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Aromaticity in Polyacene Analogues of Inorganic Ring Compounds

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The aromaticity in the polyacene analogues of several inorganic ring compounds (BN-acenes, CN-acenes, AlN-acenes, BO-acenes, BS-acenes, and Na_6-acenes) is reported here for the first time. Conceptual density functional theory-based reactivity descriptors and the nucleus-independent chemical shift (NICS) values are used in this analysis. The nature of the site selectivity is understood through the charges and the philicities.

Introduction

The concept of aromaticity[1] was introduced into the chemistry literature through the pioneering works of Kekule,[2] Pauling,[3] and Hückel[4] to explain the exceptional stability and extraordinary reactivity pattern of benzene. In comparison to the nonaromatic molecules, the aromatic systems are chemically more stable with appreciable local magnetic field with a cyclic planar structure containing $(4n + 2)$ π- electrons whereas the corresponding antiaromatic systems are more reactive with $4n$ π- electrons.[1]

Although the aromaticity concept was originally restricted to cyclic aromatic molecules, attempts have been made in analyzing the behavior of the corresponding analogues like borazine ("inorganic benzene"). Aromaticity/antiaromaticity in various metal clusters like Al_4^{2-}/ Al_4^{4-} has also become a very important field of research in recent years.[5,6]

Most popular benzene like inorganic aromatic compounds include s-triazine, borazine, $Al_3N_3H_6$, boraxine, Na_6, etc. with planar D_{3h} (D_{6h}) symmetry. Because of their similar connectivity patterns[7] as that of benzene, these molecules are expected to show aromaticity.[1,8] Several experiments authenticate their aromatic behavior, albeit with some qualitative differences like more electron localization around the more electronegative atoms and preference of addition over substitution reactions. Aromaticity in the polyacene analogues of borazine is also studied.[9]

Some of these inorganic benzene compounds (only single ring) are studied by Fowler et al.[10] using valence bond and ring current based description of aromaticity. Although Phukan et al.[9] considered compounds like borazine to be aromatic on the basis of resonance energy, nucleus-independent chemical shift (NICS), and molecular electrostatic potential values and similar conclusion obtained by Gimarc and Trinajstic[7] through molecular orbital calculations, Fowler et al.[10] are of the opinion that borazine is nonaromatic whereas N_6 is aromatic, which is again shown to be[7] unknown due exceptional stability of N_2. Moreover, the optimized structure[10] of N_6 contains two imaginary frequencies and hence is not the minimum energy structure on the potential energy surface.

Understanding chemical reactivity and stability is the essence of chemical education including that of aromatic systems. Popular concepts like electronegativity,[11] hardness,[12,13] electrophilicity,[14,15] etc. have been introduced for this purpose. Quantitative definitions and theoretical bases for these otherwise qualitative concepts have been provided by conceptual density functional theory (DFT).[16,17] These concepts are often better appreciated in terms of various associated electronic structure principles. Sanderson's electronegativity equalization principle[18] states that, "During an electron-transfer process in a chemical reaction, electrons flow from a species of lower electronegativity (higher chemical potential) to one with higher electronegativity (lower chemical potential) until the electronegativities get equalized to a value approximately equal to the geometric mean of the electronegativities of the isolated species." Pearson introduced the hard−soft-acid−base (HSAB) principle,[19,20] which in general can describe a variety of acid−base reactions. This principle is stated as, "Hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases for both their thermodynamic and kinetic properties." The

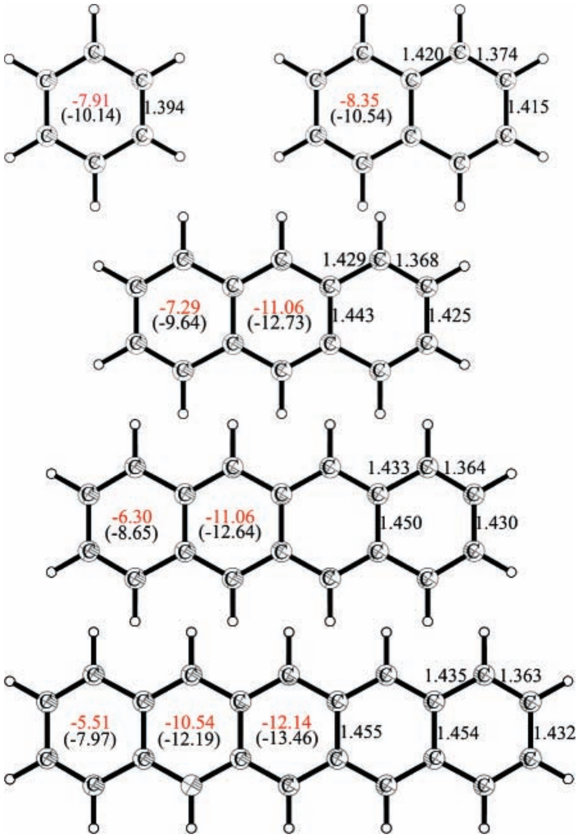

Figure 1. Minimized geometries of the polyacenes, $C_{4n+2}H_{2n+4}$ ($n = 1-5$), with their NICS (0) (in red color) and NICS (1) (in bracket) at the center of the rings.

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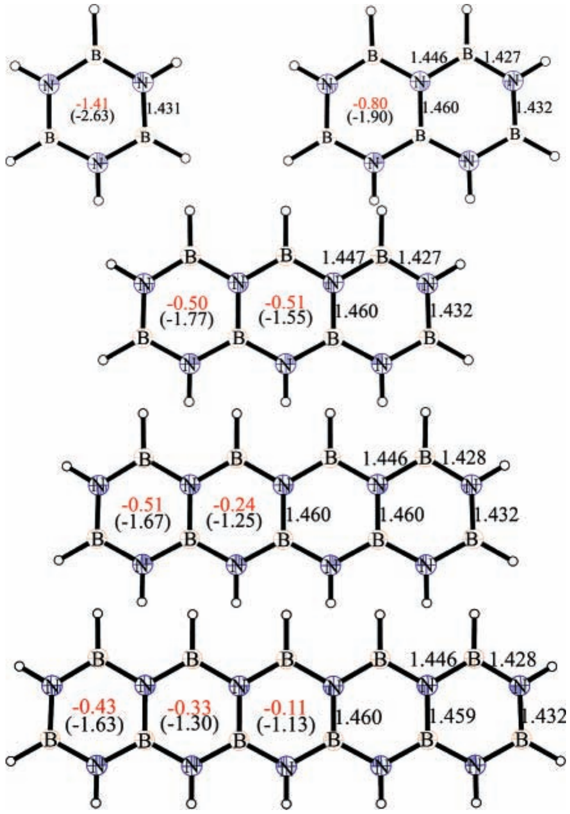


Figure 2. Minimized geometries of the BN-acenes, $(BN)_{2n+1}H_{2n+4}$ ($n = 1-5$) with their NICS (0) (in red color) and NICS (1) (in bracket) at the center of the rings.

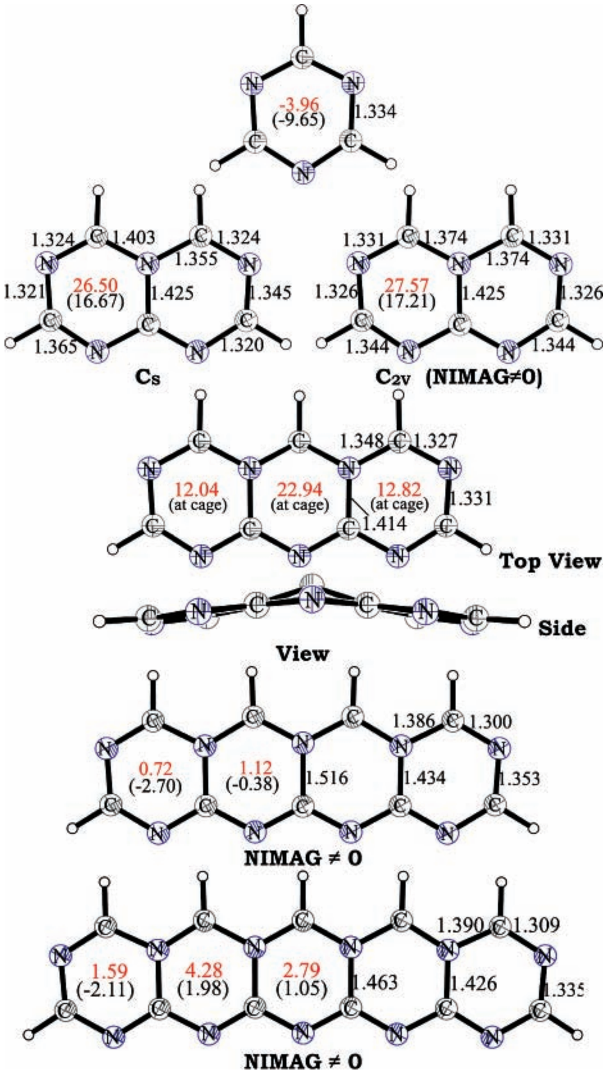


Figure 3. Minimized geometries of the CN-acenes, $(CN)_{2n+1}H_{n+2}$ ($n = 1-5$) with their NICS(0) (in red color) and NICS (1) (in bracket) at the center of the rings.

maximum hardness principle (MHP) is stated[21,22] as "There seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible." The minimum polarizability principle (MPP) is stated as,[23] "The natural direction of evolution of any system is toward a state of minimum polarizability." The minimum electrophilicity principle[24] is stated as "Electrophilicity will be a minimum (maximum) when both chemical potential and hardness are maxima (minima)." In this paper, we analyze the aromaticity/antiaromaticity of polyacene analogues of various inorganic ring compounds using these conceptual DFT-based reactivity descriptors.

