

Structure, Reactivity and Aromaticity of Acenes and Their BN Analogues: A Density Functional and Electrostatic Investigation

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Density functional calculations have been carried out on a series of linearly annelated acenes and their BN analogues. Even though borazine shows aromatic and reactivity behavior parallel with that of benzene, its condensed derivatives show patterns different from those of their hydrocarbon analogues. Nucleus independent chemical shift (NICS) values in acenes suggest that the aromaticity of the inner rings is more than that of benzene, whereas in BN-acenes there is no substantial change in the aromaticity of the individual rings. Molecular electrostatic potential (MESP) is employed to obtain further insights into the bonding and reactivity trends for these systems. The MESP topography patterns of acenes and BN-acenes are substantially different, with BN-acenes showing more localized π electron features compared to those of acenes. The MESP values at the critical points (CPs) indicate overall lowering of aromaticity in these annelated systems. However, this change is gradual among the BN-acenes.

Introduction

Benzene and borazine are representative planar aromatic organic and inorganic molecules containing six π electrons delocalized over the six-membered ring.¹ However, due to the large electronegativity difference between boron (2.0) and nitrogen (3.0), the π electron delocalization may be expected to be reduced in borazine as compared to benzene. Despite their polarity, all the B–N bonds in borazine are of the same length justifying its description as “inorganic benzene”. The extent of aromaticity of borazine in relation to benzene is still debated.² The aromatic stabilization energy (ASE) of borazine is approximately half of that for benzene.³ With this in view, the present article attempts to extend this debate to polycyclic aromatic hydrocarbons (PAHs, also known as acenes) and the corresponding B–N analogues. Recently, the linearly annelated benzene rings have received much attention because of their role as pollutants and, in

particular, as carcinogens.⁴ Owing to their remarkable stability, these PAHs are found in substantial quantities in the interstellar space⁵ and are of substantial chemical interest.

While the chemistry of benzene and its linearly annelated compounds is well-developed,⁶ the corresponding B–N analogues are relatively unknown. There is a renewed interest in the study of borazine-based polycyclic compounds because of their use as precursors for boron-containing polymers and ceramics.⁷ Almost four decades ago, Laubengayer and

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co-workers⁸ reported the isolation of the BN analogues of naphthalene and biphenyl, viz. borazanaphthalene (B₅N₅H₈) and diborazine (B₆N₆H₁₀), respectively. These were further detected in the gas-phase mass spectrometric analysis of borazine.⁹ Recently, Sneddon and co-workers reported the synthesis and X-ray characterization of these two molecules.¹⁰ To the best of our knowledge, there is only one theoretical report on the structure and aromaticity of BN analogues of PAHs, viz., that of BN-naphthalene.¹¹ We present here a density functional theory (DFT)^{12,13} based study of the structure, stability, and reactivity of benzene, its linearly condensed compounds, viz. naphthalene, anthracene, tetracene, and pentacene, and their BN analogues. For obtaining aromatic stabilization energies, the corresponding *trans*-perhydro derivatives are considered. Also included for a comparison are cyclohexene and 1,3-cyclohexadiene. The emphasis is to compare and contrast the properties of the borazines with those of their PAH counterparts.

With the increasing popularity of nucleus independent chemical shift (NICS)¹⁴ as a scale of aromaticity in conjugated hydrocarbons, NICS has been used further to investigate aromaticity in BN-acenes. The electronic charge distribution in these molecules is also probed by topographical analysis of the molecular scalar field of molecular electrostatic potential (MESP), which is known to provide valuable insights into the bonding and reactivity of molecular systems.^{15a,b}

Computational Details

All the structures (1–24) were fully optimized using the hybrid HF-DFT method B3LYP.¹² This is based on Becke's three-parameter functional^{12a} including Hartree–Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke^{12b} together with the nonlocal correction for the correlation energy suggested by Lee, Yang, and Parr.^{12c} Initially, the molecules were optimized at the 6-31+G* basis set which uses one diffuse and polarization function for each atom as implemented in the

Gaussian 94 suite of programs.¹³ They have been further optimized using the triple- ζ quality 6-311+G** basis set. The optimized structures were characterized as minima on their respective potential energy surfaces by vibrational frequency calculation at the B3LYP/6-31+G* level of theory. The total energies are calculated by adding the zero point vibrational energy (ZPVE) obtained from B3LYP/6-31+G* level to the energy values obtained from B3LYP/6-311+G** level. The condensed polycyclic hydrocarbons and their BN counterparts were optimized under the *D*_{2h} and *C*_{2v} symmetry constraints, respectively. To judge the aromaticity of the individual rings, nucleus independent chemical shift (NICS)¹⁴ calculations (B3LYP/6-311+G**) were carried out at the ring center and 1 Å above the plane of each ring.

Molecular Electrostatic Potential (MESP).¹⁵ The electrostatic potential, *V*(**r**) at a point **r**, generated by the molecular charge distribution, is given by

