

A comparative study on the $B_{12}N_{12}$, $Al_{12}N_{12}$, $B_{12}P_{12}$ and $Al_{12}P_{12}$ fullerene-like cages

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Abstract The stability, geometry and electronic structure of the title nanoclusters were compared by using density functional theory (DFT) calculations. Their electrical property analysis showed that the relative magnitude of the HOMO-LUMO gaps (eV) that are average values from the calculated results with five different DFT functionals is as follows:

$$B_{12}N_{12}(7.02) \gg Al_{12}N_{12}(4.09) > B_{12}P_{12}(3.80) > Al_{12}P_{12}(3.39).$$

Computing the standard enthalpy and the Gibbs free energy of formation, it was found that the $B_{12}N_{12}$ structure is thermodynamically stable at 298 K and 1 atmosphere of pressure, while the $Al_{12}N_{12}$ structure may be stable at low temperatures. Due to positive values of change of enthalpy and entropy of formation for both the $B_{12}P_{12}$ and $Al_{12}P_{12}$ clusters, it seems that their formation from the consisting atoms is not spontaneous at any temperature.

Keywords Density functional theory · Enthalpy of formation · Fullerene-like nanoclusters · Gibbs free energy · Stability

Introduction

The large-scale isolation of C_{60} in 1985 [1] makes nanocluster science very interesting and the literature in the field is growing rapidly. In recent years, numerous efforts have been devoted to the study of possible fullerene-like structures constructed of other elements, rather than carbon, for their specific physical and chemical properties [2–5]. Specially, studies of small III–V clusters have become routine works in the literature as they are used in fast micro-electronic devices and light-emitting diodes [6, 7].

Theoretical studies of several $(XY)_n$ clusters ($X=B, Al, \dots$ and $Y=N, P, \dots$) predicted the fullerene-like cages $X_{12}Y_{12}$ to be the most stable ones [8, 9]. These facts show that the fullerene-like cages $(XY)_n$ may be magic clusters, having inherent special stability when n is equal to 12. Oku et al. [10] synthesized nanocage clusters of $B_{12}N_{12}$ detected by laser desorption time-of-flight mass spectrometry. They showed that $B_{12}N_{12}$ clusters consisted of 4- and 6-membered rings of BN. Other papers on the $B_{12}N_{12}$ nanocluster topics are available in the literature [11, 12].

If boron and nitrogen atoms of the BN cluster are replaced by the heavier elements of Groups III and V, the clusters are expected to be less strained. Wu et al. have studied the structure and energy of $(AlN)_n$ cages ($n=2-41$), theoretically, showing that the $Al_{12}N_{12}$ is energetically the most stable cluster in this family and would thus be an ideal inorganic fullerene-like cage. Wang et al. suggested that these clusters are ideal materials for hydrogen storage applications under ambient thermodynamic conditions [13].

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However, to the best of our knowledge there is no report on the synthesis of these nanocages.

AIP clusters are prominent targets of study with heavier atoms due to their higher vibrational frequencies, facilitating the observation of vibrational progressions in photoelectron spectra. Additionally, the smaller number of electrons makes them more amenable to electronic structure calculations. So far, several *ab initio* calculations have been carried out on the properties of Al_nP_m clusters by several groups [14–16].

BP 4- and 6-membered rings have been made available previously [17]. Th BP is a refractory semiconductor compound with peculiar properties. It is a III–V material with a strong covalent binding character, its zinc blende structural phase is the most stable one, and it is a promising material for use in optoelectronic and microelectronic devices working under difficult conditions such as high temperatures or aggressive environments [18].