Theoretical Background. For an N-electron system with total energy E and external potential $v(\vec{r})$, the chemical potential[25] (μ, negative of electronegativity[11] (χ)) and the hardness[12,13] (η) are respectively defined by the following first-order and second-order derivatives:

$$-\chi = \mu = \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \tag{1}$$

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} \tag{2}$$

A finite difference approximation to the above definitions leads to,[12,25,26]

$$\chi = \frac{I + A}{2}$$

and

$$\eta = \frac{I - A}{2} \tag{3}$$

where I and A are the ionization potential and the electron affinity respectively. Above relations may be further simplified using Koopmans' approximation,[27] in terms of the highest occupied ($\in_{\mathrm{HOMO}}$) and the lowest unoccupied ($\in_{\mathrm{LUMO}}$) molecular orbital energies as,

$$\chi = -\frac{\in_{\mathrm{HOMO}} + \in_{\mathrm{LUMO}}}{2}$$

and

$$\eta = \frac{\in_{\mathrm{LUMO}} - \in_{\mathrm{HOMO}}}{2} \tag{4}$$

Electrophilicity index (ω) is defined as,[14]

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{5}$$

and a local variant of this quantity, condensed to the atom k in a molecule, is given by,[28]

$$\omega_{\mathrm{k}}^{\alpha} = \omega . f_{\mathrm{k}}^{\alpha} \tag{6}$$

where f_{k}^{α} is the condensed Fukui function and α (= +, −, 0) refers to nucleophilic, electrophilic, and radical attacks respectively. The condensed Fukui functions are calculated in terms

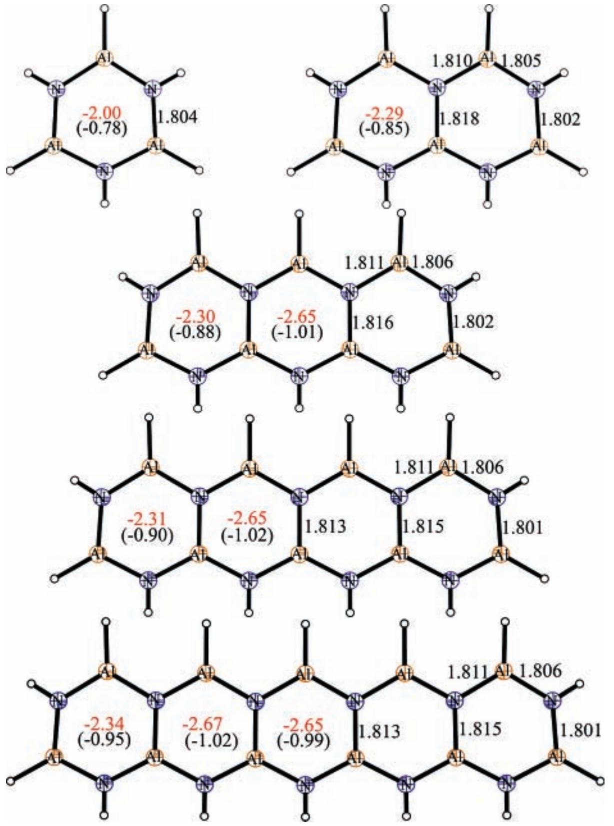


Figure 4. Minimized geometries of the AlN-acenes, $(AlN)_{2n+1}H_{2n+4}$ ($n = 1-5$) with their NICS (0) (in red color) and NICS (1) (in bracket) at the center of the rings.

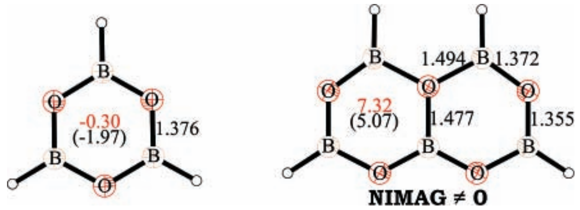


Figure 5. Minimized geometries of the BO-acenes, $(BO)_{2n+1}H_{n+2}$ ($n = 1-2$) with their NICS(0) (in red color) and NICS (1) (in bracket) at the center of the rings.

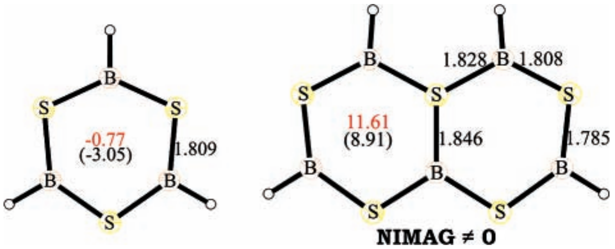


Figure 6. Minimized geometries of the BS-acenes, $(BS)_{2n+1}H_{n+2}$ ($n = 1-2$) with their NICS(0) (in red color) and NICS (1) (in bracket) at the center of the rings.

of the associated electronic population q_k of atom k in a molecule, as[29]

$$f_k^+ = q_k(N+1) - q_k(N) \text{ for nucleophilic attack} \quad (7a)$$

$$f_k^- = q_k(N) - q_k(N-1) \text{ for electrophilic attack} \quad (7b)$$

$$f_k^o = [q_k(N+1) - q_k(N-1)]/2 \text{ for radical attack} \quad (7c)$$

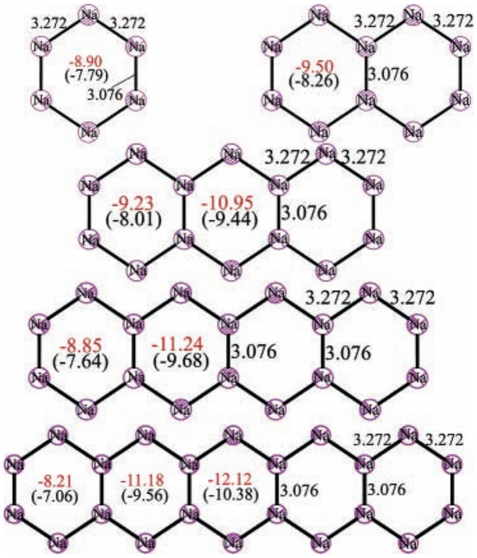


Figure 7. Experimental geometries without the metalloligands[33] of the Na$_6$-acenes, Na_{4n+2} ($n = 1-5$), with their NICS (0) (in red color) and NICS (1) (in bracket) at the center of the rings.

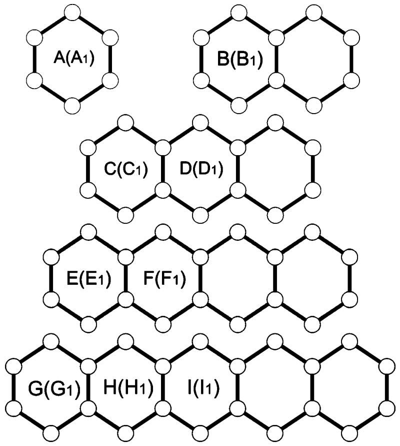


Figure 8. Template providing the NICS(0)(NICS(1)) values at the ring center and 1 Å above the plane respectively of all the polyacenes. Please see Table 6 for the actual values.

The electric dipole polarizability is a measure of the linear response of the electron density in the presence of an infinitesimal electric field F and it represents a second-order variation in energy

$$\alpha_{a,b} = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right)$$

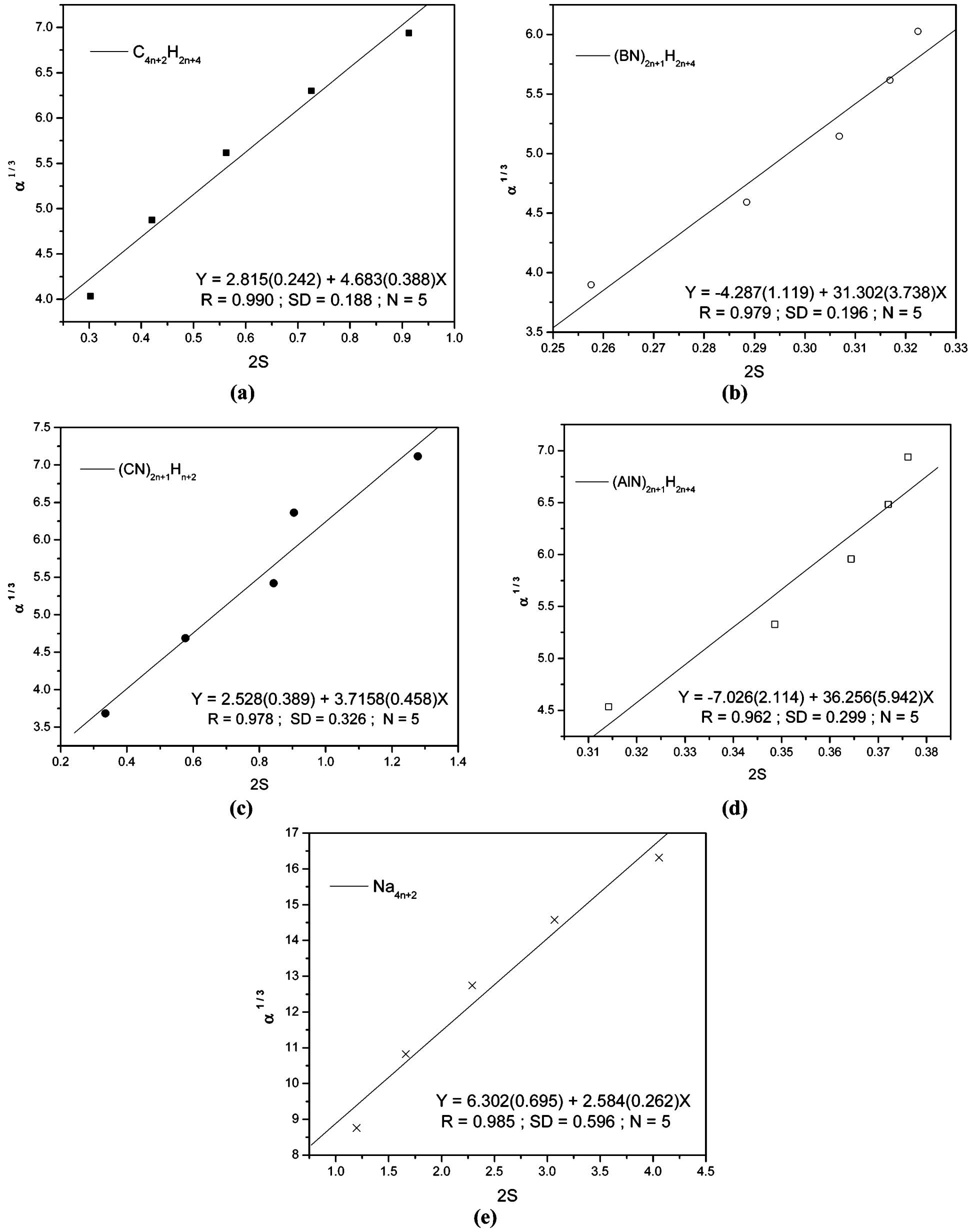
$$a,b = x,y,z \quad (8)$$

The polarizability α is calculated as the mean value as given in the following equation

$$\langle\alpha\rangle = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3} \quad (9)$$