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \quad (1)$$

where the first term denotes the contribution due to nuclei of charges {*Z*_A} located at {**R**_A} and the second term arises due to the continuous electronic charge density distribution, $\rho(\mathbf{r})$. The topographical analysis of *V*(**r**) is based on locating and characterizing the critical points (CPs). These are the points where the gradient of the function vanishes, viz., $\nabla V(\mathbf{r}) = 0$. The CPs can be characterized on the basis of the number and nature of the nonzero eigenvalues of the Hessian matrix *A*, where *A*_{ij} = ($\partial^2 f / \partial x_i \partial x_j$) evaluated at the CP.^{12a} If none of the eigenvalues is zero, it represents a nondegenerate CP. A typical CP is labeled as (*R*, σ), where the rank *R* is the number of nonzero eigenvalues and σ is the sum of signs of the eigenvalues. Nondegenerate MESP CP can be of type (3, +3), viz. a minimum, that typically represents electron localization at a non nuclear site or (3, –1) and (3, +1) saddles. By locating maximal and minimal points of MESP, one can precisely identify the electrophilic and nucleophilic binding sites on a molecule. MESP has long been employed in the chemical literature as a meaningful descriptor of molecular reactivity. Tomasi¹⁶ and Pullman¹⁷ pioneered the use of MESP for predicting the sites of electrophilic attack. Politzer¹⁸ suggested mapping of the MESP on the van der Waals surface of a molecule for locating probable sites of nucleophilic attack. The nature, value, and distribution of the CPs give valuable information about the π electron delocalization and hence the aromatic character in conjugated systems. Gadre et al.¹⁹ have earlier explored the MESP topography of PAHs for defining total aromaticity of the individual rings. A closely related concept of aromatic sextets has been explored by using MESP topography which is explained in detail in the next section.¹⁹ In the present study, the MESP distribution and the corresponding CPs of acenes and BN-acenes have been

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computed using the program INDPROP.^{15c} Further, an electrostatics-based model, called electrostatic potential for intermolecular complexation (EPIC) has been employed for obtaining the possible dimer structures of borazine as well as BN-naphthalene.²⁰ EPIC interaction energy is expressed as a summation of discrete point charges (q) on one molecule multiplied by the MESP (V) at these points due to the other molecules:²⁰

$$E_{\text{int}} = 1/2 \sum_{\substack{i \in A \\ j \in B}} (V_{A,i} q_{B,j} + V_{B,j} q_{A,i}) \quad (2)$$

The second molecule is moved around the first without changing the internal geometry of either of them, so as to minimize E_{int} . More details for the EPIC model may be found elsewhere.^{20c}

Results and Discussion

The optimized geometries of the hydrocarbons (1–12) and their BN counterparts (13–24) are shown in Figures 1 and 2, respectively. The energies are shown in Table 1. The calculated C–C bond lengths, which range from 1.363 to 1.455 Å, are comparable to those reported earlier.²¹ Compared to the acenes, the changes in the corresponding B–N bond lengths of the BN-acenes are very small (1.425 to 1.460 Å). The stabilization or resonance energies of the linear acenes and their BN analogues were evaluated by using eq 3, as suggested by Schleyer and co-workers.²² The basis for using eq 3 for the estimation of stabilization energies is that being a cyclic conjugated diene 1,3-cyclohexadiene is a better standard reference for the evaluation of stabilization energies of benzenoid hydrocarbons than the usually employed *s-trans*-butadiene or other acyclic *s-trans*-polyenes.

$$E(\text{acene}) = E(n \text{ 1, 3-cyclohexadiene}) + E(\text{trans-perhydroacene}) - E(n \text{ cyclohexene})$$

$$n = 3, 5, 7, \dots \quad (3)$$

It is seen that the resonance energies of both the acenes and their BN analogues increase linearly from benzene (1) to pentacene (5) and from borazine (13) to BN-pentacene (17), respectively. However, the resonance energies/ π electron (RE_{π}) of the two systems do not go parallel to each other. While the RE_{π} of the acenes is almost constant throughout the series, that of the BN analogues increases nonuniformly in going from borazine to BN-pentacene (cf. Figure 3). It increases significantly from (13) to (14) and then uniformly to (17). This dramatic change in RE_{π} in going from (13) to (17) may be attributed to different degrees of electron delocalization in these systems.

Schleyer and co-workers¹⁴ have proposed the use of absolute magnetic shieldings, computed at ring centers (nonweighted mean of the heavy atom coordinates) with the standard quantum mechanics programs, as a new aromaticity/antiaromaticity criterion. They have correlated these values

