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The Stability and Properties of M^{n+}@ $C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0, 3) Complexes for Synthesis Application

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Abstract

The structural and electronic properties of $C_{24-2n}B_nN_n$ and M@ $C_{24-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=3 and 6) molecules are studied using the Density Functional Theory (DFT). It was found that the most interaction is in M@ $C_{24-2n}B_nN_n$ complexes (M=Be, Mg; n=3 and 6). The negative nucleus-independent chemical shifts confirm that $C_{24-2n}B_nN_n$ (n=3 and 6) cages exhibit aromatic characteristics. The molecular analysis reveals a linear correlation between isotropic polarizability values and HOMO-LUMO gaps energies in stable complexes.

Keywords: *C_{26} molecule, $C_{20}B_3N_3$ molecules, Density Functional Theory (DFT), interaction energies.*

Introduction

Among the small fullerenes, C_{26} might be another substance with potential applications. According to Kent's research, the C_{26} fullerene is the smallest energetically stable fullerene and may potentially possess superconducting properties [1]. However, the C_{26} fullerene has been synthesized, but its characterization is currently in dispute [2]. Therefore, it is significant to additional theoretically explore the endohedral complexes of C_{26} fullerene theoretically which may provide guidance for

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further experimental research in this field.

In this paper, we described a systematic theoretical study on the stability and properties of M^{n+}@ $C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0, 3) to gain insights into the understanding of the unusual chemical properties of small fullerenes and to facilitate experimental investigations on these promising new materials. The purpose of this study was to gain insight into the understanding of the unusual chemical properties of endohedral complexes of C_{26} and $C_{26-2n}B_nN_n$ to facilitate experimental investigations of the promising new materials.

Computational methods

The structures of the $C_{26-2n}B_nN_n$ and M@ $C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0 and 3) molecules were optimized by the B3LYP method[3], and 6-31G(d,p) [4, 5] is chosen as basis set. Input files have been created by Nanotube modeler version 1.6.4[6] and Gaussian viewer 3.0 softwares.

The optimization was done along with a frequency calculation for each complex to verify that the geometry was a real minimum. All electronic structure calculations have been performed using the Gaussian 2003 suite of program [7].

The interaction energy, IE, can be evaluated from the difference between energy of the complex and sum of the energies of the $C_{26-2n}B_nN_n$ and metals:

$$I.E = E(\text{complex}) - [E(C_{26-2n}B_nN_n) + E(M^{n+})]$$

The calculated interaction energies were corrected for basis set superposition errors (BSSE), which were computed for all calculations using the counterpoise correction method of Boys and Bernardi [8] .

The nucleus independent chemical shift (NICS) was used as a descriptor of aromaticity from the magnetic point of view. The index is defined as the negative value of the absolute magnetic shielding computed at ring centers [9, 10].

Results and discussion

Energetic aspect

Table 1 presents the computed energies $C_{26-2n}B_nN_n$ and M^{n+}@$C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0, and 3) molecules (Figure 1). Also, interaction energies (I.E), basis set superimposition error (BSSE) and corrected interaction energies of the complexes have been gathered.

Table 1. Calculated Energy (Hartree), interaction energy (kcal/mol), basis set superimposition error (BSSE, Hartree), and corrected interaction energy (kcal/mol), M^{n+}@ $C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0, 3) by the method B3LYP with 6-31G(d,p) basis set.

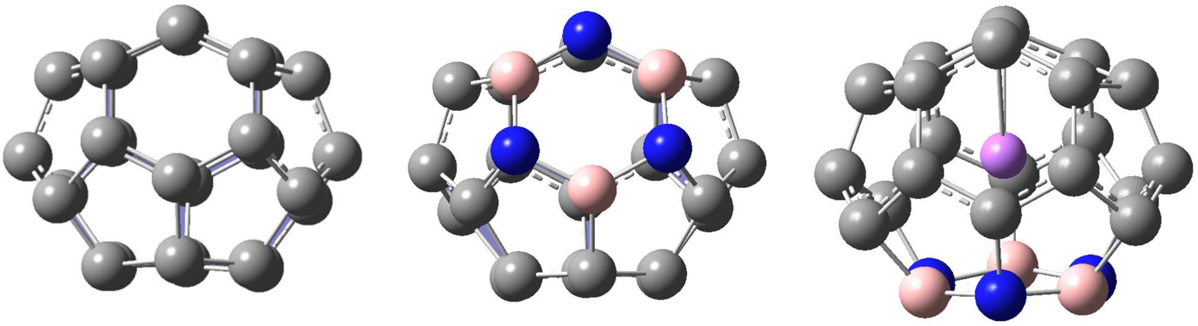
	E	BSSE	IE	$IE^{correted}$
C_{26}	-990.058	-	-	-
Li@C_{26}	-997.356	0.00512	-8.72	-5.51
Na@C_{26}	-1152.054	0.00853	53.34	58.70
K@C_{26}	-1589.415	0.00764	230.59	235.38
Be@ C_{26}	-1004.083	0.00465	-234.16	-231.24
Mg@C_{26}	-1189.437	0.00723	-95.66	-91.13
Ca@C_{26}	-1666.796	0.01003	80.42	86.72
$B_3N_3C_{20}$	-1000.540	-	-	-
Li@$B_3N_3C_{20}$	-1007.823	0.00517	0.94	4.19
Na@$B_3N_3C_{20}$	-1162.520	0.00801	63.95	68.97
K@$B_3N_3C_{20}$	-1599.891	0.00768	234.94	239.75
Be@$B_3N_3C_{20}$	-1014.562	0.00372	-231.86	-229.52
Mg@$B_3N_3C_{20}$	-1199.898	0.00704	-81.74	-77.32
Ca@$B_3N_3C_{20}$	-1677.262	0.00889	91.33	96.91