The nucleus-independent chemical shift[30] values are calculated at the ring center, NICS(0), and 1 Å above the ring, NICS(1). NICS is obtained[30] as the "absolute magnetic shieldings, computed at *ring centers* (nonweighted mean of the heavy atom coordinates) with available quantum mechanics programs,[31] as a new aromaticity/antiaromaticity criterion."

In the present work, we study the nature of the reactivity descriptors χ, η, and ω and the associated electronic structure principles in understanding the possible aromatic/antiaromatic



(a) (b) (c) (d) (e)

Figure 9. $\alpha^{1/3}$ vs $2S$ of (a) $C_{4n+2}H_{2n+4}$, (b) $(BN)_{2n+1}H_{2n+4}$, (c) $(CN)_{2n+1}H_{n+2}$, (d) $(AlN)_{2n+1}H_{2n+4}$, and (e) Na_{4n+2} ($n = 1-5$) clusters.

TABLE 1: Energy (*E*, hartree) and Energy(Ring)$^{-1}$ (hartree) Values of the Polyacenes and their Inorganic Analogues

n	$C_{4n+2}H_{2n+4}$	$(BN)_{2n+1}H_{2n+4}$	$(CN)_{2n+1}H_{n+2}$	$(AlN)_{2n+1}H_{2n+4}$	$(BO)_{2n+1}H_{n+2}$	$(BS)_{2n+1}H_{n+2}$	Na_{4n+2}
				Energy (*E*, hartree)			
1	−232.3007	−242.7343	−280.4352	−895.4968	−302.3982	−1271.1736	−973.8179
2	−385.9749	−403.3926	−466.7487	−1491.3407	−503.3016	−2117.9461	−1623.0316
3	−539.6428	−564.0503	−653.0886	−2087.1845	–	–	−2272.2440
4	−693.3084	−724.7081	−839.4113	−2683.0281	–	–	−2921.4560
5	−846.9727	−885.3659	−1025.7320	−3278.8718	–	–	−3570.5125
				Energy(Ring)$^{-1}$ (hartree)			
1	−232.3007	−242.7343	−280.4352	−895.4968	−302.3982	−1271.1736	−973.8179
2	−192.9875	−201.6963	−233.3744	−745.6704	−251.6508	−1058.9730	−811.5158
3	−179.8810	−188.0168	−217.6962	−695.7282	–	–	−757.4147
4	−173.3271	−181.1770	−209.8528	−670.7570	–	–	−730.3640
5	−169.3945	−177.0732	−205.1465	−655.7744	–	–	−714.1025

behavior of $C_{4n+2}H_{2n+4}$, $(BN)_{2n+1}H_{2n+4}$, $(CN)_{2n+1}H_{n+2}$, $(AlN)_{2n+1}H_{2n+4}$ and Na_{4n+2}: $n = 1-5$; $(BO)_{2n+1}H_{n+2}$ and $(BS)_{2n+1}H_{n+2}$: $n = 1,2$. Polarizability and NICS (0,1) are also analyzed for gaining additional insights. Local reactivity trends and the site selectivity are analyzed using the atomic charges (q_k) and the philicities (ω_k^α).

Computational Details

The geometries of all the polyacenes and their BN-, CN-, AlN-, BO-, and BS- analogues are minimized at the Becke's[32] three-parameter hybrid functional (B3) with the nonlocal correlation of Lee−Yang−Parr (LYP)[32] level of theory and the 6-311+G* basis set using GAUSSIAN 03[31] suite of program.

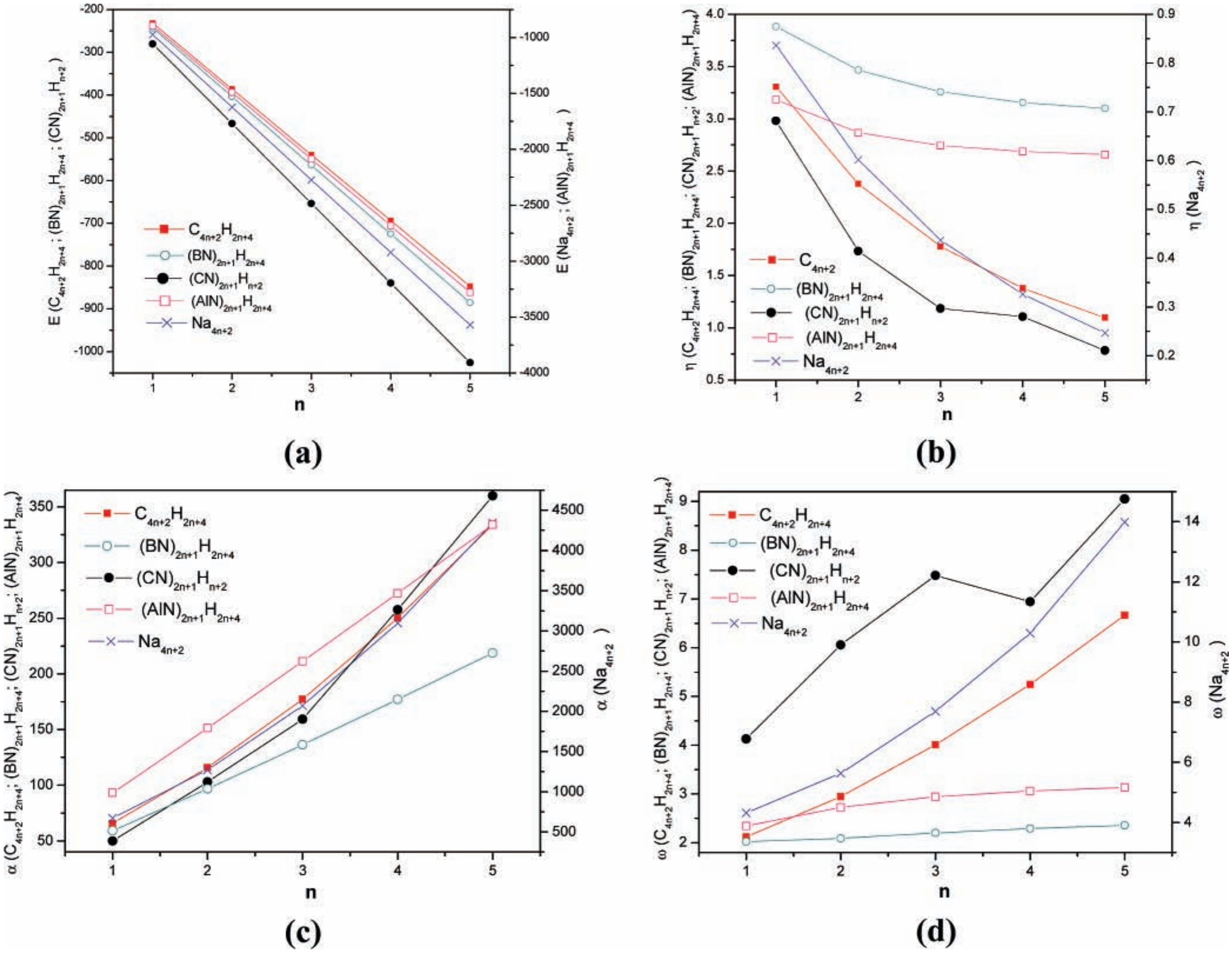


Figure 10. (a) Energy (E, hartree), (b) hardness (η, eV), (c) polarizability (α, a.u.), and (d) electrophilicity (ω, eV) profiles of $C_{4n+2}H_{2n+4}$, $(BN)_{2n+1}H_{2n+4}$, $(CN)_{2n+1}H_{n+2}$, $(AlN)_{2n+1}H_{2n+4}$, and Na_{4n+2}, $n = 1-5$.