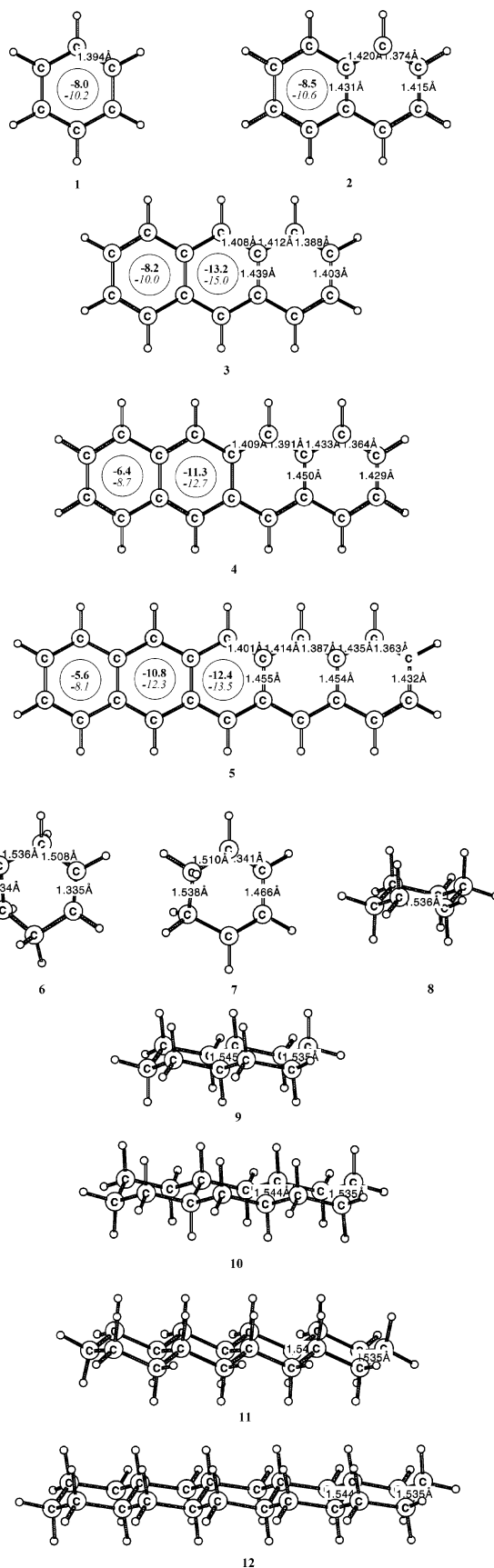


Figure 1. Optimized (B3LYP/6-311+G**) structures for the hydrocarbons (1–12) along with important bond lengths (Å). NICS values for the individual rings were given within the circle. The upper number in bold and the lower number in italics indicate the NICS values in the plane and 1 Å above the plane of the ring, respectively.

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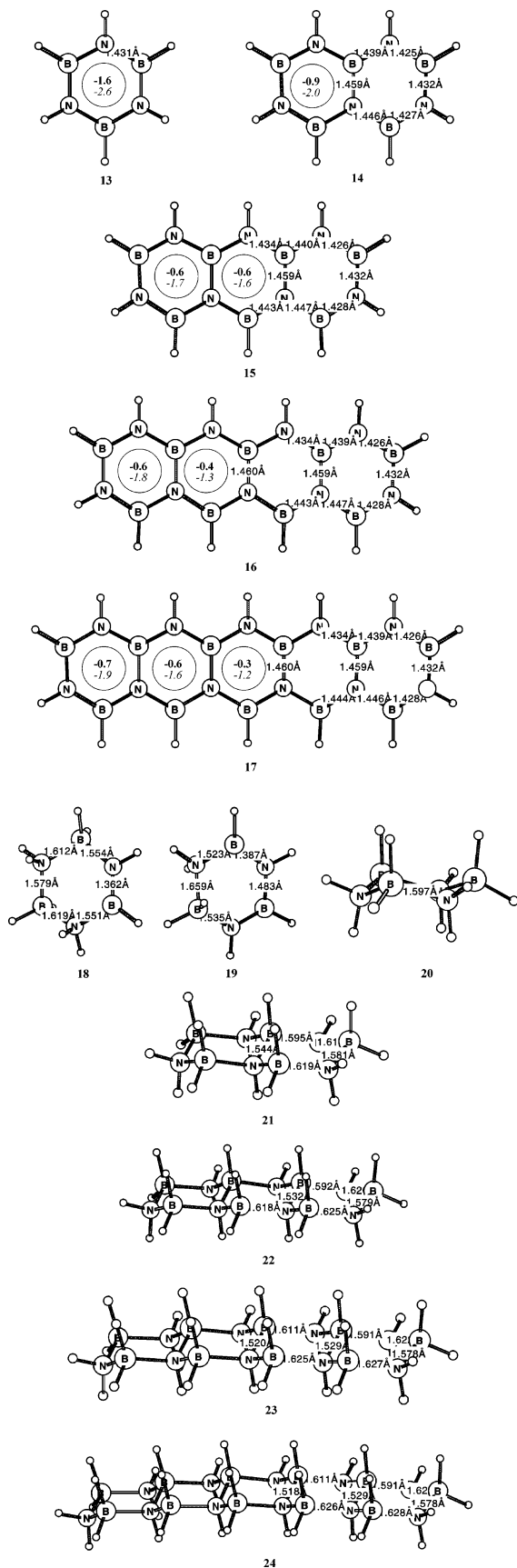


Figure 2. Optimized (B3LYP/6-311+G**) structures for the BN analogues of the hydrocarbons (**13–24**) along with important bond lengths (Å). NICS values for the individual rings were given within the circle. The upper number in bold and the lower number in italics indicate the NICS values in the plane and 1 Å above the plane of the ring, respectively.

Table 1. Total Energies (B3LYP/6-311+G**) Including Zero Point Vibrational Energy (B3LYP/6-31+G*) and Resonance Energies (kcal·mol⁻¹), Total (RE_T) and per π Electron (RE _{π}) for the Aromatic Hydrocarbons and Their Corresponding B–N Analogues

molecule	tot. energy (au)	RE _T (RE _{π})
C ₆ H ₆ (1)	-232.210 71	32.7 (5.45)
C ₁₀ H ₈ (2)	-385.841 15	59.8 (5.98)
C ₁₄ H ₁₀ (3)	-539.466 01	83.5 (5.96)
C ₁₈ H ₁₂ (4)	-693.088 50	105.5 (5.86)
C ₂₂ H ₁₄ (5)	-846.709 84	127.6 (5.80)
C ₆ H ₁₀ (6)	-234.566 59	
C ₆ H ₈ (7)	-233.361 39	
<i>trans</i> -C ₆ H ₁₂ (8)	-235.774 22	
<i>trans</i> -C ₁₀ H ₁₈ (9)	-391.771 79	
<i>trans</i> -C ₁₄ H ₂₄ (10)	-547.769 35	
<i>trans</i> -C ₁₈ H ₃₀ (11)	-703.767 09	
<i>trans</i> -C ₂₂ H ₃₆ (12)	-860.309 43	
B ₃ N ₃ H ₆ (13)	-242.655 25	13.3 (2.22)
B ₅ N ₅ H ₈ (14)	-403.275 02	33.2 (3.32)
B ₇ N ₇ H ₁₀ (15)	-563.894 43	56.2 (4.0)
B ₉ N ₉ H ₁₂ (16)	-724.513 86	80.1 (4.45)
B ₁₁ N ₁₁ H ₁₄ (17)	-885.133 13	104.2 (4.74)
B ₃ N ₃ H ₁₀ (18)	-244.932 55	
B ₃ N ₃ H ₈ (19)	-243.773 39	
<i>trans</i> -B ₃ N ₃ H ₁₂ (20)	-246.110 68	
<i>trans</i> -B ₅ N ₅ H ₁₈ (21)	-409.016 41	
<i>trans</i> -B ₇ N ₇ H ₂₄ (22)	-571.916 85	
<i>trans</i> -B ₉ N ₉ H ₃₀ (23)	-734.815 91	
<i>trans</i> -B ₁₁ N ₁₁ H ₃₆ (24)	-897.714 53	

