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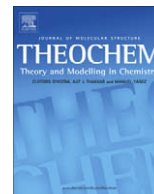**10** PUBLICATIONS **19** CITATIONS

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Ab initio studies of BN-acenes and cyclo BN-acenes electronic properties and their dependence on the molecular size and the number of electrons

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ABSTRACT

In this account, the energy properties (total electronic energy, zero point energy correction, thermal energy correction, the change in ΔH_f^0 on going from 0 to 298 K, atomization energy, and frontier orbital energies), dipole polarizability, and several important bands in the UV spectra (p, α, and β bands) of linear and zigzag BN-acenes and their corresponding cyclic structures have been calculated at several levels of theory. Various correlations have been reported among these properties for BN-acenes and cyclo BN-acenes versus the total number of electrons and the number of rings as well. It has been demonstrated that all studied molecular properties of these series, change linearly with the number of ring as well as the number of electrons, except for frontier molecular orbital energies and excitation energies between them (UV bands). The linear changes of these properties with the number of rings and the total number of electrons were used to generate fit equations. Extracting these equations makes it possible to estimate aforementioned properties for large homologues of the series which satisfy chemical accuracy, yet requiring much less computational work. Also, it has been found that, the quality of the linear equations (values of linear correlation coefficients) with respect to either the number of electrons or rings is insensitive to the combination of methods and basis sets employed to derive the mentioned molecular electronic properties.

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1. Introduction

Borazine, the inorganic analogue of benzene, is obtained by replacing the carbon atoms with alternating boron and nitrogen atoms [1]. Having the same number of π electrons delocalized over the six-membered ring, structural similarities, and observed resemblance in some physical (e.g., density, surface tension) and chemical (e.g., hexahapto ligands in organometallic complexes) [2,3] properties for borazine and benzene have had a powerful draw for chemists. According to these similarities, it has been of great interest to inquire theoretical and experimental novel findings of the chemistry of benzene and its derivatives (polycyclic aromatic hydrocarbons) for the corresponding B–N analogues.

For example, many indices for aromaticity quantification have been introduced [4] which give completely opposite results for the local aromaticity of benzenoid rings in the linear polyacenes, i.e., naphthalene, anthracene, and tetracene [5–9]. According to the numerical values of some indices, the aromatic character of the benzenoid rings in these molecules increases from the outer rings to the inner rings, while for others, the trend is completely reversed. This controversial subject has recently inspired quantum chemists to investigate aromaticity in corresponding B–N analogues (BN-acene) [10–13].

Currently, much attention has been paid to cyclopolyacenes (constructed by rolling a polyacene molecule into a ring) [14–17] because of their role to form the basic cylindrical carbon units of single-wall nanotubes and possible utility of their cyclical cavities in host–guest phenomena [18,19]. Consequently, corresponding B–N analogues (cyclo BN-acene) as important applied materials in above mentioned fields, have been preoccupation of many experimental [20–23] and theoretical chemists [24–29].

As a contribution to this field, we have recently demonstrated [30] that some electronic properties of polyacenes increase linearly with the number of rings and the number of total electrons as well. We have also generated fitting equations on the basis of linear changes of polyacenes' energy properties to estimate them for the higher linear polyacenes and to extrapolate a value for "infinite polyacene". Successful application of our approach to these systems will justify applying this approach to inorganic compounds. To this end, we have calculated some electronic properties of linear and zigzag BN-acenes, made up of laterally fused borazines, and their corresponding cyclic structures. Calculated results show striking resemblance of their changing trend dependence on molecular size to the corresponding hydrocarbon, polyacenes [30] and metal cluster chain $(Na)_{4n+2}$ analogues [31].

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2. Computational methods

The geometries have been fully optimized at the HF and B3LYP [32,33] levels using two basis sets, 6-31G(d) [35,36] and cc-pVDZ [34] by Gaussian suite of programs [37]. These methods and basis sets are sufficient to achieve our goal in the present work, as it has been shown before [30,38–42] that higher level of computation methods do not bear fruit as far as the linear fittings are concerned. All molecules have been optimized employing tight criteria (for details of optimization procedure see Gaussian's internal help). Harmonic frequencies have been computed to discern the nature of optimized geometries only for linear and zigzag BN-acenes (for cyclo BN-acenes the calculations of second derivatives of energy were out of range of our computational power). The molecules are found to present planar conformers with no imaginary frequencies at each of the employed computational levels. Only singlet spin states with C_1 symmetry point group have been considered throughout this study.

3. Discussion

3.1. Electronic energies

We have presented sample structures of studied linear (L_n) and zigzag (Z_n) BN-acenes ($n = 1$–8) along with their corresponding cyclic structures, cyclo-linear BN-acenes (LC_n) and cyclo-zigzag BN-acenes (ZC_n) ($n = 6$–16), where n refers to the number of hexagonal rings, in Scheme 1.

A compilation of the absolute values of calculated energy properties (total electronic energy, zero point energy correction, thermal energy correction, and the change in ΔH_f^0 on going from 0 to 298 K) and optimized geometries for the ground state of all compounds at all employed levels of theory can be found in Supporting information (See Tables T1 and T2).

Here we focus on the total electronic energies (without zero point energy) for the homologous series, although the findings are general for the other energy properties of all series. Fig. 1 displays the plot for the total electronic energy of the ground state of linear and zigzag BN-acenes and cyclo BN-acenes against the number of rings as well as the number of total electrons on the basis of the results of the fourth column in Table T2.

