

## **DFT Study of Phenanthrene adsorption on a BN Nano-Ring**

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### **ABSTRACT**

To investigate non-bonded interaction of Phenanthrene and BN nanostructure, geometric structure of Phenanthrene and B12N12 nano-ring with B3LYP method and 6-31g\* basis set are optimized by using ab initio gaussian quantum chemical package. The main purpose of this study was to evaluate changes of electronic properties of aromatic compound in presences Nano ring field. Therefore reactivity and stability of Phenanthrene alone and in the presence of B12N12 nanoring checked by density functional theory. To studying the non-bonded interaction energies between Phenanthrene and B12N12 nano-ring at the first time we determined the best orientation and distance of optimized structure and then NBO and NMR calculations have been done that explains reduce the reactivity, increase stability of Phenanthrene. So that shows HOMO orbitals matches the Phenanthrene and LUMO orbitals matches the Nano ring. Then charge transfer of Phenanthrene and Phenanthrene - B12N12 studies that represents the flow of electrons from the Nano ring to the Phenanthrene.

**Keywords:** DFT; Ab initio; NMR; NBO; PAHs

### **INTRODUCTION**

Fullerene compounds as nano-structures that have special properties considered Late Twentieth Century. Boron nitride Fullerenes is also one of the most stable fullerene structures that in recent years due to their inherent capabilities and special properties compared to similar carbon compounds in the fields of scientific and theoretical research has been done on them. Carbon Fullerenes bonds are non-polar, While boron nitride fullerenes due to electronegativity difference between the atoms, are polar bonds and can have an effective interactions. Polycyclic Aromatic Hydrocarbons (PAHs) occur naturally in

coal, Crude oil and gasoline. PAHs compounds are also products made from fossil fuels, asphalt and pitch. By converting coal to natural gas and the incomplete combustion of fossil fuels and garbage, PAHs compounds are released into the air. Which is much more incomplete combustion process more compounds released. PAHs compounds in the environment, water, soil and air are found and the months and years will remain in these areas. The amount of these compounds in urban air is 10 times higher than non-urban air. Subject carcinogenic poly nuclear aromatic compounds are still

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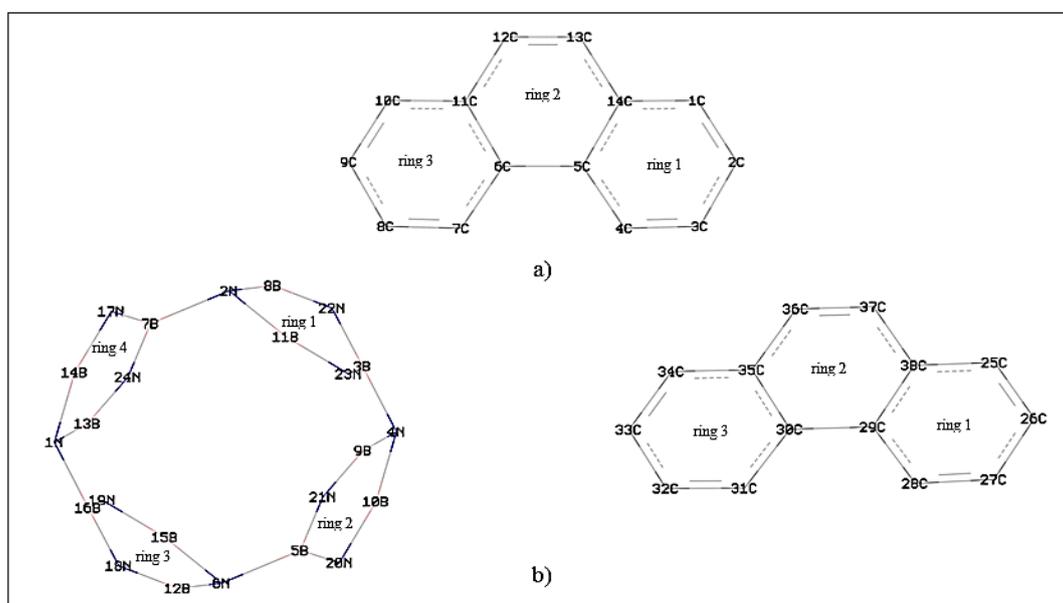
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requires further study. The carcinogenic effects of a number of compounds of this group, in laboratory animals has been proven, but it is not known whether humans as a result of exposure to these compounds is cancer or not. In this study, changes in the properties one of these compounds in the presence of nanostructures reviewed. After the discovery of C60 [1], carbon nano structures such as fullerene clusters, nanotubes, nano-capsules, cones and cubes have been reported [1-4]. Boron nitride Nanostructure has a band gap energy of about 6 eV it is expected that different electronic, optical and magnetic properties reveal [4]. Therefore, many studies on BN nanomaterials such as BN nanotubes [4,5], BN nanocapsules [4], BN clusters [3,4] and BN nanoparticles [6,7] have been reported, it is expected that these compounds to be useful for the electronics, semiconductor with high thermal stability and nanowires. The number of BN clusters [8-12] and BN nano-rings [13-16] have been studied using theoretical methods. In this study, the Phenanthrene aromaticity