We are interested in a comparative study on the thermochemistry of $B_{12}N_{12}$, $Al_{12}N_{12}$, $B_{12}P_{12}$ and $Al_{12}P_{12}$ nanoclusters by means of density functional theory method. We also comparatively will investigate their structural and electrical properties under identical conditions. Previously, using semiempirical AM1 method, Dumitrescu et al. have studied some properties and enthalpy of formations of these clusters [19]. It seems that AM1 method cannot efficiently describe such systems and accurate methods are needed to

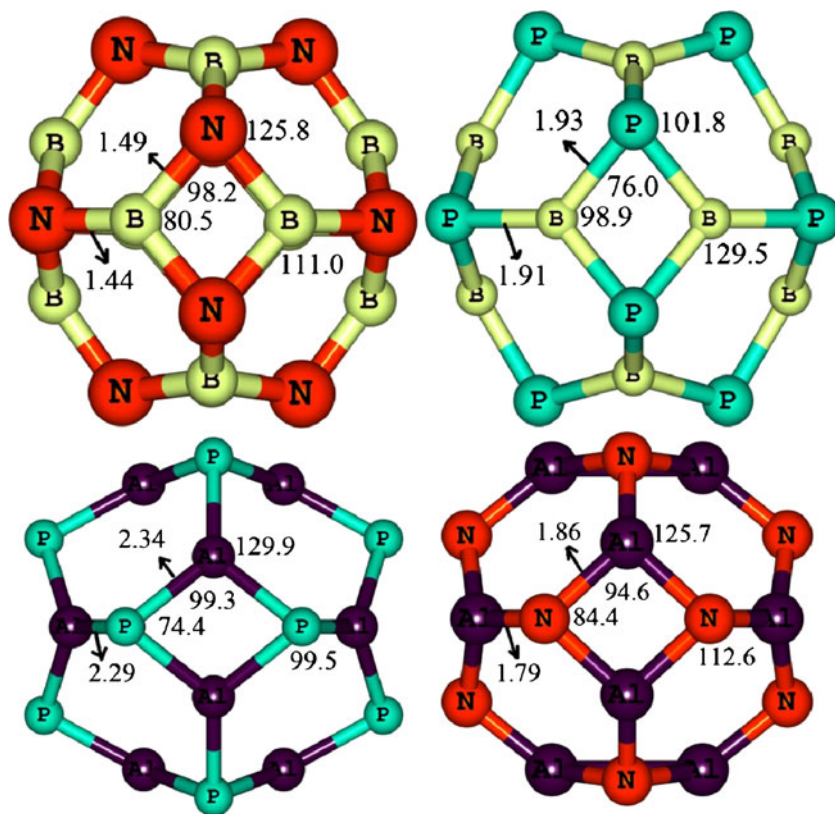
gain nearly exact results. However, we achieved different results in comparison to those of Dumitrescu et al.

Computational details

We selected four fullerene-like $X_{12}Y_{12}$ ($X = B$ or Al and $Y = N$ or P) nanocluster; their optimized parameters were shown in Fig. 1. Structure optimizations and all energy calculations were performed using spin-unrestricted B3LYP/6–31 G* level of theory. Harmonic vibrational frequency calculations confirmed the stationary points as a minima structure on the potential energy surfaces. The B3LYP functional, is a combination of HF with a DFT based on the Becke three-parameter exchange coupled with the Lee–Yang–Parr (LYP) correlation potential [20–22], and is one of the most popular hybrid DFT methods in the study of nanostructured materials [23–26]. Previously, it has been shown that the geometrical structure of fullerene (C_{60}) predicted by the B3LYP calculations is in very good agreement with experiment [27]. The spin-unrestricted formalism has been used here, because in calculation of binding energy of clusters, we have to calculate the energy of open shell atoms with spin multiplicity more than one.

Furthermore, we have shown that 6–31 G* is the most optimal basis set from the standpoints of calculation time and accuracy [28]. Previously, benchmark calculations of

Fig. 1 Geometrical parameters of optimized structures of the $B_{12}N_{12}$, $Al_{12}N_{12}$, $B_{12}P_{12}$ and $Al_{12}P_{12}$ inorganic fullerene-like cages. The distances and angles are in angstrom and degree, respectively



Wu et al. on the $B_{12}N_{12}$ cages have shown that the B3LYP results have the same trend as those of MP2 calculations, and B3LYP/6-311+G* gives both qualitative and quantitative agreement with the B3LYP/6-31 G*, and therefore the basis set effect is negligible [29]. In addition, other four DFT functionals were used in the HOMO-LUMO gap (E_g) calculations that are listed in Table 1. All calculations reported here were carried out using a locally modified version of the GAMESS electronic structure program [30].