As it is shown in Fig. 1, there is a clear correlation between total electronic energies with both the number of rings and the number of total electrons. The straight lines can be fitted to the empirical linear regression equations:

$$E(N_e) = h \times N_e + s \qquad (1)$$
$$E(N_r) = a \times N_r + b \qquad (2)$$

In these equations, $E(N_e)$ and $E(N_r)$ denote the total electronic energy of the compound with N_e, number of electrons and N_r, number of borazine rings, respectively, whereas h, s, a and b are regression parameters. These parameters have been offered in Table 1 at all levels of theory (and Tables T3–T5 in Supporting information). It is worth mentioning that, in two independent researches [30,38] above equations have previously been obtained for polyacenes.

What might seem surprising at first glance from the entries in Table 1 (and Tables T3–T5) is significant closeness of R^2 to 1. Such excellent and almost perfect linearity of regression lines justify that these expressions can be applied to reexamine the computational findings or to estimate the missing energy values of large molecules. Therefore, one can readily calculate total energy of very large compounds merely by the regression parameters determined for a set of known energy properties of smaller compounds which belong to the same homologous series.

As it can be seen in Table 1 (and Tables T3–T5), R^2s obtained by both HF and B3LYP methods are identical. The influences of methods and basis sets on the linear correlation coefficient, R^2, are very small and the linear relation applies satisfactorily to all four exam-

L_n
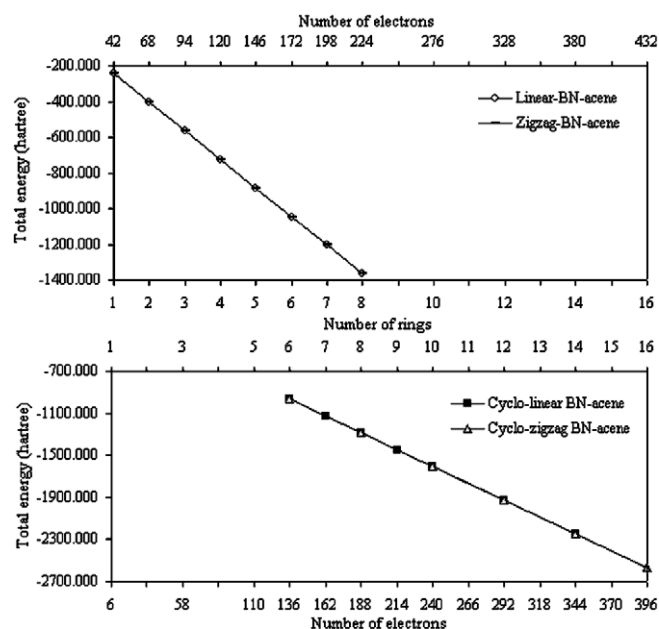
Z_n

CL_n

CZ_n
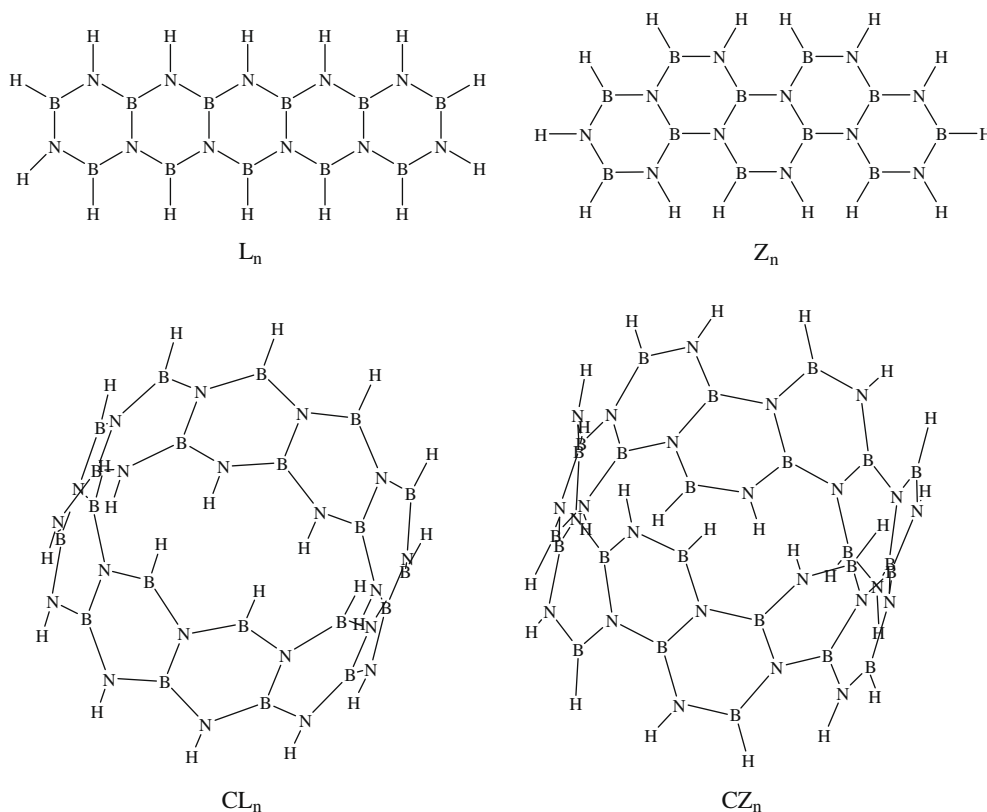
Scheme 1.

Fig. 1. B3LYP/6-31G(d) calculated total electronic energy vs. number of electrons and number of repeating units as well.

ined levels of theory. This finding is in agreement with previous reports at domains of additivity and linear relations [30,38–42] that the success of the linear fittings is insensitive to level of theory.