TABLE 2: Hardness (η, eV) and Hardness(Ring)$^{-1}$ (eV) Values of the Polyacenes and their Inorganic Analogues

n	$C_{4n+2}H_{2n+4}$	$(BN)_{2n+1}H_{2n+4}$	$(CN)_{2n+1}H_{n+2}$	$(AlN)_{2n+1}H_{2n+4}$	$(BO)_{2n+1}H_{n+2}$	$(BS)_{2n+1}H_{n+2}$	Na_{4n+2}
			Hardness (η, eV)				
1	3.3058	3.8821	2.9816	3.1829	4.2572	3.0077	0.8362
2	2.3787	3.4669	1.7336	2.8686	2.4407	1.6447	0.6018
3	1.7776	3.2588	1.1864	2.7443	–	–	0.4367
4	1.3780	3.1553	1.1059	2.6877	–	–	0.3260
5	1.0957	3.1011	0.7823	2.6584	–	–	0.2465
			Hardness(Ring)$^{-1}$ (eV)				
1	3.3058	3.8821	2.9816	3.1829	4.2572	3.0077	0.8362
2	1.1893	1.7334	0.8668	1.4343	1.2203	0.8224	0.3009
3	0.5925	1.0863	0.3955	0.9148	–	–	0.1456
4	0.3445	0.7888	0.2765	0.6719	–	–	0.0815
5	0.2191	0.6202	0.1565	0.5317	–	–	0.0493

Harmonic vibrational frequency analyses are also performed at the same level of theory to check whether the obtained structure is a minimum on the potential energy surface. For $C_5N_5H_4$, two different geometries with C_S (NIMAG = 0) and C_{2V} (NIMAG ≠ 0) are obtained. Single point calculations at the same level of theory on the experimental geometries[33] of polyacene analogues of Na_6 are performed for the Na_6 units without the ligands. The crystal structure of $[Na_2MoO_3L(H_2O)_2]_n$ {L = iminodiacetate} is used as the input.[33] We use only the $(Na_6)_n$ unit for the present work. Geometry optimization of the Na_6-acenes without the metalloligand may not yield the planar structure. The Mulliken charges are calculated using the GAUSSIAN 03[31] program. The Fukui functions using Hirschfeld population analysis scheme (HPA) are calculated using the DMol^3 program[34] package at the BLYP level of theory with the DND basis set.

Results and Discussion

The geometrical parameters, energies and other DFT descriptors are provided in Figures 1–6 and Tables 1–5. Experimental geometries of the Na-acenes[33] (without the metalloligand,

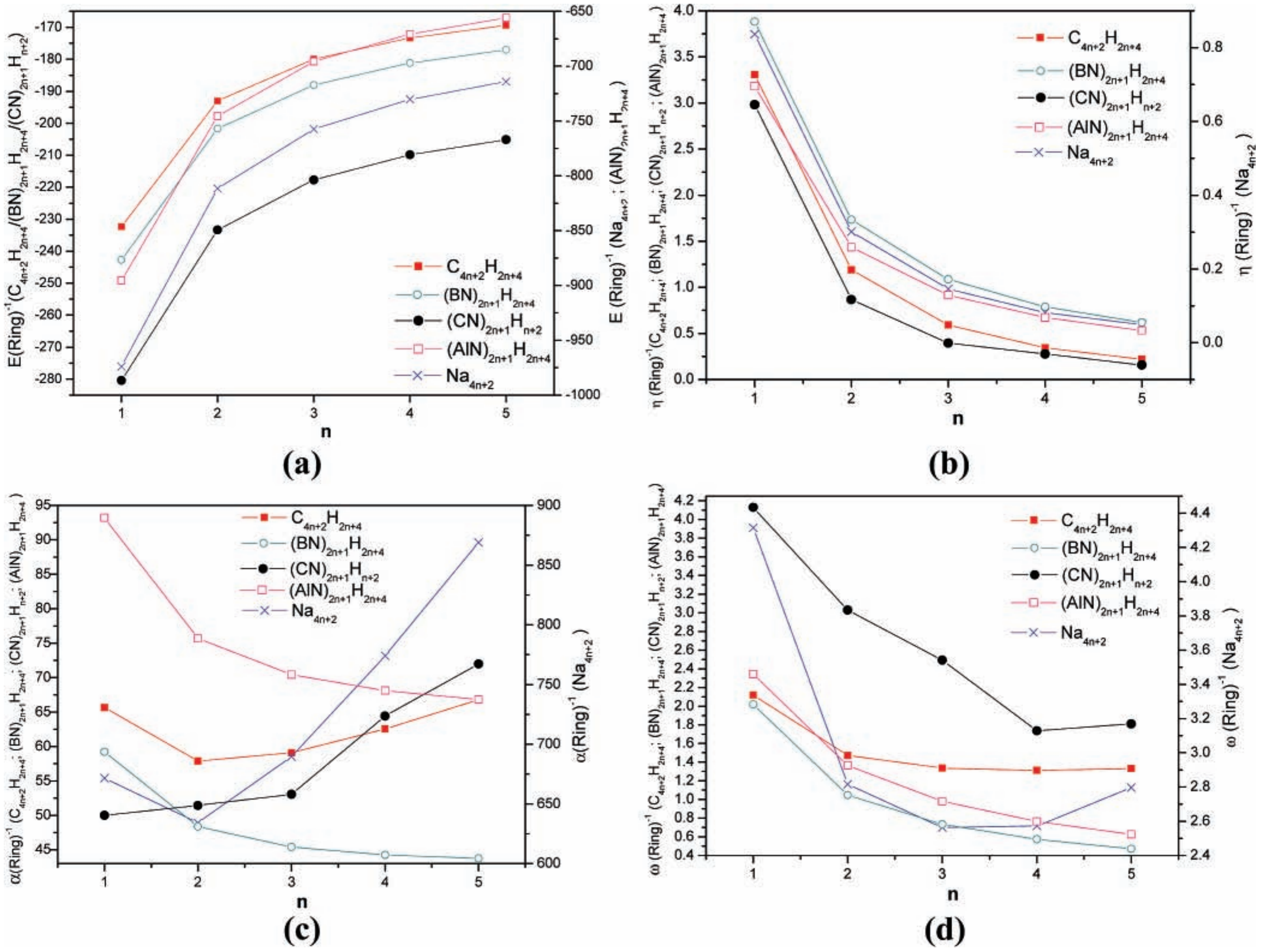


Figure 11. (a) Energy (*E*, hartree), (b) hardness (*η*, eV), (c) polarizability (α, a.u.), and (d) electrophilicity (*ω*, eV) profiles per unit ring of $C_{4n+2}H_{2n+4}$, $(BN)_{2n+1}H_{2n+4}$, $(CN)_{2n+1}H_{n+2}$, $(AlN)_{2n+1}H_{2n+4}$, and Na_{4n+2}, $n = 1-5$.

TABLE 3: Chemical Potential (*μ*, eV) and Chemical Potential(Ring)$^{-1}$ (eV) Values of the Polyacenes and their Inorganic Analogues

n	$C_{4n+2}H_{2n+4}$	$(BN)_{2n+1}H_{2n+4}$	$(CN)_{2n+1}H_{n+2}$	$(AlN)_{2n+1}H_{2n+4}$	$(BO)_{2n+1}H_{n+2}$	$(BS)_{2n+1}H_{n+2}$	Na_{4n+2}
				Chemical Potential (*μ*, eV)			
1	−3.7431	−3.9605	−4.9628	−3.8616	−5.2050	−5.3117	−2.6866
2	−3.7422	−3.8089	−4.5836	−3.9571	−3.9861	−4.4631	−2.6035
3	−3.7752	−3.7886	−4.2131	−4.0186	−	−	−2.5919
4	−3.8020	−3.8024	−3.9188	−4.0569	−	−	−2.5903
5	−3.8214	−3.8236	−3.7631	−4.0813	−	−	−2.6259
				Chemical Potential(Ring)$^{-1}$ (eV)			
1	−3.7431	−3.9605	−4.9628	−3.8616	−5.2050	−5.3117	−2.6866
2	−1.8711	−1.9045	−2.2918	−1.9785	−1.9931	−2.2316	−1.3017
3	−1.2584	−1.2629	−1.4044	−1.3395	−	−	−0.8640
4	−0.9505	−0.9506	−0.9797	−1.0142	−	−	−0.6476
5	−0.7643	−0.7647	−0.7526	−0.8163	−	−	−0.5252

$[LMoO_3(H_2O)_2]^{2-}$ {L = iminodiacetate}) are provided in Figure 7. In most cases, the molecules are planar and the expected symmetry is obtained. In general, for all the systems studied, the systems become less energetic, softer, more polarizable, and more electrophilic as the number of rings increases. Figure 8 contains a generic template for the NICS values, which are explicitly provided in Figures 1−7 and Table 6. All the single ring ($n = 1$) compounds (C_6H_6, $B_3N_3H_6$, $C_3N_3H_3$, $Al_3N_3H_6$, $B_3O_3H_3$, $B_3S_3H_3$, and Na_6) reveal negative NICS(0) and NICS(1) values and hence are aromatic. Although the negative signs for NICS[9,30] of BN-, CN-, BO-, BS-, and AlN-acenes suggest those molecules to be aromatic, their small magnitude would render them to possess essentially nonaromatic behavior. Like polyacenes, all the borazine analogues are aromatic, but as shown earlier,[9] the inner rings of borazine analogues are less aromatic than the corresponding outer rings unlike in polyacenes.[35] However, a perfect resemblance with the polyacene aromatic behavior is observed in the related Na_6 analogues. Most of the CN-acenes and BO- or BS-naphthalene are antiaromatic. Note that the structures with nonzero imaginary frequencies as obtained in a couple of cases do not correspond to potential energy minima (cf. Table 7).