Results and discussion

The optimized structures of the title nanoclusters with the geometrical parameters were shown in Fig. 1. In general, a significant difference between the XY fullerene and the carbon fullerenes is that XY fullerenes are composed from two different atoms. Y has a lone pair pointing out from the surface of the spheroid, while X has an empty orbital. Thus, dimers containing X facing Y would be more stable than those having Y to Y, because of the repulsion between the two lone pairs. Generally, a $X_{12}Y_{12}$ nano-cage is formed from eight 6-membered rings and six 4-membered rings with T_h symmetry so that the calculated electric dipole moment is zero. The computed nuclear magnetic resonance (NMR) spectrums of the all clusters consist of two single peaks, confirming their T_h symmetry. The smaller and greater size of angles around the Y and X atoms, respectively, is related to their hybridization. The natural bonding orbital (NBO) analysis shows that the hybridization of Y and X atoms is nearly sp^3 and sp^2 , respectively.

There are two distinct X–Y bonds in the optimized structures of $X_{12}Y_{12}$ clusters (Fig. 1); one is shared by two 6-membered rings (B_{66}) and another by 4- and 6-membered rings (B_{46}) where length of the B_{46} is somewhat greater than that of the B_{66} . As shown in Table 2, they are both shorter than the single bond in H_3X-YH_3 , but longer than the double bond in H_2X-PY_2 at spin-unrestricted B3LYP/6-31 G*. It indicates that the $X_{12}Y_{12}$ clusters have aromatic nature stabilizing by the p electron conjugation. The Mulliken charges are transferred from electropositive atom (X) to electronegative one (Y). The Mulliken charges in the

Table 1 HOMO-LUMO gap (E_g) of the $B_{12}N_{12}$, $Al_{12}N_{12}$, $B_{12}P_{12}$ and $Al_{12}P_{12}$ clusters calculated using different DFT functionals. The E_g values are in electron volts

Cluster	B3LYP	X3LYP	O3LYP	M05	M06	Mean
$B_{12}N_{12}$	6.84	6.99	6.15	7.65	7.46	7.02
$Al_{12}N_{12}$	3.93	4.05	3.43	4.69	4.37	4.09
$B_{12}P_{12}$	3.71	3.81	3.19	4.22	4.08	3.80
$Al_{12}P_{12}$	3.39	3.49	3.04	3.73	3.31	3.39

Table 2 Lengths of two individual bonds in the surface of $X_{12}Y_{12}$ clusters in comparison to that of H_3X-YH_3 and H_2X-YH_2

Cluster	B_{66}	B_{46}	H_3X-YH_3	H_2X-YH_2
$B_{12}N_{12}$	1.44	1.49	1.39	1.67
$Al_{12}N_{12}$	1.79	1.89	1.73	2.00
$B_{12}P_{12}$	1.91	1.93	1.87	1.96
$Al_{12}P_{12}$	2.30	2.34	2.33	2.57

surfaces of $B_{12}N_{12}$, $Al_{12}N_{12}$, $B_{12}P_{12}$ and $Al_{12}P_{12}$ clusters are 0.44, 0.75, 0.12 and 0.21 e, respectively (Table 2). The ionicity of the Al-N and B-N bonds is significantly more than those of the others.

To gain an accurate E_g for every studied nanocluster, we applied different DFT functionals including: B3LYP, X3LYP, O3LYP, M05 and M06 combined with the 6-31 G* basis set. The calculated results are summarized in Table 1, indicating that the E_g values are strongly dependent on the type of used functional. The O3LYP and M06 yield the smallest and largest values, respectively. Since there are no experimental data for the E_g , we calculated the average value of the results of these functionals in every case and suggested it as E_g of cluster. The relative order of magnitudes for E_g (in eV) are as follows:

$$B_{12}N_{12}(7.02) \gg Al_{12}N_{12}(4.09) > B_{12}P_{12}(3.80) > Al_{12}P_{12}(3.39).$$

The $Al_{12}P_{12}$ nanocluster has the smallest E_g among all types; therefore, it is the most electrically conductive cluster. The $B_{12}N_{12}$ case has the most electrical resistivity due to the largest E_g . All the above suggest that the $B_{12}N_{12}$ nanocluster is insulator material but the others are semiconductors. It seems that there is a definite correlation between the size of consisting atoms and E_g of clusters, i.e., the clusters that consist of the atoms with greater covalent radius have smaller E_g . It can be rationalized by this fact that the larger atoms have high polarizability and their valence electrons can freely contribute in electrical conductivity.