properties as a known carcinogen combination, in interaction with B12N12 Nanoring theoretically studied. Because prolonged contact to Phenanthrene, causes detrimental effects on manufacturer tissue of blood cells.

## COMPUTATIONAL METHOD

Geometric structure of Phenanthrene molecule and B12N12 nano-ring with B3LYP method and 6-31g\* basis set is optimized. The aim of this study is determination the electronic structure, structural stability or reduction in reactivity of Phenanthrene in the presence B12N12 Nano ring by using theoretical methods. The best angle and distance values for the two adsorbed molecules equal to the  $0.0^\circ$  and  $3.0 \text{ \AA}$ , respectively. Optimized structure shown in (Fig. 1) and adsorption energy for optimized structure of Phenanthrene -B12N12 equal to  $-0.2735 \text{ kcal/mol}$ . So other calculations related to NBO, NMR, Freq and NICS for optimum structure at the level of B3LYP / 6-31g \* was used.



**Fig. 1.** a) optimized structure of Phenanthrene b) optimized structure of Phenanthrene - B12N12 nanoring.

## RESULT AND DISCUSSION

Thermodynamic data such as Sum of electronic and zero-point Energies (E+ZPE), Sum of electronic and thermal Energies (E+T), Sum of electronic and thermal Enthalpies (E+H) and Sum of electronic and thermal Free Energies (E+G) values of Phenanthrene, B12N12 and B12N12- Phenanthrene at B3LYP method with 6-31g\* basis set have been calculated. The energy values are given in Tables 1. Energy values reflect the stability of compounds.

In this study GIAO method for the measurement NMR parameters of Phenanthrene and Phenanthrene - B12N12 nano ring used. The results are reported in Table 2 and 3. According to the data of the table it is clear that 14 carbon atom that is shared between 1 and 2 rings and 11 carbon atom that is shared between 2 and 3 rings in Phenanthrene molecule appeared at  $\sigma = 64.864$  ppm and with the lowest chemical shift. When the Phenanthrene is located adjacent to B12 N12 Nanoring, lowest chemical shift related to 35 and 38 carbon atoms and appeared at  $\sigma = 64.843$  ppm. So, chemical shift of 31 and 32 carbon atoms increases which due to its position in the center of the magnetic field

of ring 2 of nano-ring B12N12. and since 31 carbon atoms is also in the aromaticity field of 2 ring of the molecule phenanthrene, as a result, chemical shifts will be more than 32 carbon atoms so that the 32 carbon atom and 31 carbon atom appeared at  $\sigma = 70.688$  ppm and at  $\sigma = 73.307$  ppm respectively. But 33 carbon atoms along the 4 nitrogen atom of Nanoring (with the effect of electron-induced attraction) is a caused deshieldings 33 carbon atoms of the phenanthrene and appears at  $\sigma = 70.785$  ppm and above than 34 carbon atoms. But 34 will appears at  $\sigma = 67.461$  ppm. Because 34 carbon is located in front of the 3 boron atom that is electropositive little impact on the 34 carbon chemical shift.

