       | 1.415, 1.100                    |
| QCISD(T)/6-31+G(d')          | -308.52139       | 1.415, 1.08                     |
| CAM-b3lyp/6-311g             | -309.24996       | 1.413, 1.099                    |
| m06x/cc-pvdz                 | -309.33567       | 1.415, 1.05                     |
| m06x/cc-pvTz                 | -309.43505       | 1.409, 1.094                    |

Table.1: continue: HOMO/LUMO and Aromaticities
SamieiSoofi and Monajjemi /// (4n +2)π Huckel’s rule of \( B_nN_nC(8-2n)H_8 \) ...129-150

| C-C-C and H-C-C angle in resonated ring | LUMO/HOMO Gap Energy \( \text{kJmol}^{-1} \) | Aromaticity |
|----------------------------------------|-------------------------------|-------------|
| 135.0, 112.5                           | 519.06                        | -14.95      |
| 135.0, 112.5                           | 519.13                        | -15.11      |
| 135.0, 112.5                           | 519.05                        | -14.87      |
| 135.0, 112.5                           | 547.1                         | -17.59      |
| 135.0, 112.5                           | 493.43                        | -15.90      |

Table 2. HOMO/LUMO and Aromaticities

| Molecule | LUMO/ HOMO Gap energy | % composit for HOMO | % composition of atoms for LUMO |
|----------|-----------------------|---------------------|---------------------------------|
| \( B_4N_4H_8^{2+} \) | 3.34 eV | 23.0(B1+B4 +B6+B7) | 7.8 (B1+ B4 + B6 + B7 ) +10.5 (N2+N3+N5+N8 ) |
| \( B_4N_4H_8^{-} \) | 3.54 eV | 25.0(B1+B4 +B6+B7) | 6.8 (B1+ B4 + B6 + B7 ) +11.5 (N2+N3+N5+N8 ) |
| \( B_4N_4H_8^{0} \) | 3.14 eV | 26.0(B1+B4 +B6+B7) | 7.1 (B1+ B4 + B6 + B7 ) +12.1 (N2+N3+N5+N8 ) |
| \( B_2N_2C_4H_8^{2-} \) | 4.055 eV | 30.0(B1+B7) + 4.0 C3+ C5) +15.9 (C4+C6) | 9.0 (B1+B7)+ 19.4 (N2+N8)- 4.7(C3+C5)+ 34.6(C4+C6)+9.1B7 |
| \( BNC_6H_8^{2-} \) | 4.59 eV | 7.0N1+8.6B2 +1.2C3+23.0 (C4+C8)+0.6C5+33.4C 6+0.9C7 | 1242B2-43N1-1580C3+99 C4+4205C5+5610C6+15 207 C7 |
In a ring with “4n+2” electrons, the HOMO and LUMO are related to “n+1” and “n”, but for a ring with “4n” electrons, the HOMO and LUMO are derived from a split degenerate (\(\lambda = n\)). For \(n=4\) or \(B_4N_4H_8\) \(\lambda\) is zero and meanwhile dia-tropic contribution arises from a transition in which \(\Delta\lambda = +1\) and a para-tropic contribution arises from a transition in which \(\Delta\lambda = 0\).

Fig1: Gradient lines map of ELF and current density induced in cyclooctatetraene (C\(_8\)H\(_8^2\)) and boron nitride in cyclooctatetraene (B\(_4\)N\(_4\)H\(_8^2\)) by a perpendicular external magnetic field.
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Calculated by the Cam-B3lyp/ 6-31G**. Anticlockwise circulations are Dia-tropic, clockwise circulations Para-tropic

| % composition of atoms for (HOMO-1) | HOMO/LUMO overlap in whole space | HOMO/HOMO-1 overlap | Molecule          |
|------------------------------------|---------------------------------|---------------------|-------------------|
| 23(N2+N3+N5+N8)                    | 0.314                           | 0.323               | B_4N_4H_8^{2+}    |
| 25(N2+N3+N5+N8)                    | 0.348                           | 0.338               | B_4N_4H_8^{2-}    |
| 26(N2+N3+N5+N8)                    | 0.316                           | 0.344               | B_4N_4H_8^{0}     |
| 0.02B1+15.3N2+28.9C3+5.7C4+28.8C5+5.7C6+0.01B7+15.3N8 | 0.333                           | 0.554               | B_2N_2C_4H_8^{2-} |
| 13.4N1+1.1B2+2.5C3+21.3C4+16.8C5+0.5C6+23.7C7+15.4C8 | 0.152                           | 0.718               | BNC_6H_8^{2-}     |