3.2. Atomizations energies

Atomization energy is the energy difference between a molecule and its constituent atoms. To compute atomization energies of all series, molecules were considered closed-shell singlet and spin multiplicity assumed for hydrogen, boron, and nitrogen atoms were doublet, doublet, and quartet, respectively. Table 2 offers atomization energies (at 0 K) for all molecules employed and at all computational levels utilized in this study. There are regularities in these data that one can formulate them by linear equations with N_r as well as N_e for each homologous series; similar to Eqs. (1) and (2). The linear correlation coefficient belonging to linear relations of cyclo BN-acenes (CL_n and CZ_n) is smaller than 0.999,999, while that of BN-acenes (L_n and Z_n) is larger than 0.999,999,9. Only

excluding the smallest member of both cyclical series in regression process ($n = 6$ in CL_n and CZ_n) makes it possible to have a larger R^2. It seems that strain resulting from curvature of the smallest cyclo BN-acenes affects R^2 magnitude. To visualize the behavior of atomization energies versus N_r and N_e, see Supporting information (Figs. F1–F4).

It is interesting to note that since atomization energy of a molecule is defined as the energy required disintegrating a molecule into its constituent ground state atoms, so it is equivalent to the total binding energy. Consequently, the total binding energy can be predicted to show linear relations with N_r and N_e.

There is, however, a subtle point here: in "frozen-core approximation" energy associated with the inner-shell (core) electrons is almost constant for atoms and molecules. So, the energy contribution of core electrons is essentially a constant factor, which drops out in atomization energy calculation (and any relative energy). Therefore, observation of linear relation for atomization energies does not result from energies of core electrons [30].

3.3. Orbital energies

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) play a dominant role in many chemical reactions [43]. The HOMO–LUMO energy separation has been used as a simple and conventional indicator of kinetic stability. A large HOMO–LUMO gap (band gap) implies high kinetic stability and low chemical reactivity.

The kinetic stability of polyacene has previously been discussed in terms of the HOMO–LUMO energy gap [44,45]. Recently, band gap in cyclo-linear-BN-acenes as a function of the size of the molecules has been studied [25,26]. In this section, we have also determined frontier molecular orbital energies and p, α, and β bands for the four types of BN-acenes as a function of the number of rings and the number of electrons as well.

Calculated frontier orbital energies for all molecules at all levels of theory are available in Supporting information (see Tables T6 and T7). The p band corresponds to the HOMO–LUMO gap and α and β bands involve mainly the HOMO−1 to LUMO and HOMO to LUMO+1. All three transitions occur between occupied and unoccupied π-type molecular orbital ($\pi \rightarrow \pi^*$). The results for these three bands are summarized in Tables 3 and 4 for BN-acenes and cyclo BN-acenes, respectively. These bands are displayed in Fig. 2 for the linear and zigzag BN-acenes as a function of the N_r and N_e. Only by discarding the two smallest members of zigzag series

Table 1
Regression analysis results of total electronic energies for all BN-acene and cyclo BN-acene series.

Homologous series	Method	Regression parameters		$1-R^2$	MAD	Regression parameters		$1-R^2$
		a	b			h	s	
Linear BN-acene	HF/6-31G(d)	−159.65290	−81.49847	0.0	0.07	−6.14050	16.74947	0.0
	HF/cc-pVDZ	−159.66337	−81.50998	0.0	0.06	−6.14090	16.74440	0.0
	B3LYP/6-31G(d)	−160.61928	−82.05132	0.0	0.08	−6.17766	16.79132	0.0
	B3LYP/cc-pVDZ	−160.63007	−82.05985	0.0	0.22	−6.17808	16.78888	0.0
Zigzag BN-acene	HF/6-31G(d)	−159.65292	−81.49840	0.0	0.07	−6.14050	16.74956	0.0
	HF/cc-pVDZ	−159.66318	−81.51025	0.0	0.09	−6.14089	16.74402	0.0
	B3LYP/6-31G(d)	−160.62105	−82.04828	0.0	0.17	−6.17773	16.79545	0.0
	B3LYP/cc-pVDZ	−160.63171	−82.05702	0.0	0.17	−6.17814	16.79326	0.0
Cyclo-linear BN-acene	HF/6-31G(d)	−159.66672	0.29235	5E−10	17.04	−6.14103	−122.52821	5E−10
	HF/cc-pVDZ	−159.67703	0.29366	5E−10	10.09	−6.14142	−122.53483	5E−10
	B3LYP/6-31G(d)	−160.63401	0.27546	4E−10	5.35	−6.17823	−123.28916	4E−10
	B3LYP/cc-pVDZ	−160.64482	0.27988	4E−10	5.25	−6.17865	−123.29306	4E−10
Cyclo-zigzag BN-acene	HF/6-31G(d)	−159.66721	0.27333	8.6E−09	15.31	−6.14105	−122.54760	8.6E−09
	HF/cc-pVDZ	−159.67860	0.29512	6E−10	9.98	−6.14148	−122.53458	6E−10
	B3LYP/6-31G(d)	−160.63309	0.26938	5E−10	7.26	−6.17820	−123.29453	5E−10
	B3LYP/cc-pVDZ	−160.64431	0.27678	6E−10	6.64	−6.17863	−123.29577	6E−10

Mean absolute deviation values (MAD) are in kcal mol^{-1}.

Table 2
Atomization energies for all BN-acene series.