The nucleus-independent chemical shift (NICS) is a computational method that calculates the absolute magnetic shielding at the center of a ring. Nucleus-Independent Chemical Shifts Values of Phenanthrene and Phenanthrene-B12N12 values in Table 3 shows that the aromaticity and reactivity of Phenanthrene compound in the presence of nano ring field reduced.

**Table 1.** Sum of thermochemical parameters of Phenanthrene, B12N12 and Phenanthrene - B12N12

Compounds	E+ZPE (Hartree/Particle)	E+T (Hartree)	E+H (Hartree)	E+G (Hartree)	S (cal/mol-Kelvin)
Phenanthrene	-539.343	-539.334	-539.333	-539.378	95.828
B12N12	-955.561	-955.544	-955.543	-955.605	130.380
Phenanthrene - B12N12	-1494.904	-1494.879	-1494.878	-1494.963	178.638

**Table 2.** NMR parameters of *phenanthrene* at B3LYP / 6-31g \* (The units are in ppm)

Atomic number	Phenanthrene						
	Isotropic	Anisotropy	$\Delta\sigma$	$\delta$	$\eta$	$\Omega$	$\kappa$
1 C	67.4616	144.3275	144.3275	96.2183	0.851181	185.2771	-0.11592798
2 C	70.6452	163.4072	163.4072	108.9381	0.754383	204.4977	-0.196263821
3 C	70.501	161.3497	161.3498	107.5665	0.772563	202.9007	-0.180861377

Continued Table 2

4 C	73.3082	160.7431	160.7431	107.1621	0.74389	200.6015	-0.205221795
5 C	65.8524	184.8751	184.8751	123.25	0.218633	198.3483	-0.728291596
6 C	65.8524	184.875	184.8751	123.25	0.218633	198.3483	-0.728291596
7 C	73.3081	160.7432	160.7432	107.1621	0.743894	200.6018	-0.205219993
8 C	70.5009	161.3498	161.3498	107.5665	0.772564	202.9008	-0.180861288
9 C	70.6452	163.4072	163.4072	108.9381	0.754383	204.4977	-0.196263821
10 C	67.461	144.3274	144.3274	96.219	0.851175	185.277	-0.115915089
11 C	64.8647	194.0071	194.0071	129.338	0.119005	201.703	-0.84738105
12 C	68.4668	136.3373	136.3373	90.8916	0.95558	179.7644	-0.033687426
13 C	68.4669	136.3373	136.3373	90.8915	0.955581	179.7644	-0.033689095
14 C	64.8645	194.0072	194.0072	129.3382	0.119007	201.7033	-0.847376815