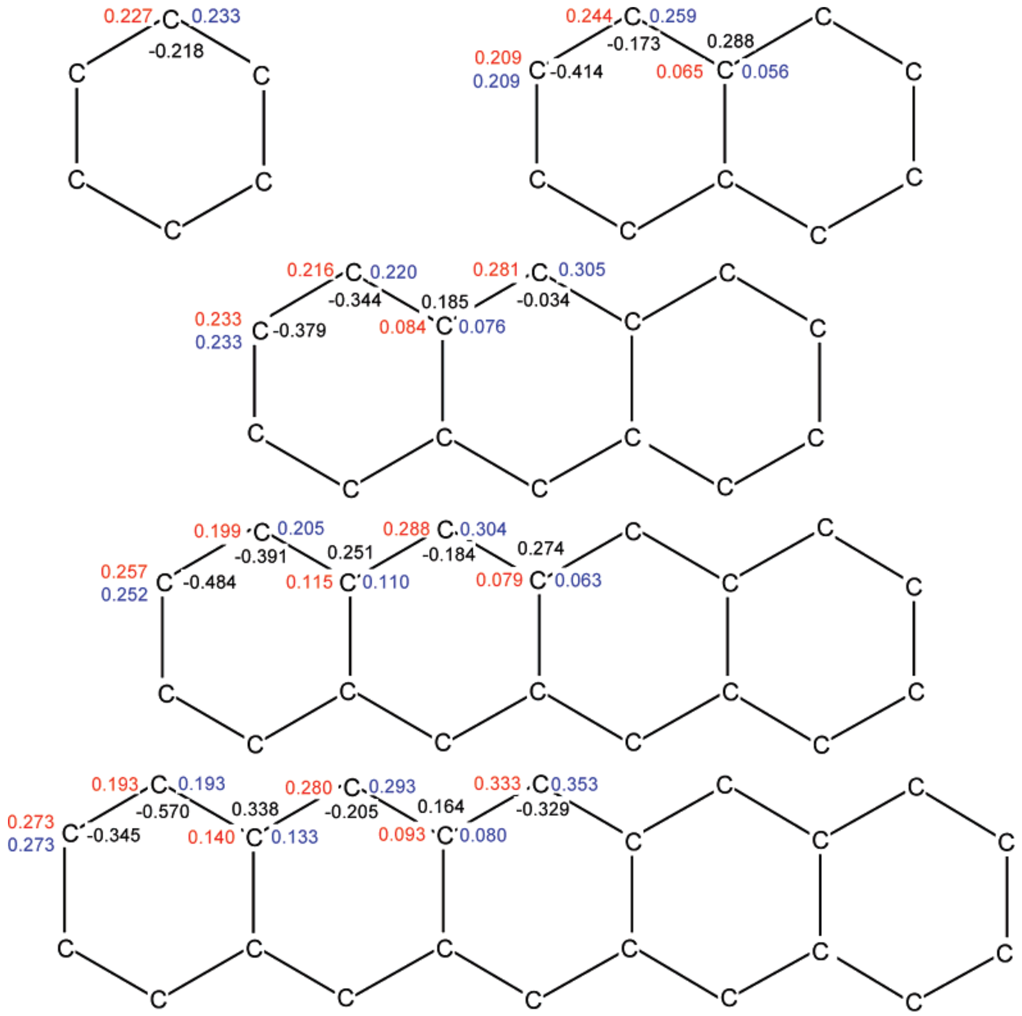


Figure 12. Mulliken charges (black) and the philicities due to nucleophilic (red) and electrophilic (blue) attacks at the different atomic sites of the polyacenes, $C_{4n+2}H_{2n+4}$ (n = 1−5).

TABLE 4: Electrophilicity (ω, eV) and Electrophilicity(Ring)$^{-1}$ (eV) Values of the Polyacenes and their Inorganic Analogues

n	$C_{4n+2}H_{2n+4}$	$(BN)_{2n+1}H_{2n+4}$	$(CN)_{2n+1}H_{n+2}$	$(AlN)_{2n+1}H_{2n+4}$	$(BO)_{2n+1}H_{n+2}$	$(BS)_{2n+1}H_{n+2}$	Na_{4n+2}
				Electrophilicity (ω, eV)			
1	2.1191	2.0202	4.1303	2.3425	3.1819	4.6903	4.3158
2	2.9437	2.0924	6.0595	2.7293	3.2551	6.0556	5.6316
3	4.0088	2.2023	7.4807	2.9423	–	–	7.6909
4	5.2450	2.2911	6.9436	3.0619	–	–	10.2910
5	6.6641	2.3572	9.0503	3.1329	–	–	13.9850
				Electrophilicity(Ring)$^{-1}$ (eV)			
1	2.1191	2.0202	4.1303	2.3425	3.1819	4.6903	4.3158
2	1.4719	1.0462	3.0297	1.3646	1.6276	3.0278	2.8158
3	1.3363	0.7341	2.4936	0.9808	–	–	2.5636
4	1.3112	0.5728	1.7359	0.7655	–	–	2.5727
5	1.3328	0.4714	1.8101	0.6266	–	–	2.7969

Table 8 delineates that ionization potential (I), electron affinity (A), hardness (η), chemical potential (μ), electrophilicity (ω), energy (E), and polarizability (α) can be expressed as quadratic functions of n (the number of rings in various polyacene analogues). Figure 9 confirms the linear behavior between $\alpha^{1/3}$ and $2S$, where S is the softness, given by $1/(2\eta)$, as expected.[36]

Although energy and hardness decrease and polarizability and electrophilicity increase with an increase in n (Figure 10), an analysis of the behavior of energy, hardness, and polarizability values per ring reveals that with an increase in n, the energy/ring value increases, whereas the hardness/ring value decreases, as expected (Figure 11) from the maximum hardness principle. The polarizability/ring also increases in most cases (except BN- and AlN-acenes) as per the minimum polarizability principle.[23] The minimum electrophilicity is not expected to hold good as the magnitude of the chemical potential does not increase monotonically with n.[24] Striking resemblance (Figures 1−11) among the behavior of various DFT-based reactivity descriptors and the associated electronic structure principles for polyacenes and their inorganic analogues highlight the possible aromatic/antiaromatic characteristics in the latter, complementing the

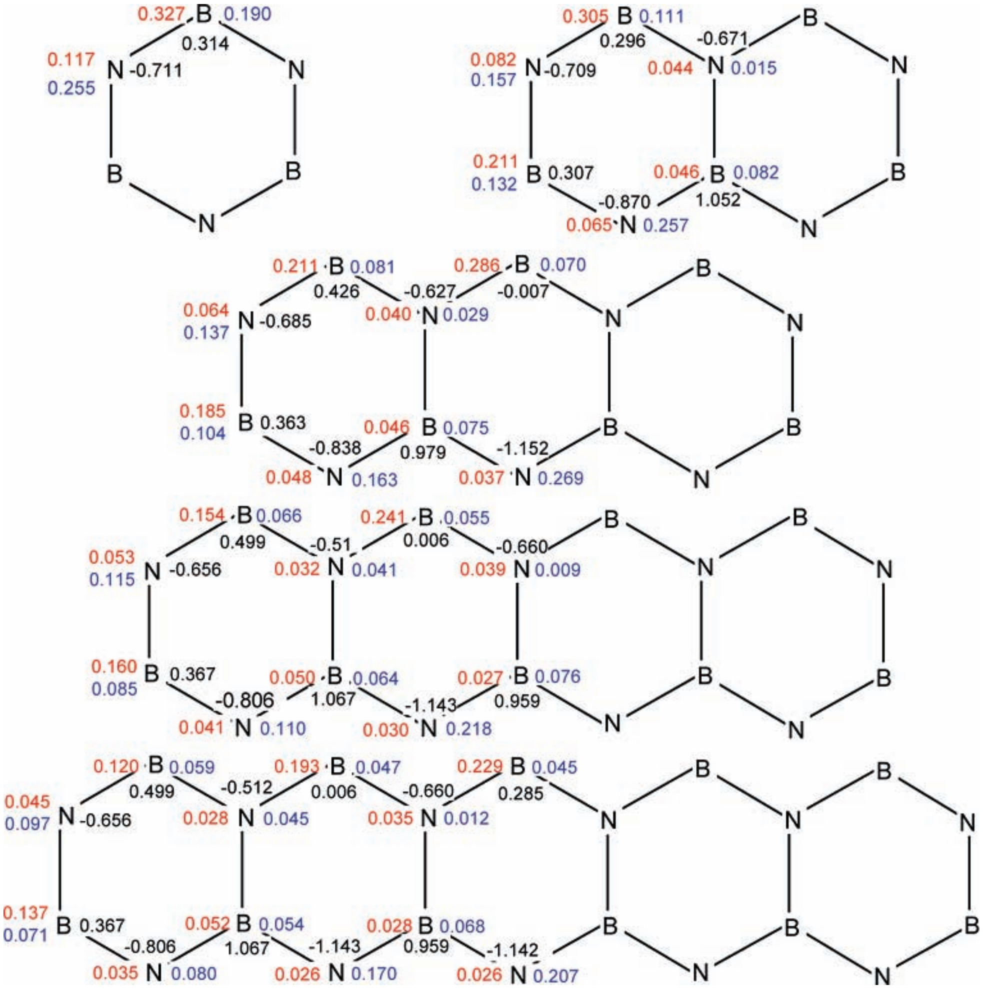


Figure 13. Mulliken charges (black) and the philicities due to nucleophilic (red) and electrophilic (blue) attacks at the different atomic sites of the BN-acenes, $(BN)_{2n+1}H_{2n+4}$ ($n = 1-5$).

TABLE 5: Polarizability (α, a.u.) and Polarizability(Ring)$^{-1}$(a.u.) Values of the Polyacenes and their Inorganic Analogues

n	$C_{4n+2}H_{2n+4}$	$(BN)_{2n+1}H_{2n+4}$	$(CN)_{2n+1}H_{n+2}$	$(AlN)_{2n+1}H_{2n+4}$	$(BO)_{2n+1}H_{n+2}$	$(BS)_{2n+1}H_{n+2}$	Na_{4n+2}
			Polarizability (α, a.u.)				
1	65.6430	59.2223	50.0013	93.1900	43.3970	95.2623	671.6630
2	115.7970	96.7543	102.8640	151.3423	155.8937	223.8090	1268.1380
3	177.2717	136.2410	159.2020	211.3143	−	−	2068.6107
4	250.2087	177.0683	257.6170	272.4417	−	−	3095.7397
5	333.9313	218.7463	359.9870	334.0597	−	−	4345.0563
			Polarizability(Ring)$^{-1}$ (a.u.)				
1	65.6430	59.2223	50.0013	93.1900	43.3970	95.2623	671.6630
2	57.8985	48.3772	51.4320	75.6712	77.9468	111.9045	634.0690
3	59.0906	45.4137	53.0673	70.4381	−	−	689.5369
4	62.5522	44.2671	64.4042	68.1104	−	−	773.9349
5	66.7863	43.7493	71.9974	66.8119	−	−	869.0113

corresponding NICS analysis. Deviations whatsoever are reported here and were similar to that observed[9] in the resonance energy per π electron for polyacenes and BN-acenes. It has also been shown[37,38] that the DFT-based reactivity descriptors, viz. hardness (η), polarizability (α), electrophilicity (ω), etc., are very useful in predicting the aromatic/antiaromatic behavior of the planar, cyclic organic molecules[37,38] as well as all-metal aluminum clusters[38] with respect to their localized/open chain reference structures.