As shown in Table 1, the values of E_g obtained from both the M05 and M06 is somewhat greater than those from the B3LYP, X3LYP and O3LYP functionals. However, the B3LYP, X3LYP [31] and O3LYP [32] are hybrid generalized gradient approximation (GGA) functionals, which include a mixture of Hartree-Fock exchange with DFT exchange-correlation. A summary of these methods is given in Table 3. Since the theory behind these functionals is explained in the original papers, we refer the readers to the original references for those details. However, the B3LYP functional has the following form as introduced in 1994 [21]:

$$E_{XC}^{B3LYP} = (1 - a) E_X^{LSDA} + a E_X^{HF} + b \Delta E_X^{B88} + (1 - c) E_C^{LSDA} + E_C^{LYP}, \quad (1)$$

Table 3 A comparison among three different density functional theory methods

Method	X ^a	Year	Ex. ^b	Corr. ^c	Ref(s).
B3LYP	20	1994	Becke88	Lee-Yang-Parr	20, 21, 23
O3LYP	11.61	2001	OPXT	Lee-Yang-Parr	31
X3LYP	21.8	2004	Becke88 + PW91	Lee-Yang-Parr	32

^aX denotes the percentage of HF exchange in the functional.

^bExchange functional. ^cCorrelation functional

where a, b, and c were optimized to 0.20, 0.72, 0.81, respectively. The O3LYP is a three-parameter functional similar in character to B3LYP, with a=0.1161, b=0.9262 (multiplying O exchange instead of B one) and c=0.8133 [32]. The X3LYP functional also uses the form of Eq. 1, with a=218, b=0.709 (multiplying a combination of 76.5% B exchange and PW (Perdew-Wang) exchange instead of pure B one) and c=0.129 [31].

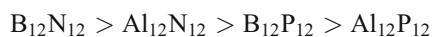
The M05 [33] and M06 [34] are hybrid meta GGA functionals in which the energy depends on the occupied orbitals not only through the HF exchange terms (as in hybrid GGAs) but also through the noninteracting spin kinetic energy densities (as in meta-GGAs) incorporate kinetic-energy density in a balanced way in the exchange and correlation functional. The M05 and M06 methods differ essentially in the inclusion of a percentage of HF exchange, in the functional forms used to represent exchange and correlation, and in parametrization.

To investigate the stability of the X₁₂Y₁₂ cages, we calculated the binding enthalpy (ΔH_b , Eq. 2) and binding Gibbs free energy (ΔG_b , Eq. 3) at 1 atm and 298 K, using the following expression. A similar equation has been used by Li et al. [35] to calculate the binding electronic energy of Al₁₂N₁₂ nanocluster.

$$\Delta H_b = [H_{\text{tot}}(X_{12}Y_{12}) - 12(H_X + H_Y)]/24 \quad (2)$$

$$\Delta G_b = [G_{\text{tot}}(X_{12}Y_{12}) - 12(G_X + G_Y)]/24 \quad (3)$$

where 12 is the number of X and Y atoms; the H_X and H_Y are enthalpy of an isolated X and Y atom also, the G_X and G_Y are the Gibbs free energies of an isolated X and Y at 1 atm and 298 K, respectively. All calculated values are negative, thus, it seems preferable to conclude that the clusters are thermodynamically stable. The relative stabilities of these clusters are as follows:

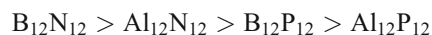


As shown from Tables 1 and 4, there is a direct relationship between the stability and E_g of clusters, namely, the greater E_g leads to more stability. Aihara et al. previously reported that T value, i.e., the E_g separation multiplied by the

Table 4 Enthalpy of binding (ΔH_b), Gibbs free energy of binding (ΔG_b), charge transfer from electropositive atom to electronegative one (Q_T), standard enthalpy of formation ($\Delta_f H^0$) and standard Gibbs free energy of formation ($\Delta_f G^0$) for the studied clusters. The energies are in kcal mol⁻¹