N_r	N_e	Method/basis set		Method/basis set	
		HF/6-31G(d)	HF/cc-pVDZ	B3LYP/6-31G(d)	B3LYP/cc-pVDZ
Linear BN-acene					
1	42	1166.02	1149.90	1423.51	1411.09
2	68	1869.63	1841.42	2272.31	2251.42
3	94	2572.95	2532.69	3120.71	3091.43
4	120	3276.27	3223.95	3969.14	3931.47
5	146	3979.58	3915.19	4817.55	4771.50
6	172	4682.88	4606.42	5665.96	5611.52
7	198	5386.17	5297.64	6514.36	6451.53
8	224	6089.46	5988.86	7362.75	7291.53
Zigzag BN-acene					
1	42	1166.02	1149.90	1423.51	1411.09
2	68	1869.63	1841.42	2272.31	2251.42
3	94	2572.95	2532.67	3122.00	3092.62
4	120	3276.27	3223.59	3971.37	3933.52
5	146	3979.58	3914.69	4820.96	4774.63
6	172	4682.88	4605.81	5670.53	5615.73
7	198	5386.15	5296.94	6520.15	6456.86
8	224	6089.49	5988.08	7369.75	7298.00
Cyclo-linear BN-acene					
6	136	4080.86	4008.69	4963.17	4909.74
7	162	4804.26	4719.86	5830.04	5768.42
8	188	5522.53	5426.11	6692.28	6622.68
9	214	6296.69	6128.99	7551.11	7473.46
10	240	6949.92	6829.53	8408.08	8322.33
12	292	8370.26	8225.87	10117.17	10015.14
14	344	9786.62	9618.17	11822.80	11704.29
Cyclo-zigzag BN-acene					
6	136	4076.41	4002.72	4962.06	4909.74
8	188	5517.23	5418.97	6692.83	6622.31
10	240	6945.61	6823.13	8412.32	8325.35
12	292	8367.22	8220.45	10125.43	10022.06
14	344	9784.68	9613.60	11834.68	11714.73
16	396	11199.47	11004.06	13541.70	13404.95

All values are in kcal mol^{-1}.

Table 3
Values of UV bands, p band (HOMO to LUMO), α and β bands (HOMO−1 to LUMO, Δ_1, and HOMO to LUMO+1, Δ_2) for both linear BN-acene and zigzag BN-acene series.

N_r	N_e	Linear BN-acene			Zigzag BN-acene		
		p Band	Δ_1	Δ_2	p Band	Δ_1	Δ_2
HF/6-31G(d)							
1	42	15.79	15.79	15.79	15.79	15.79	15.79
2	68	14.71	15.07	15.19	14.71	15.07	15.19
3	94	14.27	14.73	14.92	14.60	14.73	14.71
4	120	14.11	14.52	14.68	14.40	14.59	14.59
5	146	14.07	14.34	14.48	14.27	14.42	14.44
6	172	14.06	14.21	14.34	14.19	14.35	14.33
7	198	14.06	14.13	14.25	14.12	14.27	14.26
8	224	14.07	14.09	14.20	14.07	14.22	14.20
B3LYP/6-31G(d)							
1	42	8.17	8.17	8.17	8.17	8.17	8.17
2	68	7.12	7.54	7.61	7.12	7.54	7.61
3	94	6.68	7.26	7.35	7.07	7.20	7.16
4	120	6.52	7.03	7.11	6.84	7.07	7.03
5	146	6.46	6.79	6.88	6.72	6.89	6.87
6	172	6.44	6.65	6.73	6.62	6.81	6.76
7	198	6.45	6.56	6.64	6.54	6.72	6.67
8	224	6.46	6.51	6.58	6.48	6.66	6.60
HF/cc-pVDZ							
1	42	15.38	15.38	15.38	15.38	15.38	15.38
2	68	14.37	14.73	14.79	14.37	14.73	14.79
3	94	13.96	14.41	14.51	14.23	14.36	14.38
4	120	13.82	14.22	14.30	14.04	14.22	14.24
5	146	13.78	14.05	14.13	13.90	14.05	14.09
6	172	13.79	13.94	14.03	13.82	13.97	13.97
7	198	13.80	13.87	13.96	13.75	13.89	13.90
8	224	13.82	13.83	13.92	13.65	13.78	13.79
B3LYP/cc-pVDZ							
1	42	8.04	8.04	8.04	8.04	8.04	8.04
2	68	6.99	7.41	7.47	6.99	7.41	7.47
3	94	6.56	7.13	7.20	6.93	7.06	7.03
4	120	6.40	6.92	6.96	6.71	6.92	6.90
5	146	6.34	6.69	6.75	6.57	6.74	6.74
6	172	6.33	6.54	6.61	6.47	6.65	6.62
7	198	6.34	6.46	6.53	6.34	6.46	6.53
8	224	6.36	6.41	6.48	6.33	6.49	6.46

All values are in eV.

(Z_1 and Z_2), we observe a monotonic decrease in the p band. Eventually, as the size of linear and zigzag BN-acenes reaches infinity, the changes in the HOMO–LUMO gap will reach a plateau. One should mention that the extrapolated orbital energies clearly indicate the presence of a non-vanishing (roughly 6–7 eV) energy gap in all structures of the two BN-acenes. Fig. 2 also shows that α and β bands for both non-cyclic series (L_n and Z_n) are continuously decreasing and almost go toward a limiting value for $n = 9$–10. An interesting feature of this figure is that α and β bands do not show the large difference between the series of compounds as found with the p bands. Similar trends have been previously obtained for linear and zigzag polyacenes by Wiberg [46].