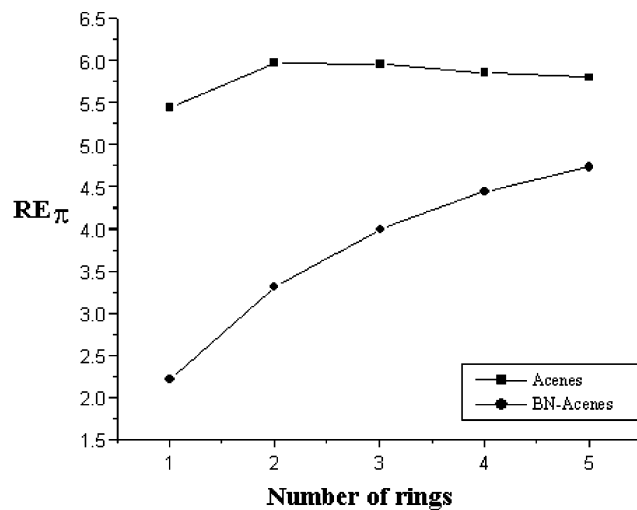


Figure 3. Comparison of the resonance energies/ π electron (RE _{π}) of acenes and their BN analogues with the increasing number of rings for systems **1–5** and **13–17**.

with the familiar NMR chemical shift convention and are known as the nucleus independent chemical shift (NICS). A negative NICS value indicates aromatic character while a positive value indicates antiaromatic character. It is observed that the NICS values are in good correlation with the ASEs and magnetic susceptibility exaltation values, which establish NICS as an effective aromaticity criterion. In this regard, we sought to quantify the amount of electron delocalization in each ring with the help of NICS calculations.¹⁴ The local effects of C–C and C–H σ bonds result in nonzero NICS values, as it is known from the NMR chemical shifts that they influence the magnetic environments. For this reason it has been recommended to calculate NICS values 1 Å above the ring centers as a more precise aromaticity index, wherein

Table 2. MESP (in au) at the CPs (at B3LYP/6-311+G**) over the Rings of Acenes and BN Acenes^a

system	ring	CP			av
		(3, +3)	(3, +1)	(3, -1)	
benzene	A	-0.0250 (6)	-0.0249 (6)	-0.0244 (1)	-0.0249
naphthalene	A	-0.0205 (1)	-0.0229 (1)	-0.0204 (1)	-0.0217
		-0.0238 (2)	-0.0204 (2)		
anthracene	A	-0.0233 (2)	-0.0218 (1)	-0.0188 (1)	-0.0209
			-0.0191 (2)		
tetracene	B	-0.0202 (2)	-0.0192 (2)	-0.0187 (1)	-0.0195
		A	-0.0229 (2)	-0.0210 (1)	-0.0179 (1)
	B		-0.0183 (2)		
			-0.0175 (1)	-0.0184 (2)	-0.0186
pentacene	A	-0.0229 (2)	-0.0208 (1)	-0.0176 (1)	-0.0196
			-0.0182 (4)		
	B	-0.0197 (2)	-0.0182 (2)	-0.0171 (1)	-0.0185
			-0.0181 (2)		
	C	-0.0189 (2)	-0.0189 (2)	-0.0170 (1)	-0.0185
			-0.0181 (2)		
borazine	A	-0.0211 (3)	-0.0044 (3)	-0.0099(1)	-0.0128
BN-naphthalene	A	-0.0211 (1)	-0.0075 (1)		-0.0141
		-0.0196 (1)	-0.0080 (1)		
	A		-0.0145 (1)		
		-0.0214 (1)	-0.0074 (1)		-0.0141
BN-anthracene	A	-0.0193 (1)	-0.0079 (1)		
		-0.0143 (1)			
	B	-0.0143 (1)	-0.0059 (1)		-0.0105
		-0.0143 (1)			
BN-tetracene	A	-0.0215 (1)	-0.0074 (1)		-0.01400
		-0.0190 (1)	-0.0078 (1)		
	B	-0.0143 (1)	-0.0056 (1)		-0.0119
		-0.0138 (1)	-0.0138 (1)		
	C	-0.0138 (1)	-0.0138 (1)		
		-0.0207 (1)	-0.0067 (1)		-0.0131
BN-pentacene	A	-0.0180 (1)	-0.0069 (1)		
		-0.0135 (1)			
	B	-0.0135 (1)	-0.0047 (1)		-0.0108
		-0.0169 (1)			
	C	-0.0129 (1)	-0.0044 (1)		-0.0106
		-0.0129 (1)			
		-0.0166 (1)			

^a Values in parentheses represent the corresponding number of CPs considered for average MESP at the CPs above each ring. See text for details.

the local contributions are diminished relative to the ring current effects. Among the acenes, the middle ring of anthracene has the highest negative NICS values, -13.2 and -15.0 in the plane and 1 \AA above the plane of the ring, respectively (Figure 1). It is found that the inner rings of all the acenes are more aromatic than the terminal ones. This is in contrast to the trends for BN acenes. Among the BN analogues, borazine (**13**) is endowed with the highest negative NICS values, -1.6 and -2.6 (Figure 2), which decrease rather gradually in the series. This indicates that, unlike the benzenoid rings, there is no appreciable change in the aromaticity of the individual rings of BN-acenes.