Cluster	ΔH_b	ΔG_b	Q _T (e)	$\Delta_f H^0$	$\Delta_f G^0$
B ₁₂ N ₁₂	-135.85	-128.7	0.44	-275.53	-48.42
Al ₁₂ N ₁₂	-98.81	-91.45	0.75	-74.67	149.29
B ₁₂ P ₁₂	-95.81	-89.03	0.12	240.08	461.03
Al ₁₂ P ₁₂	-72.62	-65.14	0.21	100.97	316.02

number of constituting atoms, is preferred as an index of kinetic stability (we mean stability against all possible chemical reactions and decomposition) of fullerene isomers [36]. They showed that fullerenes with a large T value have large minimum bond resonance energy [37]. In this study, as the number of atoms is equal in all clusters, thus, we think that the absolute values of E_g may be an appropriate factor to compare the kinetic stability of these clusters. As a result their relative kinetic stability is as follows:



this is consistent with their relative thermodynamic stability.

It seems that the binding energies are not a suitable factor for predicting the thermodynamic stability of systems; because it misses the entropic effects and the effects of vibrational, rotational energies, ect. That is, we calculated the standard enthalpy and Gibbs free energy of formation for the studied clusters. Theoretical enthalpy of formation at 298 K is calculated by subtracting calculated atomization energies (ΣD_0) from known enthalpy of formation of the isolated atoms. For any cluster, X₁₂Y₁₂, the $\Delta_f H^0$ at 1 atm and 298 K is given by:

$$\begin{aligned} \Delta_f H^0(X_{12}Y_{12}, 298K) = & 12 \Delta_f H^0(X, 298K) \\ & + 12 \Delta_f H^0(Y, 298K) - \Sigma D_0. \end{aligned} \quad (4)$$

The JANAF (NIST-JANAF Thermochemical Tables) [38] values for the atomic $\Delta_f H^0$ were used with the exception of boron, for which we used a revised value recommended by Ruscic et al.[39] based on new experimental results of Storms and Mueller [40]. The numerical values are listed in Table 5. Previously, this strategy has been frequently used to determine the $\Delta_f H^0$ of several molecules [37, 38]. Here, the JANAF values were used because determination of the $\Delta_f H^0$ for atoms of clusters is not straightforward, theoretically. For example, the reference structure for boron atom is crystal and its $\Delta_f H^0$ determination is a controversial issue [41, 42].

However, to examine the reliability of our used method in determination of $\Delta_f H^0$, we calculated the $\Delta_f H^0$ of some

Table 5 Enthalpies of formation at 298 K for gaseous atoms and ($H^{298}-H^0$) values for elements in their standard states from experiment (Ref. 3)

Atoms	$\Delta_f H^0$ (0 K)	$H^{298}-H^0$
B	136.2 ^a	0.29
N	112.53	1.04
Al	78.23	1.08
P	75.42	1.28

^a Reference 4 and 5

small atoms (including H, N, O, F) which their reference point of zero $\Delta_f H^0$ is diatomic molecules in gaseous phase. Subsequently, we compared them with the experimental values of JANAF. The calculated values and the experimental ones were listed in Table 6. Application of the statistical t-paired test [43] for the values at 0 and 298 K rendered calculated t values of 0.27 and 0.23, respectively, which are below the critical value for three degrees of freedom (viz., 3.18) at the 0.05 significance level, thus revealing the inexistence of a good consistency between experimental and uB3LYP/6–31 G* with 95% confidence. It is also noteworthy to say that Xu et al. have shown that B3LYP is one of the accurate functionals in calculation of the heat of formation [32].

