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Theoretical Study of the Electronic and Molecular Structures of BC Polygonal Membered Rings

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The *ab initio* molecular orbital calculations have been carried out to clarify the molecular planarity of the B and C polygonal membered ring (MR) clusters by varying their charged states as well as spin configurations. The highly anionization or higher spin states enhances the planarity of the BC skeleton because of an increase in the number of the occupied π bonding orbitals (BOs). Moreover, the BC polygonal networks composed of 6MR or 5–7MR units prefer to form the electron attracting stages.

Keywords: B and C polygonal networks; electronic and molecular structures; *ab initio* calculations

INTRODUCTION

Boron (B) and Carbon (C) layered compounds of MBC (M: metal) have BC network stages, whose forms are characteristically changed by the intercalated metal M atoms. Hexagonal six-membered-ring (6MR) networks[1] are formed when M being Li or Mg, while Ca, Y or Ln atom forms tetra-octa (4-8MR) BC networks[2], and also Sc does a penta-hepta (5-7MR) one[3] (Fig. 1(a)). It can be understood that several amounts of the charges are transfered from these intercalated metals into the BC polygonal network stages, because the three valence electrons of B atoms inevitably cause an incomplete electron occupation of π bonding orbitals (BOs). Moreover, these

charge transfers (CTs) are easily thought to provide a molecular planarity in this BC polygonal network system.

If so, how does the topological difference among these polygonal MRs change the electron occupation, or which MRs would prefer to provide the molecular planarity? We here investigate this problem via the following minimum composing BC units by filling the empty π BOs with electrons, *i.e.*, varying their anionized states or spin configurations. The corresponding units are the 6MR, dimerized 5MRs and 8MR shown in Fig. 1(b). They become the basic units of the polygonal network stages, because the proper translations can cover a full plane of the 6MR, 5-7MR, and 4-8MR network, respectively. In the present work, all the cluster edges are also terminated by H atoms to dissipate the dangling bonds, and the Hartree-Fock level calculations have been carried out with the 6-31G** basis sets by using the Gaussian98 program[4].

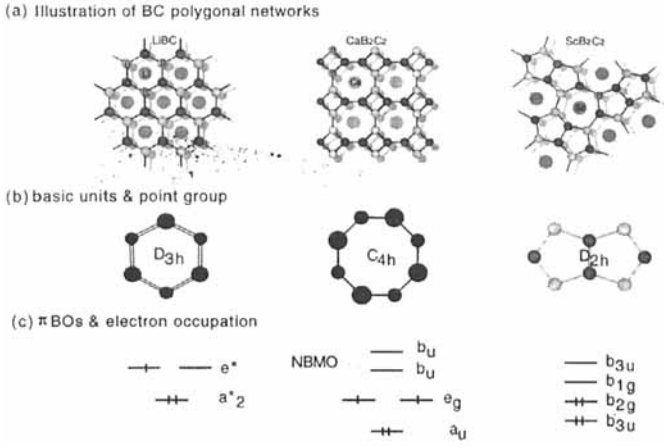

Fig. 1 Illustration of BC polygonal networks(a) and basic units in which all terminated H atoms are omitted(b), and the corresponding π bonding orbitals(c).

BC 6 MR NETWORK

The BC 6MR in which B and C atoms are alternately arranged gives the

point group symmetry of D_{3h}. In the charge neutral state, one of the doubly degenerated π BOs should be occupied singly by an electron (e'' in Fig. 1(c)). This incomplete electron filling lets the 6MR unit be instable, and the deformation should be induced to resolve the degeneracy. Under the geometrical restriction of the planar skeleton, the unit is distorted from D_{3h} to C_{2v} symmetry, and two structures having an elongated or a compressed BC skeleton are produced (Fig. 2). Both give a doublet spin state having the

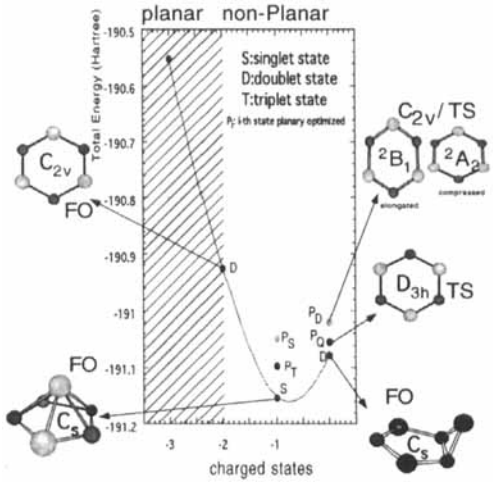

Fig. 2 Illustration of optimized structures and total energy diagram of BC 6MR. The transition state and the fully optimized structures are noted by TS and FO, respectively. All terminated H atoms are omitted for a simplification.

electron configuration of $^2B_1$ and $^2A_2$, respectively. Energetically, the former is stable than the latter by 0.012 Hartree in the present HF calculation, but both of these are still transition states (TSs). The stable higher-spin-state of the quartet one is possible under the restriction of the planar symmetry (D_{3h}). However, such a higher spin state is also a TS. The deformation of one of B atoms towards the out-of-plane (B_1 mode) should be induced, and the fully optimized (FO) non-planar structure results in. Thus, the neutral BC 6MR unit can not conserve its molecular planarity because of the lack of π electrons.