Atomic charges obtained using the Mulliken Population Analysis (MPA) scheme for various systems studied are provided in Figures 12−18. The charges are expected to be the right indicators for possible electrostatic interactions.[39] Sites with large negative (positive) charge would be preferred sites for the attack of a positively (negatively) charged species or a hard electrophile (nucleophile). For $C_{4n+2}H_{2n+4}$ systems, C-atoms in the terminal rings, except for those that are shared by two rings, contain negative charges. For benzene, all the C-atoms are equally reactive due to symmetry. For $(BN)_{2n+1}H_{2n+4}$ systems, B-centers are positively charged and N-centers are negatively charged as expected from their electronegativity difference and would properly explain the addition product when reacted with a system like HCl. Positive charges lie on Al, B, and S whereas negative charges lie on N, O, and B for the

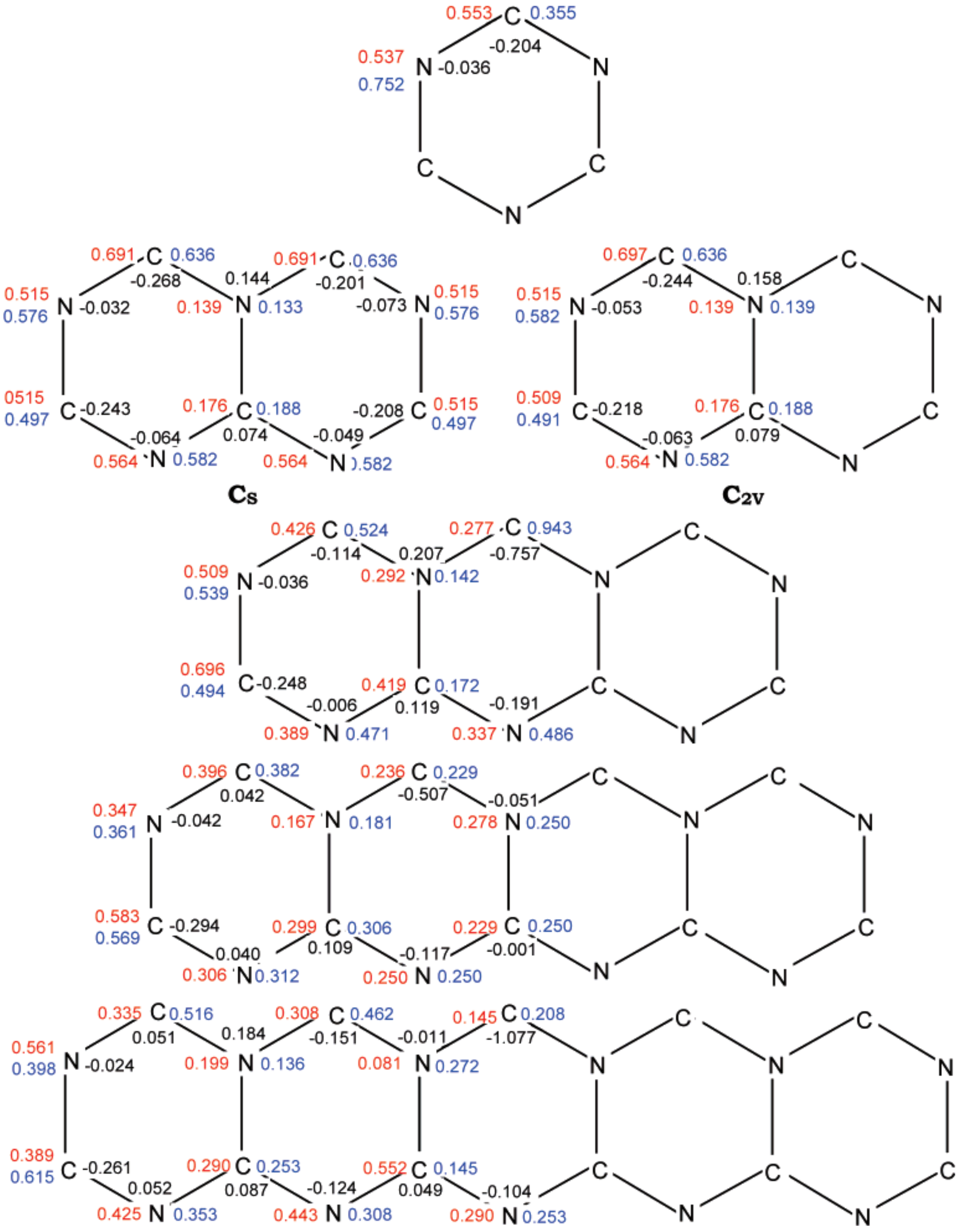


Figure 14. Mulliken charges (black) and the philicities due to nucleophilic (red) and electrophilic (blue) attacks at the different atomic sites of the CN-acenes, $(CN)_{2n+1}H_{n+2}$ ($n = 1-5$).

$(AlN)_{2n+1}H_{2n+4}$, $(BO)_{2n+1}H_{n+2}$, and $(BS)_{2n+1}H_{n+2}$ systems, respectively. In general, atoms with negative charges are more reactive for the outer rings whereas those with positive charges are more reactive for the inner rings. This fact reveals in a peculiar way in the $(CN)_{2n+1}H_{n+2}$ systems where in general both C and N atoms carry negative charges on the outer rings (especially along the periphery) and positive charges in the inner rings. In the Na_{4n+2} system, some Na atoms are positively charged and some are negatively charged determined by the metalloligand surrounding it.

Because hard−hard interactions are charge controlled and the process is ionic in nature, the charge is considered to be the right descriptor.[39] However, soft−soft interactions are frontier controlled[39] to provide essentially covalent bonding. For this reason, philicity patterns are also provided in Figures 12−18. To have a better understanding of the intermolecular reactivity trends, philicity is preferred[28,40] over Fukui functions. Necessary Fukui functions are calculated using a Hirschfeld population analysis (HPA)[41] scheme to minimize the number of negative Fukui functions albeit with the problems related to HPA.[42] It may, however, be noted that philicity and Fukui function will provide identical intramolecular reactivity trends.[40] In polyacenes, $C_{4n+2}H_{2n+4}$, C-atoms common to two rings are less reactive than those belonging to one ring. The C-atom of the latter type in the inner rings are becoming more reactive (slightly more for the electrophilic attack). In the BN-acenes, B-centers are suitable for nucleophilic attack whereas N-centers are suitable for electrophilic attack. There are two competing factors operative here. As the size increases, the system becomes softer. However, individual centers are becoming harder as the total number of probable attacking sites increases in this process. Therefore, the BN-acenes become globally softer but locally harder as the size increases. This fact requires a closer scrutiny. Other reactivity patterns are similar to that in polyacenes.

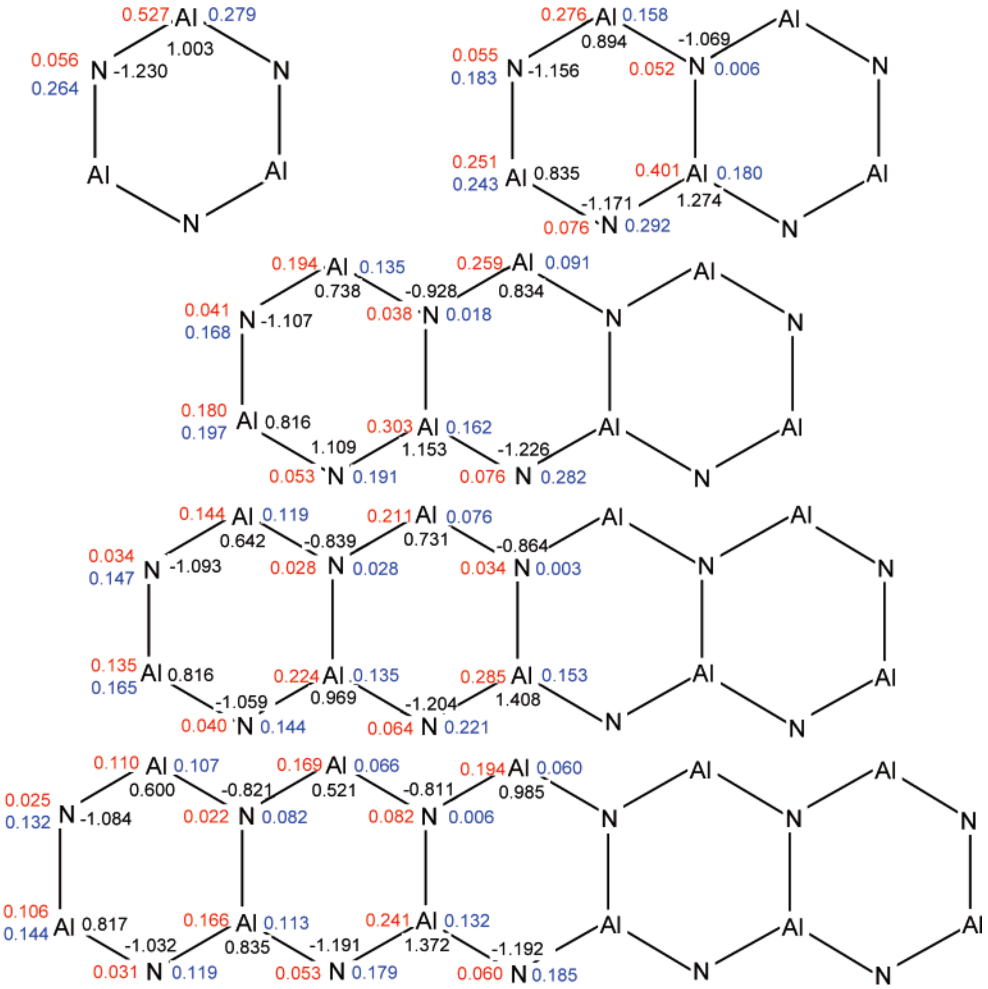


Figure 15. Mulliken charges (black) and the philicities due to nucleophilic (red) and electrophilic (blue) attacks at the different atomic sites of the AlN-acenes, $(AlN)_{2n+1}H_{2n+4}$ ($n = 1-5$).