These calculations show the negative interaction energies (I.E) values for L^{i+}@ C_{26}, Be^{2+}@C^{26}, Mg^{2+}@C_{26}, Be^{2+}@$C_{20}B_3N_3$, and Mg^{2+}@$C_{20}B_3N_3$ complexes. These values indicate to decreasing of interaction between cage and metal decreases with the increasing of atomic number of metal. Also, the increasing of interaction has been seen with increasing of charge and size of metal.

On the other hand, the positive interaction energies for the other complexes signify the other interactions between metals and of cages are unstable. This instability increases with the increasing of atomic number of metal. Therefore, it can be found that the size and charge of the cation are influential factors determining the strength of the binding interaction in these systems, as in most complexes [11].

Structures

The vibrational frequencies analysis of complexes reveals no imaginary vibrational frequency, therefore, are a true minimum on the molecular potential energy surface.The optimized results show that the M atom places in the center of cage in M@C26 complexes. But, metal atom moves from center toward the pentagon ring and then binds over this position (Figure 1).



(a) (b) (c)

Figure 1. Structures of (a)C_{26}, (b)$B_3N_3C_{20}$ and (c)M^{n+}@ $C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0, 3).

Thermochemical analysis

Thermochemical analysis is studied for $C2_{6-2n}B_nN_n$ and M@ $C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0 and 3) molecules. The reaction can be considered as:

$$Mn^{+} + C_{26-2n}B_nN_n \rightleftharpoons M@\ C26\text{-}2nBnNn$$

The values of ΔH, TΔS and ΔG are reported in Table 2 in which the individual terms are referred to a temperature of 298 K.

As can be verified, the ΔS values are similar for all complexes. Since in this reaction two particles form one, ΔS should be a negative value.

The equilibrium constants of the all complexes are given in Table 2. This shows the most equilibrium constants for M=Be, and Mg complexes.

The value of ΔG increases with increasing metal ion radius which shows that the stability of the complex decline (See Table 2).

Table 2. Thermodynamic parameters for the M^{n+}@ $C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0, 3) by the method B3LYP with 6-31G(d,p) basis set.

	G	H	ΔG	ΔH	ΔS	K
C_{26}	-989.94	-989.90	-	-	-	-
Li@C_{26}	-997.24	-997.19	1.68	-7.83	-0.03	0.058555
Na@C_{26}	-1151.94	-1151.89	65.27	53.95	-0.04	1.35E-48
K@C_{26}	-1589.30	-1589.25	240.85	228.91	-0.04	2.3E-177
Be@ C_{26}	-1003.96	-1003.92	-222.22	-232.54	-0.03	9.4E+162
Mg@C_{26}	-1189.32	-1189.27	-83.91	-95.00	-0.04	3.46E+61
Ca@C_{26}	-1666.68	-1666.63	92.14	79.91	-0.04	2.66E-68
$B_3N_3C_{20}$	-1000.43	-1000.38	-	-	-	-
Li@$B_3N_3C_{20}$	-1007.71	-1007.66	10.00	1.34	-0.03	4.65E-08
Na@$B_3N_3C_{20}$	-1162.41	-1162.36	73.89	63.65	-0.03	6.49E-55
K@$B_3N_3C_{20}$	-1599.78	-1599.73	243.19	232.32	-0.04	4.5E-179
Be@$B_3N_3C_{20}$	-1014.45	-1014.40	-222.79	-230.64	-0.03	2.5E+163
Mg@$B_3N_3C_{20}$	-1199.79	-1199.74	-72.31	-82.14	-0.03	1.08E+53
Ca@$B_3N_3C_{20}$	-1677.15	-1677.10	100.06	89.39	-0.04	4.12E-74