MESP Topography of Acenes and Their BN Analogues.

A systematic description of MESP topography of the systems in this study is given in Table 2 and Figure 4. The MESP isosurfaces of various function values displayed in Figure 5 have been generated by using the visualization package UNIVIS.²³ Benzene, the paragon of aromatic systems, shows a circular arrangement of six (3, +3) minima connected by

the six (3, +1) saddles all observed at a typical distance of 1.94 \AA above the ring (cf. CPs labeled as a and b in Figure 4a). Interestingly, the MESP values at these CPs remain almost constant with a function value of -0.0249 au (cf. Table 2). The MESP isosurface corresponding to value -0.0185 au (cf. Figure 5a) is continuous showing π electron cloud over the entire carbon framework on either side of the ring. This indeed brings out a very smooth distribution of π electrons in benzene that renders extra stability to the molecule. However, in borazine, due to the large electronegativity difference between boron and nitrogen, the localization of π electrons is predominantly seen on nitrogen. As clearly noticed from the MESP isosurface, the prominent regions of negative electrostatic potential are on the nitrogen atoms and the hydrogens bound to boron. The CP function values in borazine are not as negative as in benzene. However, the hydrogen atoms attached to borons show a pronounced hydride character in terms of MESP value. These distinctive features seem to endow borazine with more reactive character than benzene. The most negative valued (3, +3) minima ("a1" of function value -0.0211 au in Figure 4a) is located above nitrogen at a distance of 1.57 \AA (cf. Figure 4) from the ring plane. The other CPs (viz. a2, b1, b2) align along the B-H bonds that are connected by the corresponding (3, +1) and (3, -1) saddles (b, c) lying above the ring center. This indicates the polar nature of B-N bond predicting to undergo addition reactions rather than electrophilic substitution in borazine.^{1e}

In the case of annelated acenes, the π electron count/ring decreases as we go to higher members of the series. For example in anthracene, tetracene and pentacene, it is $14/3$, $18/4$, and $22/5$, respectively. This leads to the noncircular distribution of CPs with the increased MESP function values as can be noted from Table 2. The most negative valued CP (a1) occurs toward the end regions at the shortest C-C bond (cf. terminal rings in Figure 4), and its distance from the nearest carbon decreases only marginally in the series, viz. in anthracene 1.85 \AA , in tetracene 1.84 \AA , and in pentacene 1.83 \AA . The deviation of the MESP at the "a1" CP from that observed at the center region of benzene, naphthalene, anthracene, tetracene, and pentacene is 0.0006 , 0.0033 , 0.0046 , and 0.0050 au , respectively. This leads to the conclusion that π electrons get more concentrated toward the terminal rings on passage to higher linear polyacenes. This behavior is also reflected in the MESP isosurfaces, depicted as distinct and prominent π electron regions at the terminal rings compared to the inner ones (cf. Figure 5). However, this is in contrast to the NICS values of acenes, which indicate the middle ring to be more aromatic. Such a feature correlates with the experimentally reported reactivity of the acene series, which increases in the order benzene < naphthalene < anthracene < tetracene < pentacene, etc.²⁵ Further, the greater reactivity of the middle rings, for example

(23) UNIVIS-2000, developed at the Department of Chemistry, University of Pune, is employed for visualization purposes in this work. See: Limaye, A. C.; Gadre, S. R. *Curr. Sci. (India)* **2001**, *80*, 1296.

(24) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1988.