In Fig. 3, p, α, and β band energies of cyclo BN-acenes are represented against the number of rings and the number of electrons as well. It is clear that no obvious correlation of these bands of cyclo-linear BN-acenes (CL_n) with the number of electrons or rings can be observed. The p band rapidly increases, until $n = 10$, then it gradually decrease. The situation is clearly different for the cyclo-zigzag BN-acenes (CZ_n). The p band in CZ_n is nearly constant around 6.6 eV, and the value increases slightly as n increases. As a final remark, it is worth mentioning that the Δ_1 band energy (HOMO−1 to LUMO) decreases in parallel with the increase in the Δ_2 band energy (HOMO to LUMO+1) for cyclo-zigzag BN-acenes.

3.4. Polarizability

Molecular polarizabilities (and hyperpolarizabilities) are of current interest in the field of non-linear optics [47]. Several ab initio studies of dipole polarizability [30,47–49] of some components of α tensor of polyacenes have demonstrated a linear relation regarding the number of benzene rings as well as the number of electrons. Absence of any theoretical or experimental investigations over electric dipole polarizabilities encouraged us to study various components of α tensor of BN-acenes and cyclo BN-acenes, for the first time.

In studies of symmetrical molecules, the principal axes of the polarizability tensor correspond to the symmetry axes. Two axes are chosen with BN-acenes (L_n and Z_n) lying in the molecule plane (ML), L axis along the axis of linear growth of the molecule and M being normal to L axis on the molecule plane. Third axis (N) is normal to the molecular plane (ML). For cyclo BN-acenes, two orthogonal axes, L and M, rest in the center of cylindrical molecule, viz., both axes are along the radius of cyclic compound. Third axis (N) is also normal to the other axes. Accordingly, dipole polarizability tensor components are referred to as α_{LL}, α_{MM} and α_{NN}. On the other hand, what is obtained experimentally is usually the mean polarizability $\langle \alpha \rangle$ that is given as $\langle \alpha \rangle = 1/3\ \langle \alpha_{LL} + \alpha_{MM} + \alpha_{NN} \rangle$. The aim of this section is to investigate relation between $\langle \alpha \rangle$ and components of α tensor with increasing N_e and N_r.

The ground state dipole polarizabilities data of all molecules at different levels and basis sets have been compiled in Tables 5 and 6. By a careful scrutiny of α tensor components of BN-acenes (L_n and Z_n), a strong correlation among components of the polarizability for $n = 1$ to $n = 8$ becomes apparent. Along the long molecular

Table 4
Values of UV bands, p band (HOMO to LUMO), α and β bands (HOMO-1 to LUMO, Δ_1, and HOMO to LUMO+1, Δ_2) for both cyclo-linear BN-acene and cyclo-zigzag BN-acene series.

N_r	N_e	Cyclo-linear BN-acene			Cyclo-zigzag BN-acene		
		p Band	Δ_1	Δ_2	p Band	Δ_1	Δ_2
HF/6-31G(d)							
6	136	12.84	12.99	14.33	14.05	14.77	14.08
7	162	13.22	13.22	14.24			
8	188	13.83	13.83	14.48	14.00	14.44	14.03
9	214	14.07	14.07	14.49			
10	240	14.34	14.34	14.47	14.06	14.34	14.12
12	292	14.35	14.35	14.37	14.10	14.27	14.16
14	344	14.28	14.28	14.29	14.13	14.24	14.20
16	396				14.16	14.22	14.22
B3LYP/6-31G(d)							
6	136	5.59	5.69	6.70	6.53	7.13	6.54
7	162	5.96	5.96	6.69			
8	188	6.52	6.52	6.99	6.57	6.92	6.58
9	214	6.72	6.72	6.88			
10	240	6.88	6.88	6.88	6.60	6.79	6.64
12	292	6.74	6.74	6.74	6.63	6.73	6.68
14	344	6.67	6.67	6.67	6.65	6.69	6.70
16	396				6.67	6.67	6.71
HF/cc-pVDZ							
6	136	12.66	12.87	13.95	13.53	14.27	13.59
7	162	12.95	12.95	13.85			
8	188	13.46	13.46	14.12	13.42	13.89	13.54
9	214	13.67	13.67	14.12			
10	240	13.93	13.93	14.14	13.57	13.87	13.64
12	292	14.04	14.04	14.08	13.69	13.88	13.72
14	344	14.01	14.01	14.02	13.72	13.85	13.73
16	396				13.79	13.87	13.79
B3LYP/cc-pVDZ							
6	136	5.56	5.65	6.64	5.56	5.65	6.64
7	162	5.90	5.90	6.63			
8	188	6.42	6.42	6.92	6.36	6.74	6.37
9	214	6.62	6.62	6.72			
10	240	6.73	6.73	6.75	6.41	6.63	6.43
12	292	6.62	6.62	6.62	6.46	6.59	6.48
14	344	6.55	6.55	6.55	6.50	6.57	6.51
16	396				6.53	6.55	6.53