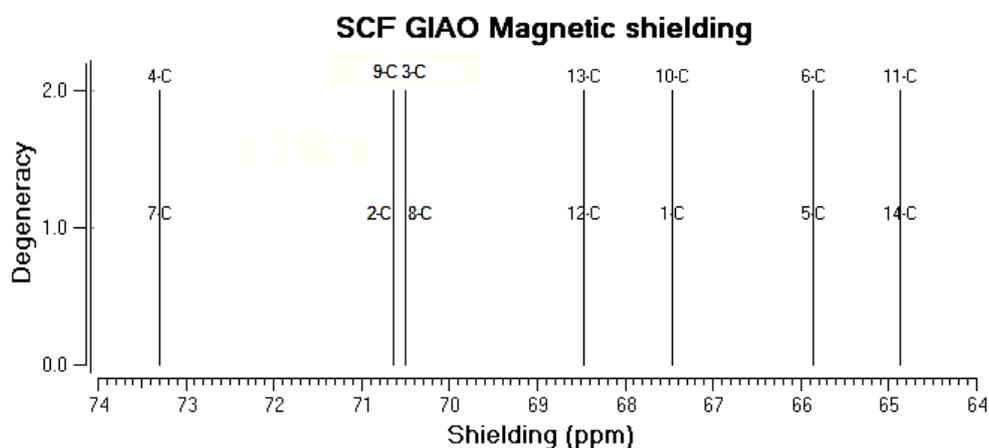
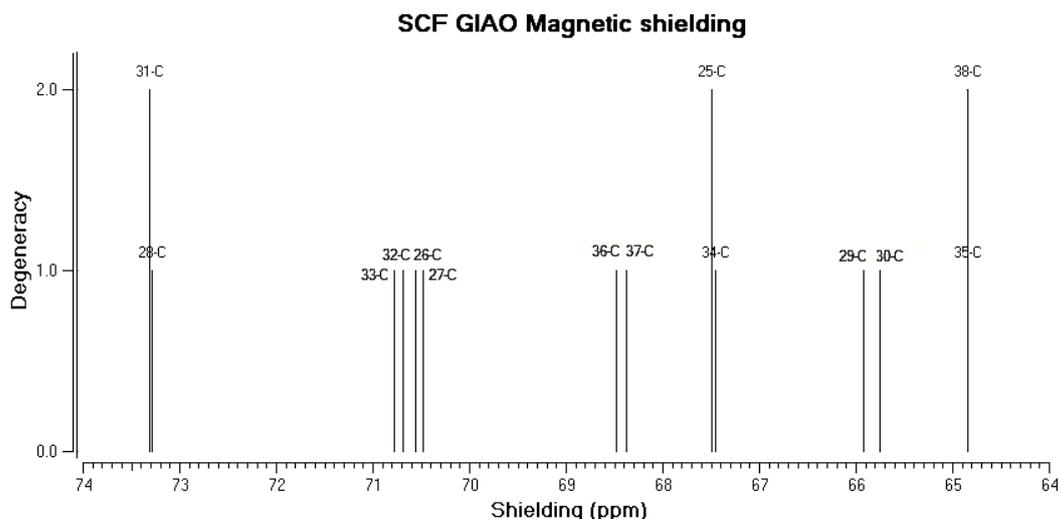


Fig. 2.: GIAO magnetic shielding of phenanthrene

Table 3. NMR parameters of phenanthrene -B12N12 nano ring at B3LYP / 6-31g \*(The units are in ppm)

Atomic number	phenanthrene-B12N12						
	Isotropic	Anisotropy	$\Delta\sigma$	$\delta$	$\eta$	$\Omega$	$\kappa$
25 C	67.4901	144.392	144.3927	96.2618	0.850888	185.3467	-0.1161
26 C	70.5544	163.259	163.2591	108.8394	0.752522	204.2111	-0.1978
27 C	70.483	161.3145	161.3145	107.543	0.773332	202.8977	-0.1802
28 C	73.2842	160.5449	160.5449	107.03	0.748153	200.5823	-0.2015
29 C	65.9266	184.7384	184.7385	123.159	0.21542	198.0039	-0.7320
30 C	65.7569	184.4465	184.4465	122.9643	0.213098	197.5482	-0.7347
31 C	73.3071	160.3762	160.3763	106.9175	0.748806	200.4065	-0.2010
32 C	70.6882	160.029	160.0291	106.6861	0.794667	202.419	-0.1623
33 C	70.7854	162.0826	162.0826	108.0551	0.735601	201.8253	-0.2123
34 C	67.4609	143.7166	143.7166	95.8111	0.862518	185.036	-0.1067
35 C	64.843	193.6259	193.6259	129.0839	0.122533	201.5344	-0.8430
36 C	68.4855	135.9775	135.9775	90.6517	0.965231	179.7274	-0.0263
37 C	68.3814	136.2239	136.224	90.8159	0.959238	179.781	-0.030
38 C	64.8436	193.7995	193.7994	129.1996	0.121773	201.6659	-0.8439



**Fig. 3.** GIAO magnetic shielding of phenanthrene -B12N12 nano ring.

**Table 4.** Nucleus-Independent Chemical Shifts Values of Phenanthrene and Phenanthrene-B12N12

Compounds	Nucleus-Independent Chemical Shifts Values / (ppm)		
	ring 1	ring 2	ring 3
Phenanthrene	-3.6193	-4.5981	-3.6193
Phenanthrene-B12N12	-3.6738	-4.3127	-2.9994