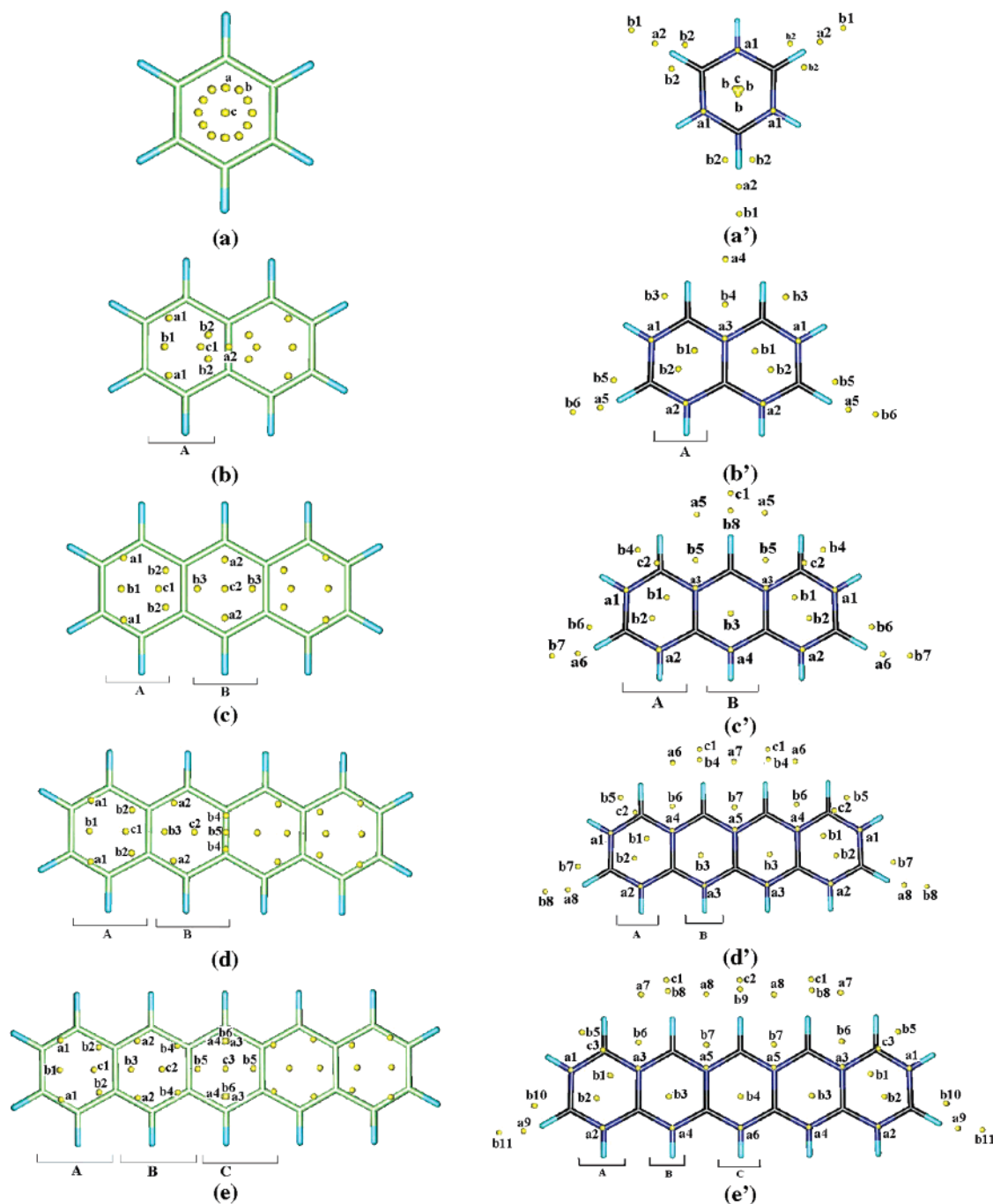


Figure 4. MESP topography (top view) of acenes 1–12 in (a) and the BN analogues in (b). a_i, b_i, and c_i represent (3, +3), (3, +1), and (3, −1) CPs, respectively. For MESP function values at CPs, see Table 2.

in anthracene, brings in the lack of correlation between aromaticity and reactivity. On the other hand, in BN annelated systems, the topography pattern remains unchanged in the series. Borazine itself shows distinct π electron distribution at the nitrogen sites and along the BH bonds. As one goes to higher members of the series, the B–H bonds pertaining to the fused rings reveal rich electrostatic features. The MESP isosurface corresponding to value -0.0100 and -0.0070 au in Figure 5 shows a “cap” like region on the

top of these B–H bonds with the increasing size in the series. The corresponding local MESP minimum becomes more negative in the higher annelated systems viz. in BN-naphthalene (a₄), BN-anthracene (a₅), BN-tetracene (a₇), and BN-pentacene (a₈) of -0.0204 , -0.0233 , -0.0260 , and -0.0260 au respectively. These values are more negative than the corresponding minima on nitrogen indicating that these becomes more prominent binding sites for the electrophilic species in these systems. However, such MESP features are observed to be diminishing at the B–H bonds (cf. Figure 5) of the terminal rings. The terminal rings show two (3, +1) saddles (b₁, b₂) whereas there is only one saddle

(25) (a) Clar, E. *Polycyclic Hydrocarbons*; Academic: London, 1964; Vols. 1 and 2. (b) Clar, E. *The Aromatic Sextet*; John Wiley and Sons: London, 1972.