Therefore for the 4n+2 systems (with higher symmetry) only the HOMO–LUMO transitions are consider (dia-tropic current) and for the “4n” ring (lower symmetry) two forms can be considered , first the HOMO–LUMO transition leads to a para-tropic contribution, and second HOMO–LUMO+1 transitions to the dia-tropic contributions (Table.2)(Monajjemi et al, 2010; Monajjemi and Khaleghian, 2011; Monajjemi, 2012). In Huckel theory it is needed to rearrange the Coulomb and resonance integral parameters as: (1) boron and nitrogen are zero- and two- electron.

Table.3: HOMO and LUMO characteristics in several molecules
Therefore in structure of $B_nN_nH_n$ with the differing electro-negativities of boron and nitrogen a symmetric changing to the Coulomb parameters yield $(\alpha - \gamma \beta)$ and $(\alpha + \gamma \beta)$ energies which $\gamma$ is a correlated parameter in various $B_nN_nH_n$ structures and varied between $0 \leq \gamma < 1$. Solution of the Hückel equation via considering the $\gamma$ parameter with a simple modification gives molecular orbitals $\{\phi\}$ and related energies $\{\varepsilon\}$ from which the consequences for cycle currents can be deduced. Canonical molecular orbitals (Streitwieser, 1961) $(\psi_{\lambda,c})$ are delocalised set with $(\gamma \neq 0)$ and in each position of $\gamma \neq 0$ a linear combinations of these set can be written for orbitals.

In the full symmetrical systems of carbocyclic, the degeneracy of $\psi_{2,c}$ and $\psi_{2,s}$ can be stabilized through several ways such as distortion to $D_{2d}$ and $D_{4h}$ geometries of “clamped”-substituted COT systems. Due to its bond alternation, planar $D_{4h}$ COT keeps delocalized orbitals and the cycle current of the equilateral carbocyclic, as Fig.1 exhibits. In the heterocyclic systems or $(\gamma \neq 0)$ $\psi_{2,c}$ and $\psi_{2,s}$ are bonding and antibonding wave function, respectively, and are belongs to the $B_{1u}$ and $B_{2u}$ symmetric on the setting of $D_{4h}$ within $D_{8h}$. It is notable wave functions $\psi_{2,c}$ and $\psi_{2,s}$, is the HOMO and LUMO, for all amounts of $\gamma$, which is completely localized, the HOMO on the nitrogen atom and the LUMO on the boron atom. Obviously, $\phi_{0,c}$, $\phi_{1,c}$, $\phi_{1,s}$, $\phi_{3,c}$, $\phi_{3,s}$ and $\phi_{4,c}$, become strongly localized on the electronegative atom. In the $\gamma$-1 the nitrogen and boron atoms Obey from Hückel’s population as $1 \pm \frac{1}{2} (\frac{1}{2} + \frac{1}{\sqrt{3}} + \frac{1}{2\sqrt{5}}) \approx 1.66$ and 0.36 electrons, respectively. In the Hückel–London approach the ring current of the eight-membered ring in small amount of $\gamma$, HOMO–LUMO contribution overcome to the bond–bond polarizability. By increasing the $\gamma$ from the planar-constrained of COT (where $\gamma = 0$) to the $B_4N_4H_8$ planer (where $\gamma = 1$), the eight-membered ring has still net para-tropic circulation. The symmetry conclusion to deduct the line currents in $4n \pi$ position includes several steps; firstly $(\gamma \approx 0)$, those currents are overmatched via the HOMO–LUMO transitions amongst small gap energies. This situation $(\Delta \lambda = 0)$ generates an intense, para-tropic intensities.
In other words, the symmetry reasoning for deducing the currents in 4n systems consist of several levels from ($\gamma$ = 0), which the current is under HOMO–LUMO transition with a small energy gap towards $\gamma$ = 1 which, the HOMO–LUMO gap opens, and the intensity of the current falls but remains paramagnetic. Here the separation of HOMO-1 and LUMO as well as HOMO and LUMO+1 increase slowly and the para-tropic or anti-aromatic cycle current is reduced significantly. (Tables 2-4), Current-density maps, ELF and LOL from ab-initio calculations on the $B_nN_nC_{(8-2n)}H_8^{2+}$, are shown in Figures 1-3 and are listed in tables 4,5.