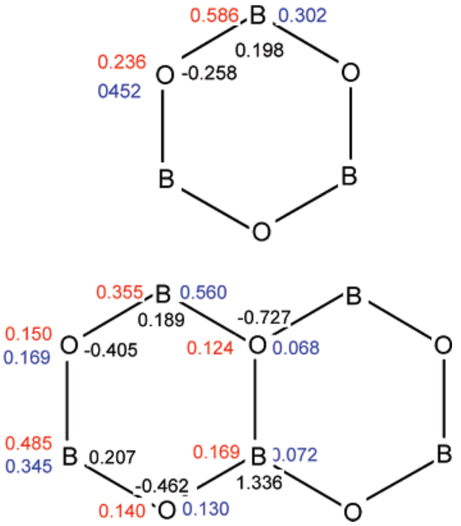


Figure 16. Mulliken charges (black) and the philicities due to nucleophilic (red) and electrophilic (blue) attacks at the different atomic sites of the BO-acenes, $(BO)_{2n+1}H_{n+2}$ ($n = 1-2$).

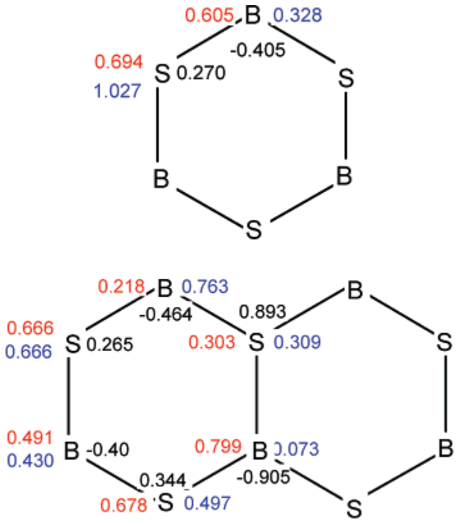


Figure 17. Mulliken charges (black) and the philicities due to nucleophilic (red) and electrophilic (blue) attacks at the different atomic sites of the BS-acenes, $(BS)_{2n+1}H_{n+2}$ ($n = 1-2$).

In the case of the CN-acenes, on an average C-atoms are marginally more preferable for the nucleophilic attack than the electrophilic attack whereas N-atoms are marginally more preferable for the electrophilic attack but for the largest system studied. This type of erratic behavior appears to stem from the nonzero-NIMAG structures. For AlN-acenes, Al-atoms are in general the preferable sites for the nucleophilic attack whereas N-atoms are the preferable sites for the electrophilic attack. For $n = 1$, in both BO- and BS-acenes, B-atoms are the preferable sites for the nucleophilic attack and O- or S-atoms

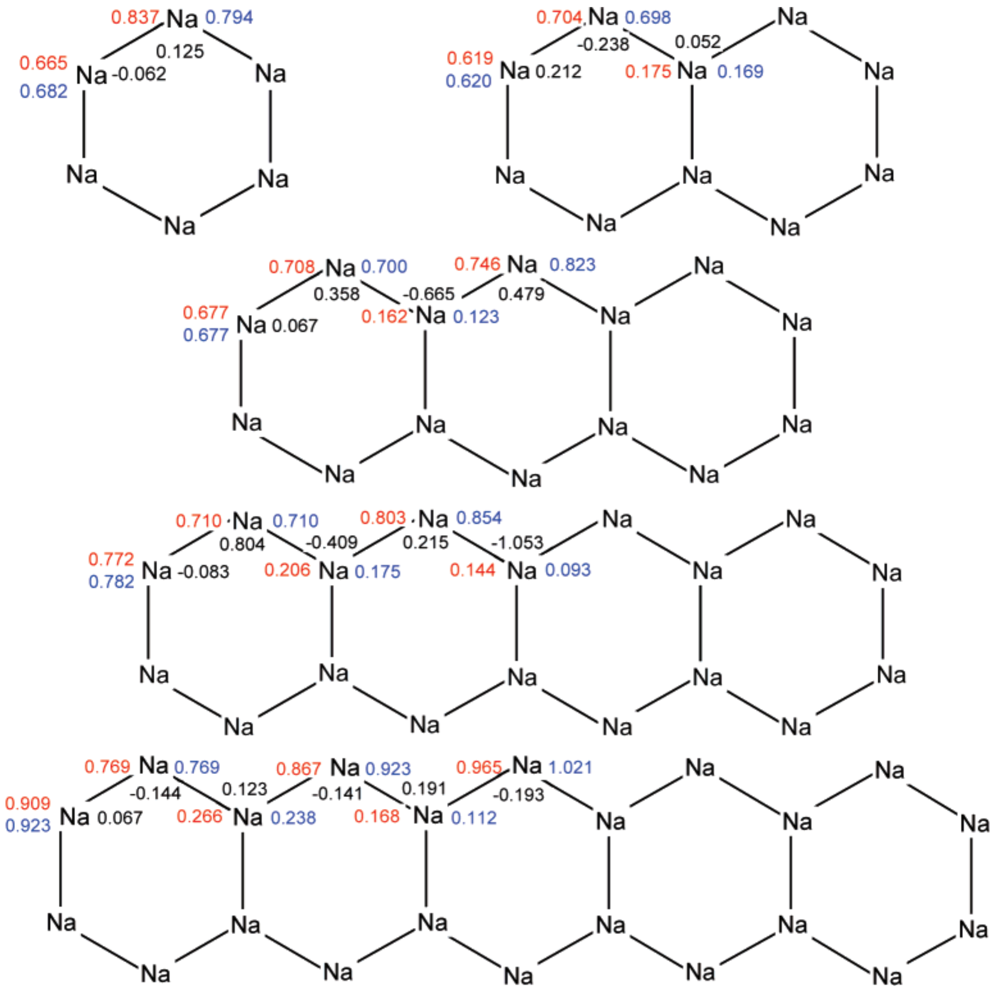


Figure 18. Mulliken charges (black) and the philicities due to nucleophilic (red) and electrophilic (blue) attacks at the different atomic sites of the Na_6-acenes, Na_{4n+2} ($n = 1-5$).

TABLE 6. NICS(0) and NICS(1) Values at Different Ring Centers of $C_{4n+2}H_{2n+4}$, $(BN)_{2n+1}H_{2n+4}$, $(CN)_{2n+1}H_{n+2}$, $(AlN)_{2n+1}H_{2n+4}$ and Na_{4n+2}, $n = 1-5$

NICS(0) (NICS(1))	$C_{4n+2}H_{2n+4}$	$(BN)_{2n+1}H_{2n+4}$	$(CN)_{2n+1}H_{n+2}$	$(AlN)_{2n+1}H_{n+2}$	Na_{4n+2}
A	−7.91	−1.41	−3.96	−2.00	−8.90
(A_1)	(−10.14)	(−2.63)	(−9.65)	(−0.79)	(−7.79)
B	−8.35	−0.81	26.50	−2.29	−9.50
(B_1)	(−10.54)	(−1.90)	(16.67)	(−0.85)	(−8.26)
C	−7.29	−0.50	12.04	−2.30	−9.23
(C_1)	(−9.64)	(−1.77)	(cage)	(−0.88)	(−8.01)
D	−11.06	−0.51	22.94	−2.65	−10.95
(D_1)	(−12.73)	(−1.55)	(cage)	(−1.01)	(−9.44)
E	−6.30	−0.51	0.72	−2.31	−8.85
(E_1)	(−8.65)	(−1.67)	(−2.70)	(−0.90)	(−7.64)
F	−11.06	−0.24	1.12	−2.65	−11.24
(F_1)	(−12.64)	(−1.25)	(−0.38)	(−1.02)	(−9.68)
G	−5.51	−0.43	1.59	−2.34	−8.21
(G_1)	(−7.97)	(−1.63)	(−2.11)	(−0.95)	(−7.06)
H	−10.54	−0.33	4.28	−2.67	−11.18
(H_1)	(−12.19)	(−1.30)	(1.98)	(−1.02)	(−9.56)
I	−12.14	−0.11	2.79	−2.65	−12.12
(I_1)	(−13.46)	(−1.13)	(1.05)	(−0.99)	(−10.38)

are responsible for electrophilic attack. In the case of $n = 2$, the nonzero-NIMAG structures do not allow to have proper reactivity analysis. For the Na_6-acenes, an Na-atom is either electrophilic or the nucleophilic in nature, depending on its environment created by the metalloligand, albeit with a marginal difference in most cases. It is also important to note that aromaticity descriptors like ring current[10] or multicenter delocalization index (MDI)[43] may provide different trends than that predicted by NICS in some cases. It is expected that for a given descriptor (say, MDI) the resemblance of its trend in polyacenes

TABLE 7: AM1 and B3LYP/3-21+G* Results of $(CN)_{2n+1}H_{n+2}$, $(BO)_{2n+1}H_{n+2}$, and $(BS)_{2n+1}H_{n+2}$ ($n = 1-5$)