NBO analysis is done for *Phenanthrene* and *Phenanthrene-B12N12* at B3LYP/6-31g\*. NBO analysis results are reported in Table 5. Electronic properties such as Ionization energy (I), Electron affinity (A), energy gap (Eg), electronic chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ), electro philicity index ( $\omega$ ), global hardness (s) and charge transfer ( $\Delta n$ ) can be obtained using NBO analysis. According to the data of Table 5 can be understood the energy gap for Phenanthrene, B12N12 and Phenanthrene - B12N12 Nano ring are 4.753 eV, 4.371 eV and 2.538 eV respectively. By comparing these values, we find that the presence of Nano ring with *Phenanthrene* is a factor for more stability and less reactivity of *Phenanthrene*. Charge transfer for *Phenanthrene* - B12N12 Nano ring is 2.83 eV, that represents the flow of electrons from the Nano ring to the *Phenanthrene*, and charge

transfer can be seen in the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) Orbitals diagram (Fig.4). So that HOMO orbitals matches the Phenanthrene and LUMO orbitals matches the Nano ring.

**CONCLUSION** Compare Carbon NMR spectra of aromatic compound alone and in the presence of nano-ring can be found that the presence of nano-rings on the side aromatic compounds can cause dishield carbon atoms is close to the nanoring and this leads to a change in chemical shift toward higher deltas is. Also results of HOMO and LUMO molecular orbitals the justification for the charge transfer of the Nano ring to the Phenanthrene. So that the shape related to molecular orbitals, HOMO orbitals based on aromatic compound and LUMO orbitals based on the Nano ring as

