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Theoretical Possibility of the Stable High Spin Multiple States in the Boron-Carbon Layered Systems

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The possibility of the high spin stable states in the Boron-Carbon layered network systems have theoretically investigated through several BC 6MR polyacene clusters. The HF/6–31G** calculations reveal that the alternant BC-benzene gives a quartet stable state rather than a doublet one, while a doublet state is more stable for the non-alternant BC-benzenes. Similarly, alternant BC-naphthalene gives a high-spin stable state (sextet) rather than lower ones (doublet, or quartet). These features are well understood by extending the Longuet-Higgins [1] theory to this BC system.

Keywords: BC-polygonal networks; high spin states

INTRODUCTION

Boron (B)-Carbon (C) intercalated compounds include BC polygonal layers, which are network stages of 6, 5-7 and 4-8 membered rings (MRs). The intercalated metals change their MR forms from 6MR for LiBC [2],[3], to 5-7 MR for ScB_2C_2 [4] or to 4-8 MR for MB_2C_2(M=Ca [5], La [6],...), respectively. Several interesting electrical [7] and magnetic [8] properties have been also reported. Stoichiometrically, these BC stages include the equivalent B and C elements. Thus, in the BC 6MR, e.g., the half number of carbon atoms are replaced by boron atoms in the graphite sheets. This atom substitution causes the electronic unsaturation in the π orbitals and produces different electronic and spin multiple structures from those of

the graphite or hydrocarbon polyacene systems. Here, for the purpose of the designing of novel BC magnetic materials, we theoretically investigate the possibility of the high-spin stable states with using several BC 6MR polyacene clusters (Fig. 1). We, first, discuss the possible spin states qualitatively by extending the Longuet-Higgins [1] theory to the above cluster systems. Next, the quantitative investigations have been performed by the *ab initio* Hartree-Fock calculations.

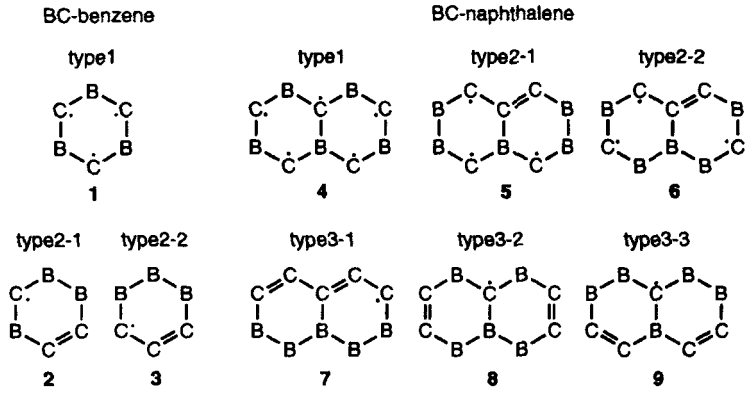

FIGURE 1 Calculated models of BC-benzene, naphthalene (terminated by H atoms, omitted).

RESULTS AND DISCUSSION

Spin States by Extended Longuet-Higgins Theory

The spin multiple-states in the π conjugated systems are well known to be described by the Longuet-Higgins(LH) theory [1]. We, here, extend this theory to the BC systems by changing the number of NBMOs (Non-Bonding Molecular Orbitals) to that of the unpaired π electrons. According to the LH theory, the number of NBMOs is $N - 2T$, where N is the number of carbon atoms and T is the maximum number of double bonds in any resonance structures. The Hund's rule results in that the total spin S of the system should be

$$S = (N - 2T)/2, \tag{1}$$

for the NBMOs degenerate within the Hückel level.

Since the regular polyacene ($(4n+2)\pi$ electrons) systems have no NBMOs, eq. 1 lets the total spin be zero. On the contrary, although the BC 6MR has also no NBMOs, the higher spin states result from the extended LH theory because of the lack of the valence electrons. The extended LH theory lets the higher spin state be feasible.

The extended LH theory (Eq. 1) gives that the resulting total spin of the BC-benzene (**1**) is $S = 3/2$ ($N = 3, T = 0$), but that of (**2**) and (**3**) is $S = 1/2$ ($N = 3, T = 1$). For BC-naphthalenes, (**4**) gives $S = 5/2$ ($N = 5, T = 0$), but (**5**) and (**6**) give $S = 3/2$ ($N = 5, T = 1$) , and also (**7**), (**8**) and (**9**) do $S = 1/2$ ($N = 5, T = 2$). Thus, the present extended LH theory predicts that the higher spin multiple-states are realized in the BC alternant arrangement structures (type1) rather than the non-alternant structures. These features are caused by that the π bonding orbitals (πBOs) have mutually closed levels especially in the type1s (Fig. 2), although there are no longer NBMOs in BC-polyacene clusters.