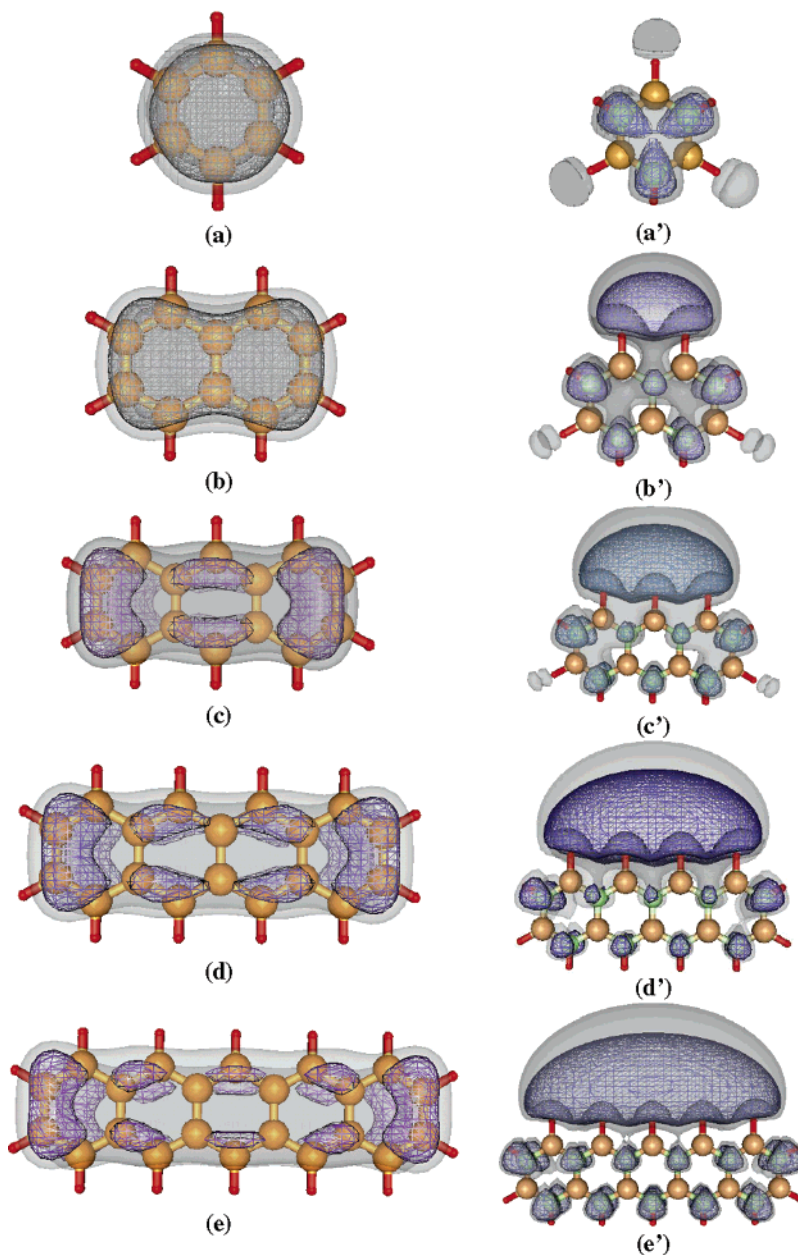


Figure 5. MESP isosurfaces (top view) corresponding to values -0.0185 au (line model isosurface) and -0.0150 au for acenes (**1–5**) and -0.0100 au (line model isosurface) and -0.0070 au for BN analogues (**13–17**).

at the inner rings with appreciably less negative function value (b3 and b4 in case of BN-pentacene) indicating major π electron concentration at the terminal rings.

Even though many studies have been reported on the reactivity trends in acenes,^{6,23} no such systematic study is available for the corresponding BN-acenes. MESP is observed to be a powerful tool in explaining various reactivity trends observed in BN systems that are studied earlier. The gas-phase reactivity of borazine and borazine-derived ions has been investigated by Fornarini et al.^{2b,c} It is observed that the most basic site in borazine ring is at nitrogen and protonation at boron is calculated to be unfavored by $28 \text{ kcal}\cdot\text{mol}^{-1}$. This is in qualitative agreement with the MESP distribution (cf. Figures 4 and 5) wherein the nitrogen atom is endowed with the most negative-valued MESP CP. Borazine displays addition reactions that are unknown in the

gas-phase chemistry of carbocyclic analogue, which can also be justified with more localized MESP features in BN acenes compared to acenes.^{2b} In ab initio studies of borazine and benzene cyclacenes, Loh et al.²⁶ observed strong delocalization of π electrons in the boron-apexed trannulene compared to the nitrogen-apexed trannulene. The present MESP-based study also finds negative-valued MESP isosurfaces only along the B–H bonds indicating delocalization of π electrons along boron-apexed side of the ring. In a recent work by Kawahara et al.,²⁷ it is observed that the gauche parallel-stacked dimer of borazine is energetically favorable with the interaction energy of $-2.73 \text{ kcal}\cdot\text{mol}^{-1}$ (at MP2/

(26) Loh, K. P.; Yang, S. W.; Soon, J. M.; Zhang, H.; Wu, P. *J. Phys. Chem. A* **2003**, *107*, 5555.

(27) Kawahara, S.; Tsuzuki, S.; Uchimaru, T. *J. Chem. Phys.* **2003**, *119*, 10081.

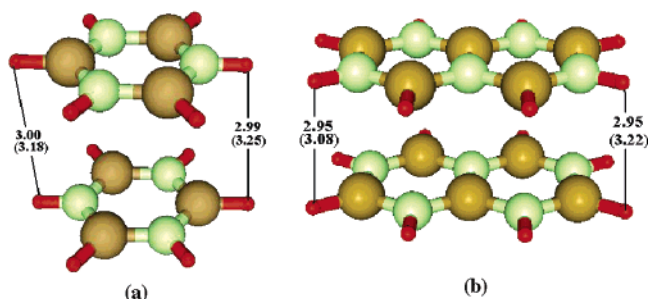


Figure 6. Gauche parallel stacked dimer geometry of (a) borazine and (b) BN-naphthalene with the interaction energy $\Delta E = -4.71$ and -10.22 kcal·mol $^{-1}$ at MP2/6-311G** level without BSSE and ZPE correction, respectively. The EPIC interaction energies are $\Delta E = -2.23$ and -8.24 kcal·mol $^{-1}$, respectively. EPIC and MP2 distances (Å) are shown with and without parentheses, respectively. See text for details.

6-311G** with BSSE correction) which is about 1 kcal·mol $^{-1}$ more negative than the benzene dimer. The strong negative valued CP with MESP of -0.0211 au centered above the nitrogen site indicates this as the obvious dimer structure for borazine. The interaction energy calculated by the EPIC²⁰ model is found to be -2.23 kcal·mol $^{-1}$ (at MP2/6-311G** level), which is also in good agreement with this study (cf. Figure 6). The possible dimer structure for BN-naphthalene is further investigated using EPIC followed by the MP2 calculation at the same level, consistent with the method employed by Kawahara et al.²⁷ In this case also the gauche parallel geometry is observed to be the energetically minimum structure (cf. Figure 5) with the interaction energy of -10.22 kcal·mol $^{-1}$ (without BSSE and ZPE corrections). This brings out the electrostatic interactions among the boron and nitrogen atoms in the lock-and-key fashion during the formation and hence similar structures seem likely for other BN acene systems.