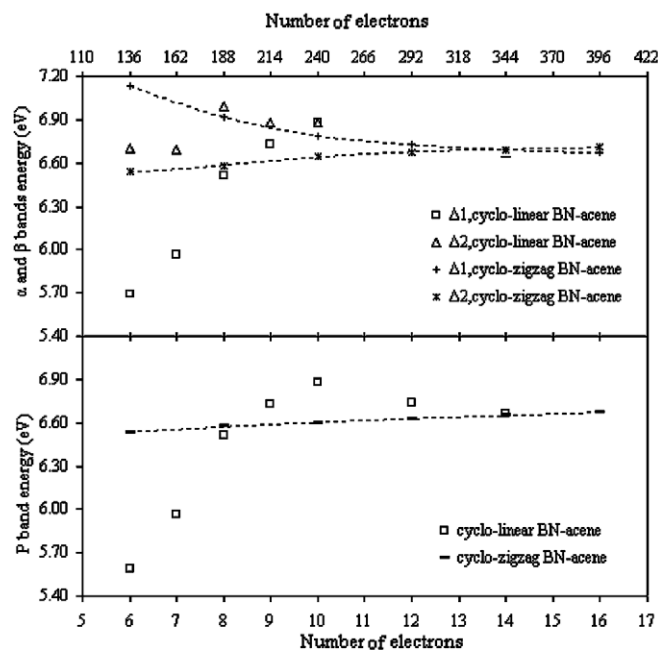All values are in eV.
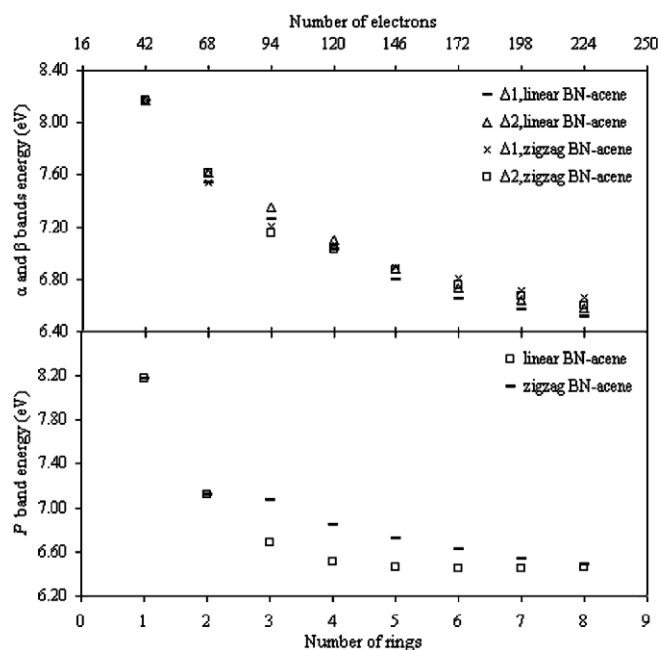
Fig. 3. B3LYP/6-31G(d) calculated p, α, and β band energies for cyclo BN-acene vs. number of electrons and number of repeating units as well.

axis, each borazine ring equally contributes to the polarizability, α_{LL}. In the medium and normal axis directions (α_{MM} and α_{NN}), however, only about half of the elementary borazine polarizability is added for an extra ring. In all, $<\alpha>$ also increases linearly with N_e and N_r (with $R^2 > 0.999$). It is also noteworthy that, the inclusion of electron correlation using density functional theory results in significant improvements in the long (α_{LL}) and medium (α_{MM}) components but has very small effect on the normal component. The various components of α tensor of cyclo BN-acenes (CL_n and CZ_n) also show interesting incremental behavior as the number of N_r and N_e increase as it is evident from data of Table 6. It is observed that α_{LL} and α_{MM} of both cyclo BN-acenes increase linearly as the ring length increases, however, the increasing rate these components of α tensor in CL_n is greater than those in CZ_n. For example, both α_{LL} and α_{MM} of CL_6 and CZ_6 equal to 148.8 a.u. (at HF/6-31G(d)), whereas those for CL_{14} and CZ_{14} equal to 408.4 and 394.7 a.u., respectively. The opposite trend is observed for α_{NN}; here, increasing rate of α_{NN} in CZ_n is greater than that in CL_n. Surprisingly, as the highlighted data entries of Table 6 suggest, there is one point for each series (see also Fig. 5) at which, value of $<\alpha>$ and all components of α tensor equal to one another; namely, $<\alpha> = \alpha_{LL} = \alpha_{MM} = \alpha_{NN}$. So, it seems as if the molecule belonging to this point, similar to a spherical top molecule (such as CH_4 and SF_6) benefits an *isotropic* polarizability, which means that all components of α tensor are the same in all directions [50]. As a result, contrary to all cyclo BN-acenes compounds, the molecules corresponding to the cross points shown in Fig. 5 (and highlighted numbers in Table 6), are predicted unable to show a rotational Raman spectrum!

The graphical representations of dipole polarizabilities (computed at B3LYP/6-31G(d)) versus the number of rings and the number of electrons are shown in Figs. 4 and 5. The same trends at other levels of theory have been avoided in the text and could be found in Supporting information (Figs. F5–F10). It is apparent from these figures that there are significant correlations among components of α tensor and the number of electrons or the number of rings. All components of α tensor have linear relation with N_e and N_r. The excellent quality of linear correlation is evident from R^2 coefficients, which are shown in Figs. 4 and 5. Based on this fact,

Fig. 2. B3LYP/6-31G(d) calculated p, α, and β band energies for BN-acene vs. number of electrons and number of repeating units as well.

Table 5
Dipole polarizabilities for both linear BN-acene and zigzag BN-acene series.