Table 4, 5: continue Localization index (LI), Ring perimeter, Aromatic fluctuation, PDI and PLR for variants of $B_nN_nC_{(8-2n)}H_8$, (n=0,1,2,3 and 4)
For each molecule, the maps indicate total p and s contributions for inducing current densities. As expected, the currents arising from the p electrons are, respectively, strongly dia-tropic in benzene and strongly para-tropic in COT. The currents are dominated by HOMO contributions in both cases. An angular-momentum analysis shows how the symmetry rules account for these features. At each successive energy level, the
quantum (Daudel et al., 1959) number, \( l (=0,1...,N/2) \), increases by one. In a cycle with \( N=4n+2 \) electrons, the HOMO and LUMO correspond to \( l=n \) and \( n+1 \), respectively. It is notable that photo-excited cyclooctatetraene relaxes toward the planar \( D_{8h} \)-symmetric and its structure appears to be identical to the thermal double bond shift transition state. This is the typical \( \pi \)-delocalized structure expected to characterize for a Hückel anti-aromatic \([4n]\) system. As it can be seen in the Table.3 the some electrons are localized and some other is not on the aza-bora-hetero-cycles variants. For benzene the low energies may only involve one delocalized allyl radical and three adjacent unpaired electrons while, in cyclooctatetraene, due to its larger size, a new and more stable tetra-radical-type configuration might be possible.

Fig.2: Density of states for \( \pi \) electrons in the rings

Table.5: Various calculations of charges for \( C_8H_{8^2} \) and \( B_4N_4H_{8^2} \)
|                  | Mayer's valance | Wiberg's bond order |
|------------------|-----------------|---------------------|
| (MK)Merz-Kollman ESP fitting Sum of values=-2 |                  |                    |
| -0.868949, -0.154367 | 3.35, 0.86     | B1-N2: 1.244        |
| 0.430606, 0.092885  | 2.98, 0.90      | B1-N3: 1.244        |
| 0.428573, 0.094883  | 2.98, 0.90      | N2-B4: 1.244        |
| -0.866058, -0.155198| 3.35, 0.86      | B4-N5: 1.244        |
| 0.421720, 0.094818  | 2.98, 0.90      | N5-B7: 1.244        |
| -0.868144, -0.154232| 3.35, 0.86      | B7-N8: 1.244        |
| -0.851509, -0.160690| 3.35, 0.86      | N8-B6: 1.244        |
| 0.417617, 0.098044  | 2.98, 0.90      | B6-N3: 1.244        |

Fig.3: ELF for variants of $B_nN_nC_{(8-2n)}H_8$, ($n=0,1,2,3,4$)

COTs have extended delocalized structures (i.e., identical 1.40 Å $\pi$-bonds and planarity, recalling an aromatics system). Therefore, it can be image that COT as being
stabilized by a kind of aromatic effects which plays against the out-of-plane deformation needed for reaching both the boat and the kink structures due to those motions which break delocalization. The total electrostatic potential for variants of $B_nN_nC_{(8-2n)}H_8$, ($n=0, 1, 2, 4$) are plotted in Fig.4. As it can be seen in the Fig.4 the stable electrostatic potential for those variants are started in positions $1.40 \text{ Å}, 1.45 \text{ Å}, 1.48 \text{ Å}, 1.50 \text{ Å}$ for $CH_8H_8$, $B_4N_4H_8$, $B_2N_2C_4H_8$ and $BNC_6H_8$ which correspond to bond length and they will be ended in the positions around $5.5$ for $CH_8H_8$ and $10.5$ for other variants.

**Fig4:** Total electrostatic potential for variants of $B_nN_nC_{(8-2n)}H_8$, ($n=0, 1, 2, 4$)

**Conclusion**
Current-density maps, ELF and LOL from ab-initio calculations on the $B_nN_nC_{(8-2n)}H_8^2$, are investigated as a novel method for understanding the aromaticity and anti-aromaticity in heterocyclic compounds by this work. For each molecule, the maps indicate total $p$ and $s$ contributions for inducing current densities. As expected, the currents arising from the $p$ electrons are, respectively, strongly dia-tropic in benzene and strongly para-tropic in COT. The currents are dominated by HOMO contributions in both cases. An angular-momentum analysis shows how the symmetry rules account for these features.

Acknowledgment

We are thankful to IAU University for supporting this work and providing the main equipment and mini computing lab for us.

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