The singly anionized BC benzene in which a foreign electron is charged shows the similar molecular deformation, but the resulting FO structure is not a 6MR, but rather a 5MR. The planar BC skeleton can be found when the 6MR unit is doubly anionized (Fig. 2).

4-8 MR NETWORK

The 8MR having the alternating B and C arrangement has the point group of C_{4h} symmetry[2]. Therefore, each of the doubly degenerated π (e_g) BOs are singly occupied and the two spin configurations of the singlet and triplet states are possible (Fig. 1(c)). The exchange term does stabilize the triplet state energetically than the singlet state by 0.244 Hartree (Hund's rule, Fig. 3). However, this triplet 8MR unit is a TS, and the deformation should occur

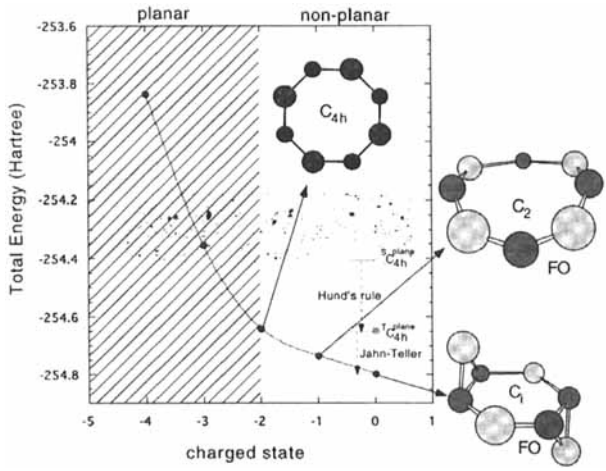

Fig. 3 Illustration of optimized structures and total energy diagram of BC 8MR. All terminated H atoms are omitted for a simplification.

to resolve the degenerated half-filled π orbitals (SOMOs). Consequently, two B atoms are moved oppositely towards the out-of-plane to break the planarity of the BC skeleton, and the "chair" form FO structure results in (Jahn-Teller distortion).

The singly anionized 8MR unit also produces a non-planar BC skeleton,

but the corresponding distortion is decreased compared with that found in the neutral unit. The planarity of the molecular can be found when the unit is anionized more than doubly.

BC 5-7 MR NETWORK

Although the symmetry of the dimerized 5MRs unit resolves the degeneracy of π BOs, the planarity of the unit is instable (Fig. 4). This is because those π BOs are not completely occupied in the charge neutral state (Fig. 1(c)). Thus, the twisting of the skeleton is induced to generate the $sp\sigma$ bondings which stabilize the total energy via lowering the one-electron π BOs' energies. Since the unit has no degenerated orbitals, the excitation into the higher spin state (quintet) has a possibility to produce a skeleton planarity (Fig. 4). However, the corresponding unit is significantly at higher

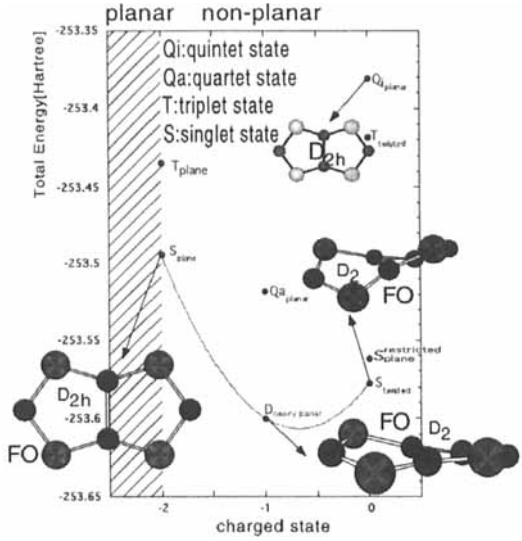

Fig. 4 Illustration of optimized structures and total energy diagram of BC dimerized5MRs. All terminated H atoms are omitted.

energy state compared with the twisted FO one. This skeleton twisting

is remarkably reduced by the single anionization (nearly flat plane), and completely disappears (flat plane of D_{2h}) by the double anionization.

DISCUSSION

In the BC polygonal basic units, the anionization causes an interesting feature. An injection of foreign electrons increases an interelectron repulsive energy. One can, however, find the "optimal" anionization in the BC 6MR and dimerized 5MRs units but not in the 8MR unit, although the composing atoms are stoichiometrically equal among these units.

This feature originates from the topological difference of the MR structures. The neutral 6MR and dimerized 5MRs units having the planar skeletons give distinct negative values of the LUMO energies, but the 8MR does not. The reason is that the former two MR units do not have non-bonding molecular orbitals (NBMOs), and all the π BOs are stabilized energetically by the orbital mixing via the π conjugation. On the contrary, the 8MR (or 4MR, *i. e.,* analogue of 4n π electrons system in the carbon aromatic compounds) has NBMOs, in which less π conjugation occurs and the "bare" atomic state would appear. Therefore, the interelectron interaction by the anionization directly destabilizes the BC 8MR and produces the monotonous increase in the total energy (Fig. 3). Thus, in the BC polygonal MR networks, those composed of 6MR or 5-7MR units prefer to form electron attracting stages rather than that of 4-8MR units does.

Acknowledgments

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[4] Gaussian MO calculation program by Gaussian Inc..