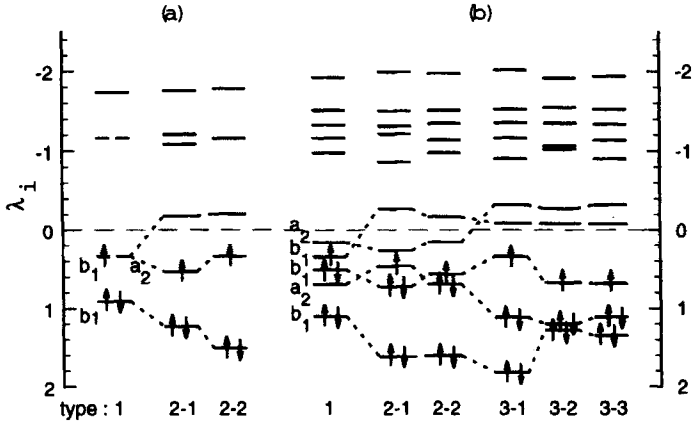

FIGURE 2 Calculated λ_i of (a)BC-benzene and (b)BC-naphthalene by using Hückel method. Bond lengths are $R_{BC} = 1.56$, $R_{BB} = 1.73$ and $R_{CC} = 1.39$Å quoted from the standard values. Electrons are in doublet occupation.

Ab initio Calculations

We carried out the *ab initio* calculations in order to investigate the quantitative stability of the higher spin multiple-state. The geometry optimizations as well as the total energy calculations have been performed by the Restricted Open-shell Hartree-Fock (ROHF) method with the 6-31G** basis set.

Table 1 and 2 show the calculated total energies of the different spin configurations, relative to that in the corresponding higher spin state, *i.e.*, the quartet for BC-benzenes or the sextet for BC-naphthalenes, respectively. All the values are those in the planary optimized structures. Two doublet states ($^2B_1$ and $^2A_2$) of the type1 BC-benzene are originated from the Jahn-Teller [9] distortion in the degenerate $^2E''$ state of the D_{3h} structure. It was found that the higher spin states in the type1s are energetically stable than the lower ones, while the opposite relation stands in other types. Thus, the present extended LH calculations can be confirmed quantitatively by the *ab inito* HF level calculations.

For understanding the mechanism of the energetical stabilization in the higher spin state for the BC alternant arrangement systems, we compare the resulting energies between the higher spin (HS) state and the lower spin (LS) state by decomposing the total energy into several energy terms ; $TE = KE + PE + EE + NE$, where TE, KE, PE, EE and NE are total, kinetic, attractive potential between electrons and nuclei, interelectron and intercore repulsive terms, respectively (Fig. 3) . It is found that EE and NE terms prefer to be a HS state. An increase in the exchange interaction (EE) also prefers to be a HS state for both types of the BC arrangement. Thus, the BC alternant arrangement systems are energetically stabilized in the HS state. On the contrary, the EE terms of the non-alternant BC arrangement systems do not overcome the one-electron attractive terms of $KE + PE$, and the LS states should appear.

TABLE 1 Total energies (kcal/mol) of the BC-benzenes relative to the quartet state.

type	doublet		quartet	
1	21.5	B_1	0	A_2"
	29.1	A_2		
2-1	-43.0	A"	0	A"
2-2	-58.6	A_2	0	A_2

TABLE 2 Total energies (kcal/mol) of the BC-naphthalenes relative to the sextet state.

type	doublet		quartet		sextet	
1	36.9	B_1	18.0	A_2	0	B_1
2-1	-5.0	B_1	-57.6	B_1	0	B_1
2-2	-19.3	B_1	-48.6	B_1	0	B_1
3-1	-115.2	B_1	-59.2	A_2	0	B_1
3-2	-86.6	B_1	12.7	A_2	0	B_1
3-3	-92.8	B_1	-22.7	A_2	0	B_1

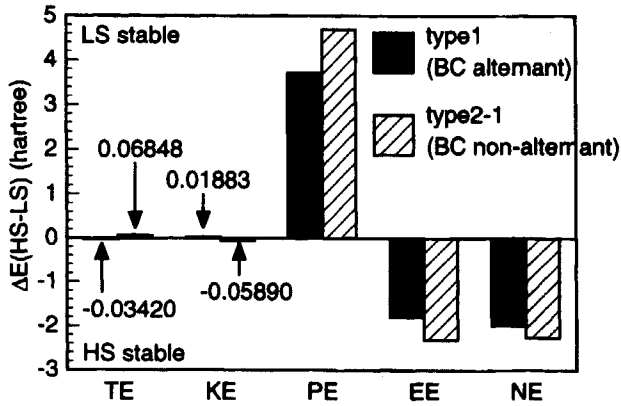

FIGURE 3 Relative energies between the high spin state (HS) and the low spin state (LS) by energy terms for type1 and type2-1 BC-benzene. $\Delta E(HS\text{-}LS)=E(^4A_2")-E(^2B_1)$ (type1), $E(^4A")-E(^2A")$ (type2-1).

CONCLUSION

The alternant BC polyacene system has the possibility of the high-spin stable state because of the coexistence of valence III and IV elements in the skeleton. The extended Longuet-Higgins theory describes this characteristics and gives the result consistent with that by *ab initio* HF calculations.

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