Polarizability

Polarizabilities describe the response of a system in an applied electric field [12]. They determine not only the strength of molecular interactions (such as the long range intermolecular induction, dispersion forces, etc.) as well as the cross sections of different scattering and collision processes, but also the nonlinear optical properties of the system [13].The isotropic polarizability <α> is calculated as the mean value as given in the following equation [14]:

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

And the polarizability anisotropy invariant is:

$$\Delta\alpha = \left[\frac{(\alpha_{XX} - \alpha_{YY})^2 + (\alpha_{YY} - \alpha_{ZZ})^2 + (\alpha_{ZZ} - \alpha_{XX})^2}{2}\right]^{\frac{1}{2}}$$

The calculated anisotropic polarizability values indicate these values decrease in complexes (Table 3). On the other hand, isotropic polarizability values decrease in complexes. Also, these values show that isotropic and anisotropic polarizability are more for C_{26} and related complexesrather than $B_3N_3C_{20}$ and its complexes.

Table 3. Isotropic and anisotropic polarizability for the M^{n+}@ $C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0, 3) by the method B3LYP with 6-31G(d,p) basis set.

	αxx	αyy	αzz	<α>	Δα
C_{26}	237.32	189.11	185.54	203.99	50.09
Li@C_{26}	242.67	193.80	193.35	209.94	49.10
Na@C_{26}	241.45	196.78	196.53	211.59	44.80
K@C_{26}	240.50	203.21	202.55	215.42	37.62
Be@ C_{26}	225.37	184.19	185.77	198.44	40.42
Mg@C_{26}	240.06	192.36	192.18	208.20	47.79
Ca@C_{26}	237.27	197.25	197.06	210.52	40.11
$B_3N_3C_{20}$	220.13	198.28	183.18	200.53	32.18
Li@$B_3N_3C_{20}$	221.11	204.67	187.77	204.51	28.87
Na@$B_3N_3C_{20}$	224.53	207.74	197.05	209.77	24.00
K@$B_3N_3C_{20}$	227.28	209.57	209.84	215.56	17.58
Be@$B_3N_3C_{20}$	216.43	184.02	178.37	192.94	35.58
Mg@$B_3N_3C_{20}$	221.07	207.12	190.39	206.19	26.61
Ca@$B_3N_3C_{20}$	222.77	207.36	204.26	211.46	17.17

Frontier orbital energies and chemical hardness. The most important frontier molecular orbitals (FMOs) such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) have an important part in the chemical stability of the molecule [15]. The HOMO represents the ability to donate an electron and LUMO as an electron acceptor represents the ability to accept an electron. The energy gap between HOMO and LUMO also determines the chemical reactivity, optical polarizability and chemical hardness-softness of a molecule [16].

According to the results, frontier orbital energies decrease in complexes (Table 4). These values increase for earth alkaline complexes rather than alkaline complexes. On the other hand, there are larger values for C_{26} and related complexesrather than $B_3N_3C_{20}$ and its complexes.

To evaluate the hardness and chemical potential of these complexes, these values can be calculated from the HOMO and LUMO orbital energies using the following approximate expression:

$$\mu=(\varepsilon_{HOMO}+\varepsilon_{LUMO})/2$$

$$\eta=(\varepsilon_{HOMO}-\varepsilon_{LUMO})/2$$

Where μ is the chemical potential (the negative of the electronegativity), and η is the hardness [17, 18].

Table 4. Frontier orbital energies (Hartree), HOMO-LUMO gap energy (eV), Hardness (eV), chemical potential (eV), and electrophilicity (eV) for the M^{n+}@ $C_{26-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=0, 3) by the method B3LYP with 6-31G(d,p) basis set.

	HOMO	**LUMO**	**ΔE**	**η**	**μ**	**ω**
C_{26}	-0.207	-0.146	1.66	0.83	-4.80	13.90
Li@C_{26}	-0.377	-0.313	1.73	0.86	-9.38	50.99
Na@C_{26}	-0.378	-0.313	1.77	0.89	-9.40	49.83
K@C_{26}	-0.385	-0.317	1.83	0.91	-9.55	49.88
Be@ C_{26}	-0.543	-0.482	1.66	0.83	-13.94	116.93
Mg@C_{26}	-0.543	-0.479	1.74	0.87	-13.89	110.76
Ca@C_{26}	-0.548	-0.481	1.81	0.91	-14.00	108.16
$B_3N_3C_{20}$	-0.194	-0.144	1.36	0.68	-4.61	15.65
Li@$B_3N_3C_{20}$	-0.360	-0.313	1.27	0.64	-9.16	65.95
Na@$B_3N_3C_{20}$	-0.358	-0.315	1.17	0.58	-9.15	71.82
K@$B_3N_3C_{20}$	-0.362	-0.319	1.15	0.57	-9.26	74.87
Be@$B_3N_3C_{20}$	-0.532	-0.471	1.66	0.83	-13.64	111.80
Mg@$B_3N_3C_{20}$	-0.520	-0.480	1.09	0.55	-13.61	169.35
Ca@$B_3N_3C_{20}$	-0.521	-0.483	1.03	0.52	-13.67	181.06