N	1	2	3	4	5
			AM1 Results		
$(CN)_{2n+1}H_{n+2}$	NIMAG $= 0$ (planar)	NIMAG $= 0$ (nonplanar)	NIMAG $= 0$ (planar)	NIMAG $\neq 0$ (planar)	NIMAG $= 0$ (planar)
$(BO)_{2n+1}H_{n+2}$	NIMAG $= 0$ (planar)	NIMAG $= 0$ (planar)	NIMAG $\neq 0$ (planar)	NIMAG $= 0$ (planar)	NIMAG $\neq 0$ (planar)
$(BS)_{2n+1}H_{n+2}$	NIMAG $= 0$ (planar)	NIMAG $\neq 0$ (planar)	NIMAG $= 0$ (planar)	NIMAG $\neq 0$ (planar)	NIMAG $= 0$ (planar)
			B3LYP/3-21+G* Results		
$(CN)_{2n+1}H_{n+2}$	NIMAG $= 0$ (planar)	NIMAG $= 0$ (planar)	NIMAG $= 0$ (planar)	NIMAG $\neq 0$ (planar)	NIMAG $\neq 0$ (planar)
$(BO)_{2n+1}H_{n+2}$	NIMAG $= 0$ (planar)	NIMAG $\neq 0$ (planar)	no convergence	no convergence	no convergence
$(BS)_{2n+1}H_{n+2}$	NIMAG $= 0$ (planar)	NIMAG $\neq 0$ (planar)	NIMAG $\neq 0$ (planar)	NIMAG $\neq 0$ (planar)	NIMAG $\neq 0$ (planar)

TABLE 8: Correlation Coefficient (R^2) with Standard Deviation (SD) of the Quadratic Behavior of the Ionization Potential (I), Electron Affinity (A), Hardness (η), Softness (S), Chemical Potential (μ), Electrophilicity (ω), Energy (E), and Polarizability (α) as a Function of n of the Acene Analogues

Regression Model: $Z = C_1(SE) + C_2(SE) \times n + C_3(SE) \times n^2$; $Z \equiv I, A, \eta, S, \mu, \omega, E, \alpha$; SE/D = Standard Error/Deviation					
			n (1−5)		
	$C_{4n+2}H_{2n+4}$	$(BN)_{2n+1}H_{2n+4}$	$(CN)_{2n+1}H_{n+2}$	$(AlN)_{2n+1}H_{n+2}$	Na_{4n+2}
I	$C_1 = 8.088(0.121)$ $C_2 = -1.174(0.092)$ $C_3 = 0.109(0.015)$ $R^2 = 0.998$; SD $= 0.056$	$C_1 = 8.459(0.137)$ $C_2 = -0.732(0.104)$ $C_3 = 0.086(0.017)$ $R^2 = 0.986$; SD $= 0.064$	$C_1 = 9.693(0.400)$ $C_2 = -2.026(0.305)$ $C_3 = 0.203(0.050)$ $R^2 = 0.990$; SD $= 0.186$	$C_1 = 7.267(0.070)$ $C_2 = -0.272(0.053)$ $C_3 = 0.034(0.009)$ $R^2 = 0.968$; SD $= 0.033$	$C_1 = 3.892(0.038)$ $C_2 = -0.421(0.029)$ $C_3 = 0.044(0.005)$ $R^2 = 0.998$; SD $= 0.018$
A	$C_1 = -0.630(0.080)$ $C_2 = 1.188(0.061)$ $C_3 = -0.104(0.010)$ $R^2 = 0.999$; SD $= 0.038$	$C_1 = -0.238(0.017)$ $C_2 = 0.351(0.013)$ $C_3 = -0.032(0.002)$ $R^2 = 0.999$; SD $= 0.008$	$C_1 = 1.246(0.522)$ $C_2 = 0.964(0.398)$ $C_3 = -0.128(0.065)$ $R^2 = 0.838$; SD $= 0.243$	$C_1 = 0.234(0.089)$ $C_2 = 0.521(0.068)$ $C_3 = -0.057(0.011)$ $R^2 = 0.990$; SD $= 0.041$	$C_1 = 1.676(0.018)$ $C_2 = 0.182(0.013)$ $C_1 = -0.008(0.002)$ $R^2 = 0.999$; SD $= 0.008$
η	$C_1 = 4.359(0.100)$ $C_2 = -1.181(0.076)$ $C_3 = 0.106(0.012)$ $R^2 = 0.999$; SD $= 0.047$	$C_1 = 4.348(0.076)$ $C_2 = -0.542(0.058)$ $C_3 = 0.059(0.010)$ $R^2 = 0.994$; SD $= 0.036$	$C_1 = 4.224(0.461)$ $C_2 = -1.495(0.351)$ $C_3 = 0.165(0.057)$ $R^2 = 0.969$; SD $= 0.215$	$C_1 = 3.516(0.079)$ $C_2 = -0.396(0.060)$ $C_3 = 0.046(0.010)$ $R^2 = 0.985$; SD $= 0.037$	$C_1 = 1.108(0.018)$ $C_2 = -0.302(0.014)$ $C_3 = 0.026(0.002)$ $R^2 = 0.999$; SD $= 0.008$
$2S$	$C_1 = 0.207(0.001)$ $C_2 = 0.084(0.001)$ $C_3 = 0.011(0.0001)$ $R^2 = 1.000$; SD $= 0.001$	$C_1 = 0.222(0.004)$ $C_2 = 0.041(0.003)$ $C_3 = -0.004(0.001)$ $R^2 = 0.998$; SD $= 0.002$	$C_1 = 0.154(0.193)$ $C_2 = 0.195(0.147)$ $C_3 = 0.004(0.024)$ $R^2 = 0.968$; SD $= 0.090$	$C_1 = 0.277(0.007)$ $C_2 = 0.044(0.006)$ $C_3 = -0.005(9.1E-4)$ $R^2 = 0.99$; SD $= 0.003$	$C_1 = 0.914(0.027)$ $C_2 = 0.200(0.020)$ $C_3 = 0.085(0.003)$ $R^2 = 1.000$; SD $= 0.012$
μ	$C1 = -3.729(0.021)$ $C2 = -0.007(0.016)$ $C3 = -0.002(0.003)$ $R^2 = 0.962$;SD $= 0.010$	$C_1 = -4.111(0.061)$ $C_2 = 0.191(0.046)$ $C_3 = -0.027(0.008)$ $R^2 = 0.919$; SD $= 0.028$	$C_1 = -5.469(0.062)$ $C_2 = 0.531(0.047)$ $C_3 = -0.037(0.008)$ $R^2 = 0.998$; SD $= 0.029$	$C_1 = -3.751(0.010)$ $C_2 = -0.125(0.007)$ $C_3 = 0.012(0.001)$ $R^2 = 0.999$; SD $= 0.004$	$C_1 = -2.784(0.023)$ $C_2 = 0.120(0.018)$ $C_3 = -0.018(0.003)$ $R^2 = 0.964$; SD $= 0.011$
ω	$C_1 = 1.4599(0.031)$ $C_2 = 0.556(0.024)$ $C_3 = 0.097(0.004)$ $R^2 = 1.000$; SD $= 0.015$	$C_1 = 1.914(0.031)$ $C_2 = 0.102(0.024)$ $C_3 = -0.002(0.004)$ $R^2 = 0.995$; SD $= 0.014$	$C_1 = 2.714(1.868)$ $C_2 = 1.760(1.423)$ $C_3 = -0.114(0.233)$ $R^2 = 0.885$; SD $= 0.871$	$C_1 = 1.905(0.060)$ $C_2 = 0.502(0.046)$ $C_3 = -0.052(0.008)$ $R^2 = 0.996$; SD $= 0.028$	$C_1 = 3.832(0.217)$ $C_2 = 0.130(0.165)$ $C_3 = 0.378(0.027)$ $R^2 = 0.999$; SD $= 0.101$
E	$C_1 = -78.626(0.002)$ $C_2 = -153.677(0.002)$ $C_3 = 0.002(0.0003)$ $R^2 = 1.000$; SD $= 0.001$	$C_1 = -82.076(0.0002)$ $C_2 = -160.658(0.0002)$ $C_3 = 8.10^{-05}(3.10^{-05})$ $R^2 = 1.000$; SD $= 0.001$	$C_1 = -94.105(0.017)$ $C_2 = -186.326(0.013)$ $C_3 = 1.10^{-04}(0.00214)$ $R^2 = 1.000$; SD $= 0.008$	$C_1 = -299.653(7.1E-5)$ $C_2 = -595.844(5.4E-5)$ $C_3 = 4.3E-5(8.9E-6)$ $R^2 = 1.000$; SD $= 3.3E-5$	$C_1 = -324.511(0.079)$ $C_2 = -649.316(0.060)$ $C_3 = 0.022(0.010)$ $R^2 = 1.000$; SD $= 0.037$
α	$C_1 = 26.574(0.296)$ $C_2 = 33.413(0.226)$ $C_3 = 5.614(0.037)$ $R^2 = 1.000$; SD $= 0.138$	$C_1 = 22.614(0.530)$ $C_2 = 35.808(0.404)$ $C_3 = 0.688(0.066)$ $R^2 = 1.000$; SD $= 0.247$	$C_1 = 24.063(13.909)$ $C_2 = 17.005(10.600)$ $C_3 = 10.078(1.733)$ $R^2 = 0.999$; SD $= 6.485$	$C_1 = 35.661(0.637)$ $C_2 = 56.818(0.486)$ $C_3 = 0.578(0.079)$ $R^2 = 1.000$; SD $= 0.297$	$C_1 = 303.695(10.014)$ $C_2 = 260.722(7.631)$ $C_3 = 109.453(1.248)$ $R^2 = 1.000$; SD $= 4.669$

with that in the corresponding inorganic ring analogues will not be disturbed.

Conclusions

Aromatic/antiaromatic behavior of polyacenes, BN-acenes, CN-acenes, BO-acenes, BS-acenes, AlN-acenes, and Na_6-acenes are analyzed in terms of nucleus-independent chemical shift and various conceptual DFT-based reactivity descriptors. Most of the polyacene analogues of the inorganic ring compounds are aromatic in nature albeit with some qualitative differences in their aromatic behavior with that of polyacenes. Some of these inorganic ring compounds are antiaromatic. Site selectivities are understood through the charge and philicity patterns.

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