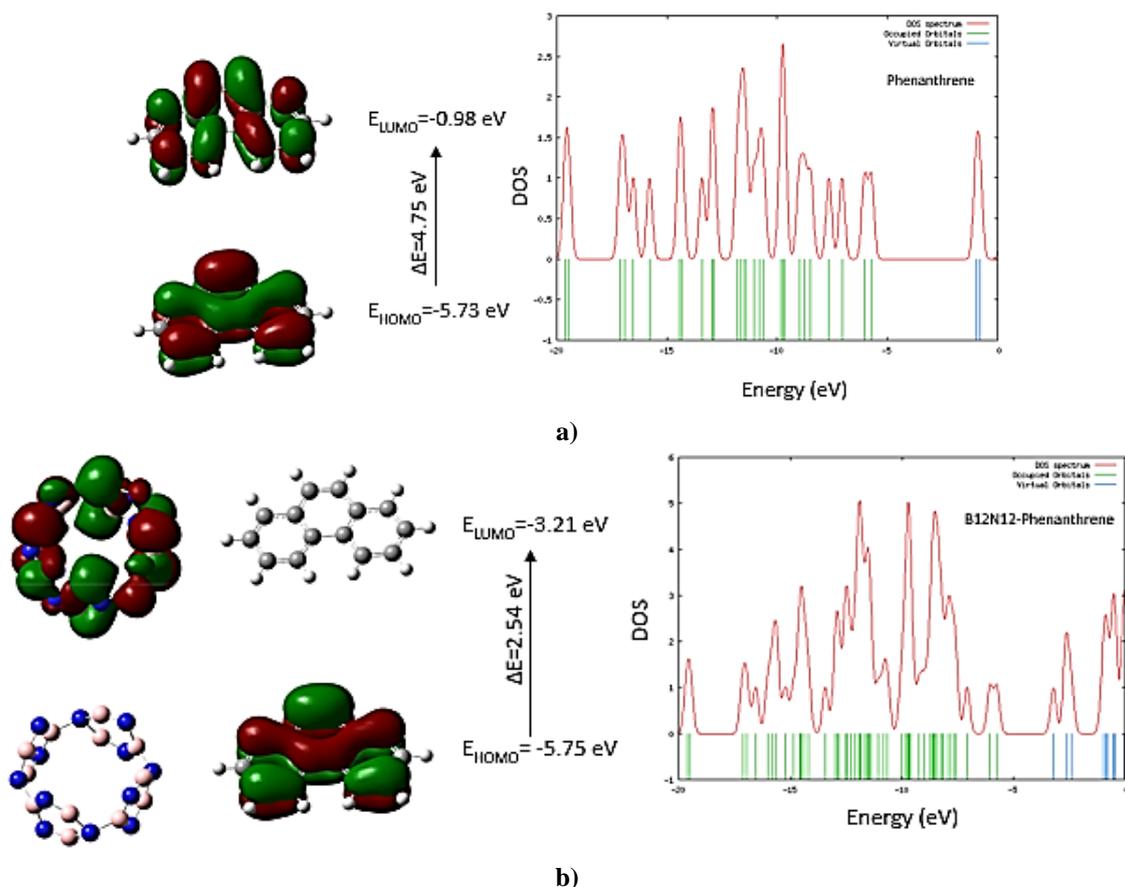


Fig .4. LUMO and HOMO molecular orbitals and DOS diagrams of a) Phenanthrene and b) Phenanthrene –B12N12.

Table 5: Electronic properties of Phenanthrene and B12N12- Phenanthrene at B3LYP / 6-31g \*

Compounds	NBO data at B3LYP / 6-31g *									
	LUMO (ev)	HOMO (ev)	I(ev)	A(ev)	Eg(ev)	EF(ev)	η(ev)	ω(ev)	s(ev <sup>-1</sup> )	Δn
Phenanthrene	-0.980	-5.733	5.733	0.980	4.753	-3.356	2.376	2.370	0.210	1.412
B12N12	-3.176	-7.548	7.548	3.176	4.371	-5.362	2.186	6.577	0.229	2.453
B12N12-Phenanthrene	-3.212	-5.750	5.750	3.212	2.538	-4.481	1.269	7.910	0.394	3.531

well as the results of the carbon NMR spectrum is justified.

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### REFERENCES

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien,

R.F. Curl and R.E. Smalley, Nature, 318 (1985) 162.

[2] S. Iijima, Nature. 354 (1991) 56.

[3] T. Oku, T. Hirano, M. Kuno, T. Kusunose, K. Niihara and K. Sugauma, Mater. Sci. Eng. B. 74 (2000) 206.

[4] T. Oku, M. Kuno, H. Kitahara and I. Narita, Int. J. Inorg. Mater. 3 (2001) 597.

[5] W. Mickelson, S. Aloni, W.-Q. Han,

- J. Cumings and A. Zettl, *Science*. 300 (2003) 467.
- [6] T. Oku, K. Hiraga, T. Matsuda, T. Hirai and M. Hirabayashi, *Diamond Relat. Mater.* 12 (2003) 1138.
- [7] T. Oku, K. Hiraga, T. Matsuda, T. Hirai and M. Hirabayashi, *Mater.* 12 (2003) 1918.
- [8] F. Jensen and H. Toflund, *Chem. Phys. Lett.* 201 (1993) 89.
- [9] M.E. Zandler, E.C. Behrman, M.B. Arrasmith, J.R. Myers and T.V. Smith, *J. Mol. Str. (Theochem)*. 362 (1996) 215.
- [10] G. Seifert, P.W. Fowler, D. Mitchell, D. Porezag and Th. Frauenheim, *Chem. Phys. Lett.* 268 (1997) 352.
- [11] Z. Slanina, M.L. Sun and S.L. Lee, *Nanostruc. Mater.* 8 (1997) 623.
- [12] H.Y. Zhu, T.G. Schmalz and D.J. Klein, *Int. J. Quantum Chem.* 63 (1997) 393.
- [13] M. Monajjemi, V.S. Lee, M. Khaleghian, B. Honarparvar and F. Mollaamin, *J. Phys. Chem. C.* 114 (2010) 15315.
- [14] M. Monajjemi, *Struct. Chem.* 23 (2011) 551.
- [15] M. Monajjemi and J.E. Boggs, *J. Phys. Chem. A.* 117 (2013) 1670.
- [16] M. Monajjemi and M. Khaleghian, *J. Cluster Sci.* 22 (2011) 673.