N_r	N_e	Linear BN-acene				Zigzag BN-acene			
		α_{LL}	α_{MM}	α_{NN}	$<\alpha>$	α_{LL}	α_{MM}	α_{NN}	$<\alpha>$
HF/6-31G(d)									
1	42	55.1	55.1	25.8	45.3	55.1	55.1	25.8	45.3
2	68	97.8	84.1	40.1	74.0	97.8	84.1	40.1	74.0
3	94	144.6	112.4	54.3	103.8	138.5	116.9	54.2	103.2
4	120	193.7	140.6	68.4	134.2	186.0	145.4	68.1	133.2
5	146	244.2	168.6	82.4	165.1	232.9	175.7	81.9	163.5
6	172	295.5	196.6	96.4	196.2	282.4	204.4	95.7	194.2
7	198	347.4	224.6	110.5	227.5	331.5	234.1	109.6	225.1
8	224	399.6	252.5	124.5	258.8	382.1	262.8	123.4	256.1
B3LYP/6-31G(d)									
1	42	62.0	62.0	27.3	50.4	62.0	62.0	27.3	50.4
2	68	116.2	94.6	42.2	84.4	116.2	94.6	42.2	84.4
3	94	178.0	126.4	57.1	120.5	167.4	133.3	57.0	119.2
4	120	244.6	157.9	71.9	158.1	229.8	165.3	71.6	155.6
5	146	314.3	189.4	86.6	196.8	291.8	200.3	86.1	192.7
6	172	385.9	220.8	101.3	236.0	358.4	232.7	100.6	230.5
7	198	458.7	252.1	116.0	275.6	424.7	266.8	115.0	268.8
8	224	532.5	283.4	130.6	315.5	493.5	299.1	129.5	307.4
HF/cc-pVDZ									
1	42	58.2	58.2	30.3	48.9	58.2	58.2	30.3	48.9
2	68	102.8	88.6	46.8	79.4	102.8	88.6	46.8	79.4
3	94	151.8	118.4	62.9	111.0	145.5	123.1	62.8	110.4
4	120	203.2	147.9	78.9	143.3	195.1	153.0	78.6	142.2
5	146	256.1	177.3	94.8	176.1	244.2	184.8	94.4	174.5
6	172	309.9	206.7	110.8	209.1	296.1	214.9	110.1	207.0
7	198	364.2	236.0	126.7	242.3	347.6	246.0	125.8	239.8
8	224	419.0	265.2	142.5	275.6	400.5	276.1	141.5	272.7
B3LYP/cc-pVDZ									
1	42	65.8	65.8	31.9	54.5	65.8	65.8	31.9	54.5
2	68	122.2	100.0	49.1	90.5	122.2	100.0	49.1	90.5
3	94	186.5	133.4	65.9	128.6	175.5	140.5	65.8	127.3
4	120	255.8	166.5	82.7	168.3	240.5	174.1	82.3	165.6
5	146	328.4	199.5	99.3	209.1	304.9	210.7	98.8	204.8
6	172	403.0	232.5	115.9	250.5	374.4	244.5	115.2	244.7
7	198	478.8	265.4	132.6	292.3	443.4	280.2	131.7	285.1
8	224	555.6	298.0	149.2	334.3	515.0	314.2	148.0	325.7

All values are in a.u.

Table 6
Dipole polarizabilities for both cyclo-linear BN-acene and cyclo-zigzag BN-acene series.

N_r	N_e	Cyclo-linear BN-acene				Cyclo-zigzag BN-acene			
		α_{LL}	α_{MM}	α_{NN}	$<\alpha>$	α_{LL}	α_{MM}	α_{NN}	$<\alpha>$
HF/6-31G(d)									
6	136	148.8	148.8	170.0	155.9	148.8	148.8	176.6	158.1
7	162	178.8	178.8	196.8	184.8				
8	188	209.9	209.9	223.7	214.5	206.2	206.2	232.6	215.0
9	214	241.9	241.9	250.9	244.9				
10	240	**274.4**	**274.4**	**278.1**	**275.7**	267.1	267.1	288.7	274.3
12	292	340.9	340.9	333.0	338.2	330.2	330.2	345.3	335.2
14	344	408.5	408.4	388.1	401.7	**394.7**	**394.7**	**402.1**	**397.2**
16	396					460.2	460.2	459.3	459.9
B3LYP/6-31G(d)									
6	136	172.2	172.1	189.9	178.1	169.9	169.6	200.7	180.1
7	162	209.4	209.1	219.5	212.7				
8	188	**249.7**	**248.8**	**248.8**	**249.1**	239.8	239.8	263.9	247.8
9	214	290.6	288.5	279.9	286.4				
10	240	332.0	331.9	310.5	324.8	316.1	316.0	327.3	319.8
12	292	419.1	419.1	372.0	403.4	**396.4**	**396.4**	**391.3**	**394.7**
14	344	509.3	508.6	433.8	483.9	480.1	479.0	455.7	471.6
16	396					565.2	563.6	520.6	549.8
HF/cc-pVDZ									
6	136	160.9	160.9	177.2	166.4	160.2	160.2	185.0	168.5
7	162	193.0	193.0	205.3	197.1				
8	188	233.6	226.3	226.3	228.7	221.9	221.9	243.8	229.2
9	214	**260.2**	**260.2**	**262.0**	**260.8**				
10	240	294.9	294.9	290.6	293.5	287.0	287.0	302.7	292.2
12	292	365.5	365.5	348.1	359.7	354.3	354.3	361.9	356.8
14	344	437.4	437.4	406.0	426.9	**425.6**	**424.8**	**424.8**	**425.0**
16	396					492.8	492.7	481.3	488.9
B3LYP/cc-pVDZ									
6	136	186.2	186.2	198.9	190.4	183.3	183.1	210.8	192.4
7	162	225.7	225.4	230.0	227.0				
8	188	**267.3**	**261.5**	**267.3**	**265.4**	257.6	257.6	277.3	264.2
9	214	311.1	309.4	293.2	304.6				
10	240	354.9	354.4	325.2	344.8	**338.3**	**338.3**	**343.6**	**340.1**
12	292	446.5	446.4	389.6	427.5	423.0	423.0	410.5	418.8
14	344	541.1	540.6	454.4	512.0	511.1	509.8	477.8	499.6
16	396					600.0	599.9	545.6	581.8

All values are in a.u.

one can extrapolate $<\alpha>$ and various components of α tensor for every unlimited BN-acenes and cyclo BN-acenes series.