The values of hardness are presented in Table 4. These values indicate complexation increases chemical hardness. C_{26} and related complexes have more hardness rather than $\mathbf{B_3N_3C_{20}}$ and its complexes. The increasing of hardness has been seen with increasing of size and decreasing of charge of metal.

The values of chemical potential are shown in Table 4. These values indicate decreasing of chemical potential in complexes. $\mathbf{B_3N_3C_{20}}$ and its complexes have more hardness rather than C_{26} and related complexes.

To evaluate the electrophilicity of these complexes, we have calculated the electrophilicity index,ω, for each complex measured according to Parr, Szentpaly, and Liu [19] using the expression:

$$\omega=\frac{\mu^2}{2\eta}$$

The values of electrophilicity index are gathered in Table 4. These values indicate the most electrophility for complexes. On the other hand, electrophlicity **$B_3N_3C_{20}$** and its complexes are more than C_{26} and related complexes. The decreasing of electrophilicity has been seen with increasing of size and decreasing of charge of metal.

Conclusion

$C_{24-2n}B_nN_n$ and M@ $C_{24-2n}B_nN_n$ (M= alkaline and earth alkaline metals; n=3 and 6) molecules have been investigated theoretically in this paper. Among the complexes M@ $C_{24-2n}B_nN_n$ complexes (M=Be, Mg; n=3 and 6) had most stability. NICS values showed aromaticity character in $C_{24-2n}B_nN_n$ (n=3 and 6) cages. The molecular analysis reveals a linear correlation between isotropic polarizability values and HOMO-LUMO gaps energies in stable complexes.

References

[1] P. R. C. Kent, M. D. Towler, R. J. Needs, G. Rajagopal, *Phys. Rev.,* B 62, 15394 (2000).

[2] Z. X. Wang, W. M. Wang, F. Y. Zhu, X. P. Li, M. L. Ruan, H. Chen, R. B. Huang, L. S. Zheng, *High Energy Phys. Nucl. Phys* , 25, 69 (2001).

[3] A. D. Becke, *J. Chem. Phys.* , 98, 5648 (1993).

[4] M. J. S. Dewar, C. H. Reynolds, *J. Comp. Chem.,* 2, 140 (1986).

[5] K. Raghavachari, J. A. Pople, E. S. Replogle, M. Head-Gordon, *J. Phys. Chem.,* 94, 5579 (1990).

[6] Nanotube Modeler software, @ Jcrystalsoft, 1.6.4 version, (2010).

[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Revision B.03 ed., Gaussian, Inc., Pittsburgh PA, 2003.

[8] S. F. Boys, F. Bernardi, Mol. Phys., 19, 553 (1970).

[9] P. V. R. Schleyer, C. Maerker, A. Dransfield, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.*, 118, 6317 (1996).

[10] M. K. Cyranski, T. M. Krygowski, M. Wisiorowski, N. J. R. v. E. Hommes, P. v. R. Schleyer, *Angew. Chem., Int. Ed.,* , 37, 177 (1998).

[11] P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong, *Inorganic Chemistry, Fourth ed.*, Oxford University Press, Oxford, (2006).

[12] C. R. Zhang, H. S. Chen, G. H. Wang, *Chem. Res. Chinese,* 20, 640 (2004).

[13] H. Cheng, J. Feng, A. Ren, J. Liu, *Acta Chim. Sin.*, 60, 830 (2002).

[14] Y. Sun, X. Chen, L. Sun, X. Guo, W. Lu, *Chem. Phys. Lett.* , 381, 397 (2003).

[15] S. Gunasekaran, R. A. Balaji, S. Kumeresan, G. Anand, S. Srinivasan, *Can. J. Anal. Sci. Spectrosc.*, 53, 149 (2008).

[16] B. Kosar, C. Albayrak, *Spectrochim. Acta A,* 78, 160 (2011).

[17] R. G. Pearson, *Chemical Hardness*, Wiley-VCH: Oxford, (1997).

[18] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press: New York, (1989).

[19] R. G. Parr, L. Szentpaly, S. Liu, *J. Am. Chem. Soc.*, 121, 1922 (1999).