The computed $\Delta_f H^0$ of the clusters are listed in Table 4, indicating that $\Delta_f H^0$ of $B_{12}N_{12}$ and $Al_{12}N_{12}$ are negative with values of -275.53 and -48.42 kcal mol⁻¹, while that of $B_{12}P_{12}$ and $Al_{12}P_{12}$ is positive. It can be concluded that the $B_{12}N_{12}$ nanocluster is thermodynamically the most stable, followed by $Al_{12}N_{12}$, and the phosphorus-containing binary cages are both unstable at room temperature. However, the synthesis feasibility of $B_{12}N_{12}$ [10] helps to rationalize our findings. Previously, using the semiempirical AM1 method, Dumitrescu et al. [19] have shown that $Al_{12}N_{12}$ cage is thermodynamically more favorable than $B_{12}N_{12}$ cluster and both the phosphorus-containing binary cages are unstable. The latter is consistent with our finding but their reported on relative stability of $B_{12}N_{12}$ and $Al_{12}N_{12}$ clusters is not. We think that the semiempirical AM1 method cannot feature the thermochemistry of materials efficiently.

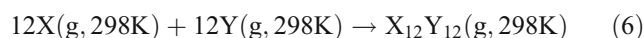
Table 6 Experimental and calculated values of enthalpy of formations (kcal mol⁻¹) of the H, N, O and F atoms at 0 and 298 K

Atom	B3LYP/6-31 G*		Experimental	
	0 K	298 K	0 K	298 K
H	51.70	52.15	51.63	52.64
N	109.67	110.12	112.53	113.57
O	61.19	61.63	58.99	60.03
F	20.33	20.77	18.47	19.52

To evaluate the entropic effect in the stability of the nanoclusters we calculated their standard Gibbs free energy of formation ($\Delta_f G^0$) using the following equation:

$$\Delta_f G^0(X_{12}Y_{12}, 298K) = \Delta_f H^0(X_{12}Y_{12}, 298K) - 298 \Delta S \quad (5)$$

where ΔS is the change of entropy for the following assumed reaction



where X and Y are atoms in the $X_{12}Y_{12}$ cluster in gas phase. Based on our calculations (Table 4) only the $\Delta_f G^0$ of $B_{12}N_{12}$ cluster is negative, demonstrating that the $B_{12}N_{12}$ formation from their consisting atoms are thermodynamically spontaneous processes at room temperature, without needing to be driven by an outside source of energy. On the other hand, formation of $Al_{12}N_{12}$ molecules from their consisting atoms may occur at low temperatures, while formation of $B_{12}P_{12}$ and $Al_{12}P_{12}$ is not thermodynamically feasible at any temperature because the ΔS is negative and $\Delta_f H^0$ is positive for this process.

It is noteworthy to say that looking at the results in Table 2. The $B_{12}P_{12}$ and $Al_{12}P_{12}$ have larger bonds compared to the other clusters. The bond H_2X-YH_2 for $Al_{12}N_{12}$ is also large. The length of the bonds for cluster $Al_{12}P_{12}$ are notably larger than the bonds of the other clusters, particularly the length of bond H_2X-YH_2 . This fact should hint that the formation of cluster $Al_{12}P_{12}$ is not likely to happen spontaneously. Also, from looking at the results in Table 4, the enthalpy of binding and Gibbs free energy of binding are negative for all the clusters, as mentioned earlier here this supports the stability hypothesis. The $\Delta_f H^0$ and $\Delta_f G_0$ for the $B_{12}P_{12}$ and $Al_{12}P_{12}$ clusters are positive. These values again hint that the formation of $B_{12}P_{12}$ and $Al_{12}P_{12}$ is not likely to happen spontaneously.

Conclusions

In summary, we have performed a DFT study on the thermochemistry and some properties of inorganic nanoclusters including $B_{12}N_{12}$, $Al_{12}N_{12}$, $B_{12}P_{12}$ and $Al_{12}P_{12}$. Their electrical property analysis showed that the relative magnitude of the HOMO-LUMO gap (eV) is as follows:

$$B_{12}N_{12}(7.02) \gg Al_{12}N_{12}(4.09) > B_{12}P_{12}(3.80) > Al_{12}P_{12}(3.39).$$

The thermodynamic stability of these inorganic clusters was studied here with calculations of their enthalpy and free energies of formation. Based on the calculations, for $P=1$ atom the $B_{12}N_{12}$ structure is thermodynamically stable at room temperature, while the $Al_{12}N_{12}$ structure may be stable at low temperatures and the two others are not stable at any temperature.

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