4. Conclusion

The observed linear relations among total electronic energies in homologous series are very topical nowadays in quantum chemistry [30,38–40,42,51–63]. Since presently, it is not possible to obtain reliable ab initio data on large molecules directly, finding such relations are useful to predict energy of large molecules.

In this paper, we have calculated the energy properties (total electronic energy, zero point energy correction, thermal energy correction, the change in ΔH_f^0 on going from 0 to 298 K, atomization energy), dipole polarizability, and the several important bands in the UV spectra (*p*, α, and β bands) for BN-acenes and cyclo BN-acenes. The results presented in this account show some interesting regularities among these properties of all homologous series versus the total number of electrons and the number of rings as well.

The HF/DFT calculations have shown that the energy properties and components of the polarizability values of all series, change linearly with the number of ring as well as the number of electrons; the same as their polyacene analogues [30]. These linear relations provide a valuable method to estimate the properties of larger molecules, where high quality quantum chemical calculations would be impractical. It is interesting to mention that by these relations; despite point group of all members of a homologous series remaining intact; it has been found that one molecule in every cyclo BN-acene series benefits an *isotropic* polarizability while the rest of molecules of that series have *anisotropic* polarizabilities.

We have shown computationally that all BN-acenes and cyclo BN-acenes exhibit a non-zero band gap. Also, we have observed that despite continuous decrease in the band gap of BN-acenes with increase of the number of rings and the electrons, band gap of cyclo-zigzag BN-acenes is nearly constant and that of cyclo-linear BN-acenes oscillates as the number of rings and the electrons increase.

Work along this line is in progress in our laboratory. Future research will determine the atomic energies and charges and their transferability of the constituent atoms of these compounds within QTAIM framework. Detailed tables with calculated properties for the molecules studied herein can be obtained from Supporting information or the authors upon request.
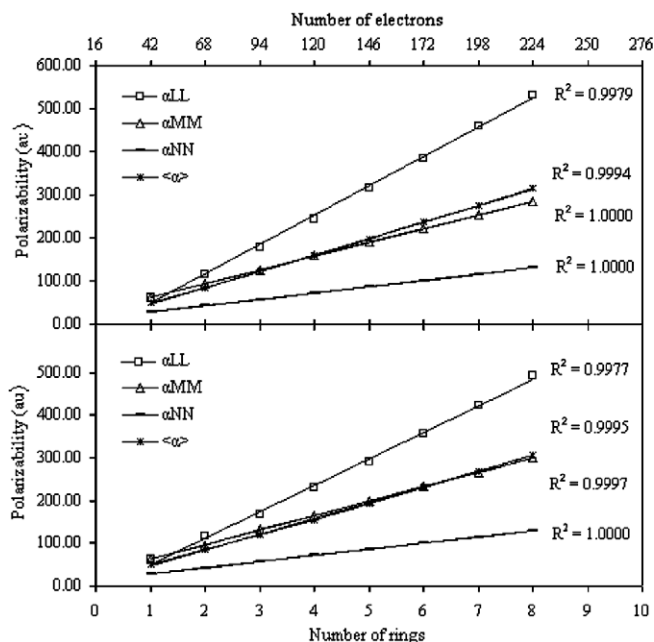
Fig. 4. Graphical representation of calculated dipole polarizabilities for both linear BN-acenes (up) and zigzag BN-acenes (down) by the B3LYP/6-31G(d).
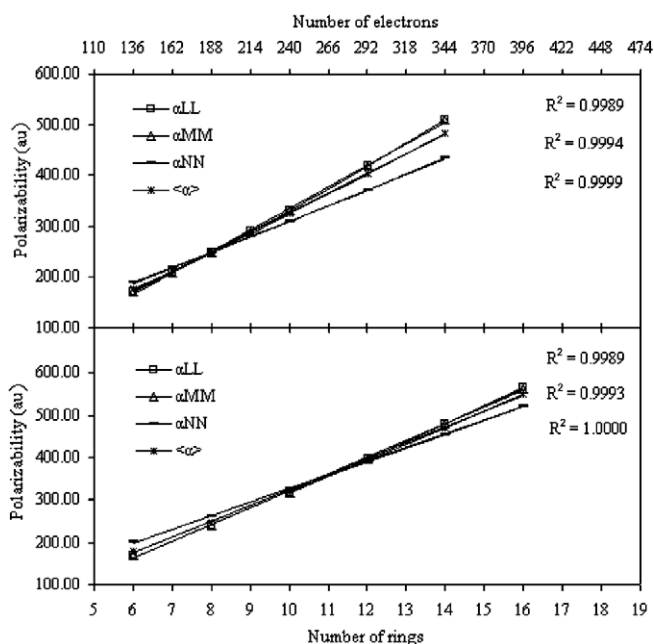

Fig. 5. Graphical representation of calculated dipole polarizabilities for both cyclo-linear BN-acene (up) and cyclo-zigzag BN-acene (down) series by the B3LYP/6-31G(d).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2009.02.042.

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