Using reactivity as a criterion of aromaticity, Jemmis et al.^{2a} observed that boracenes show parallel reactivity behavior with acenes and changes are observed are only in the quantitative details. Protonation and methylation reaction energies considered confirm that borazine is less aromatic than benzene but sufficiently aromatic to show a similar gas-phase reactivity pattern. MESP values at CP show similar trend in acenes and their corresponding BN analogues only with a quantitative difference.

Aromaticity Based on MESP Topography. One of the aspects of aromaticity is the extra stability gained by a closed loop of π electrons. It can be quantified as π electron delocalization energy or resonance energy. However, in fused ring systems, as one goes to higher members, the resonance energy does not increase uniformly with the number of rings. For example, for it is 36, 61, and 84 kcal·mol $^{-1}$ for benzene, naphthalene, and anthracene, respectively. Clar's theory describes the aromaticity of a benzenoid hydrocarbon on the basis of the maximum number of sextets (six π -electrons represented by a circle) drawn for a system. A structure with maximum number of sextets is considered as the most appropriate representation of the system. In the case of higher linear polyacenes, one such sextet will be shared among several rings that lead to gradual loss of benzenoid character or aromaticity. This phenomenon is known as "aromatic

dilution".²⁸ In our earlier studies,¹⁹ it has been observed that various aspects of Clar's aromatic sextet theory correlate well with the MESP topographical feature of PAHs. The average values of MESP at CPs of the π region calculated for each ring and the entire molecule have been employed as a measure of aromaticity. The values are in good agreement with local aromaticity values estimated by Li and Jiang^{19c} as well as the global aromaticity values reported by Zhou and Parr,^{19d} in terms of the respective hardness indices. In particular, larger aromatic character of the terminal rings seen in the present MESP topography-based work has also been noticed earlier by Li and Jiang.^{19c} It is observed that the average MESP increases numerically in the PAH series, in line with aromatic dilution effect expected for polyacene series.²⁸ Further the terminal rings are endowed with more negative values compared to the inner ones. These MESP-based values are in good agreement with the local and global aromaticity values estimated by Li–Jiang and Zhou–Parr, respectively.¹⁹ Even though the earlier study was performed at HF/6-31G** level, the calculations carried out at B3LYP/6-311+G** in this study show similar topographical patterns with appreciable increase in MESP function values. However, the trend in the average function values remains the same (cf. Table 2). The MESP-based criterion is applied to the BN-acenes wherein the average MESP function value at CP is numerically much higher compared to that of the respective PAH. The (3, +3) minima on the nitrogen and (3, +1) saddles at the ring top are considered for the average MESP calculation at CPs corresponding to each ring. The middle and terminal rings contribute to all four and five CPs, respectively. Borazine has almost half the average MESP value (-0.0127 au) of that for benzene (-0.0249 au) indicating its reduced aromatic character. In annelated BN-systems, it does not reduce much compared to the acene series. However, within the BN-systems, the terminal rings have much higher average negative function values (-0.0140 au) compared to the middle rings (-0.0119 au) indicating more aromatic character, a trend similar to that of acenes.

It may be noticed that the NICS values indicate inner rings to be more aromatic than the terminal rings for acenes (cf. Figures 1 and 2). In terms of reactivity, the middle ring in anthracene is more likely to undergo substitution reactions indicating lesser aromatic character than the terminal rings.²⁸ However, there is no direct relationship between aromaticity and reactivity as pointed out in a recent work by Schleyer et al.²² explaining that aromaticity is a ground-state phenomenon and reactivity is governed by the loss of aromaticity during reactions. Factors such as the electronegativity of the constituent atoms, charges on them, and separation of the frontier orbitals (HOMO–LUMO gap) are also crucial in determining the reactivity of a molecule.

Concluding Remarks

The stability and aromaticity of benzene (1), naphthalene (2), anthracene (3), tetracene (4), pentacene (5) and their

(28) March J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*; Wiley Eastern Limited: New Delhi, 1992.

BN analogues (**13**–**17**) were evaluated by using density functional theory. Even though the stabilization energy of the acenes and their BN analogues increases linearly from **1** to **5** and **13** to **17**, respectively, the resonance energy/ π electron remains constant for the acenes. However, it increases steadily for the BN-acenes. On the other hand, NICS calculations show that the aromaticity of the inner rings of the acenes is more than that of benzene, but the aromaticity of the individual rings in the BN-acenes remains constant and it is less than that of borazine.

MESP topography is observed to be a powerful tool for the analysis of variety of chemical phenomena, in particular, the local π electron concentrations explaining the aromatic character. The MESP topography patterns for acenes (**1**–**5**) differ substantially from their respective BN-analogues (**13**–**17**). BN-annelated systems show more localized π electron features than the corresponding acene analogues. The average MESP function value at the CPs of individual ring indicates lowering of aromatic character in annelated acenes and their BN-analogues thereby explaining “aromatic dilution effect” as known in the literature.²⁵ However, the NICS values for acenes suggest that the middle rings of these systems are more aromatic (even than benzene) than the terminal ones.

MESP topography offers a satisfactory explanation to various reactivity features of these annelated systems brought out by the earlier experimental and theoretical studies.

It is hoped that this study will be helpful in understanding the distinctive features of π electrons in annelated BN acenes as against their hydrocarbon counterparts. The present analysis of these systems brings out such alterations in the structure, reactivity, and aromaticity patterns by the use of NICS and MESP topography mapping.

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Supporting Information Available: Tables of optimized structural parameters and MESP function values (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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