

Stability of boron and nitrogen substituted buckminsterfullerene

D. Inomata, N. Kurita^A, M. Fujita, S. Suzuki and K. Nakao

Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

^AEnergy Research Laboratory, Hitachi Ltd., 7-2-1 Omika, Hitachi 319-12, Japan

Introducing a spring model in C_{60} and $C_{12}B_{24}N_{24}$ (CBN), we discuss their relative stability from the dynamical point of view. The spring constants are evaluated based on the first principle calculation of binding energy. We show that the bonding of CBN is weaker than that of C_{60} , reflecting the ionic character in CBN in contrast with the covalent one in C_{60} . We also discuss the possibility of synthesizing CBN.

1. INTRODUCTION

After the synthesis of C_{60} , new interesting materials such as hetero-fullerenes and endohedral metallofullerenes have been exploited. Guo *et al.* doped boron in C_{60} and obtained mass spectral evidence for $C_{60-x}B_x$, where x ranges between 1 and 6 [1]. Since BN is stabilized by forming graphite-like sheets, also it seems reasonable that C_{60} substituted by BN units, e.g., $C_{58}BN$, $C_{56}B_2N_2$, $C_{54}B_3N_3$ and so on, could be synthesized, although their syntheses have not been achieved.

Recently Xia *et al.* have proposed the cluster $C_{12}B_{24}N_{24}$ (CBN); it contains the largest possible number of boron and nitrogen under the constraint that there are no B-B or N-N bonds [2]. They also calculated the total energy of CBN by using the modified neglect of differential overlap method and suggested that CBN is more stable than C_{60} thermodynamically. On the other hand, Kobayashi and Kurita showed that CBN is less stable than C_{60} , employing the first principle calculation adopted the self-consistent-field (SCF)-molecular-orbital (MO) method based on the non-local-density-functional formalism [3]. Thus the relative stability of CBN to C_{60} is controversial at present.

Furthermore it was shown by Kobayashi and Kurita that the charge transfer from boron to nitrogen is caused significantly in the CBN cluster, so that CBN reveals strong an ionic character [3]. It is noticed that this property contrasts sharply with the perfectly covalent character of C_{60} . Thus

it seems important to investigate how the dynamics such as intramolecular vibrations are affected by the ionic or the covalent character of the cluster.

The purpose of this paper is to study the stability of CBN by comparing with C_{60} in reference to the dynamics rather than the energetics. We first introduce a spring model in order to describe the dynamical properties of CBN and C_{60} and determine the spring constants by using the first principle MO calculations. Then we elaborate on the difference between the spring constants of CBN and those of C_{60} in connection with the ionic character of the former and the covalent character of the latter. Finally we discuss the relative stability of CBN to C_{60} by comparing the spring constants of CBN with those of C_{60} .

2. SPRING MODEL

In our model for the C_{60} cluster, the springs are classified into two groups; four kinds of springs for bond-stretching motion and two kinds of springs for angle-bending motion. The symbol k_{sp} in Fig. 1(a) means the spring constant corresponding to the single bond-stretching motion, where subscripts s and p denote stretching and pentagon, respectively. Similarly the subscript h is used for the spring constant with respect to hexagon. It is noticed that k_{sh} is the spring constant of the bond connecting two pentagons. Other two stretching spring constants are k_{s2p} and k_{s2h} between the second nearest neighbor atoms inside a pentagon and a hexagon, respec-

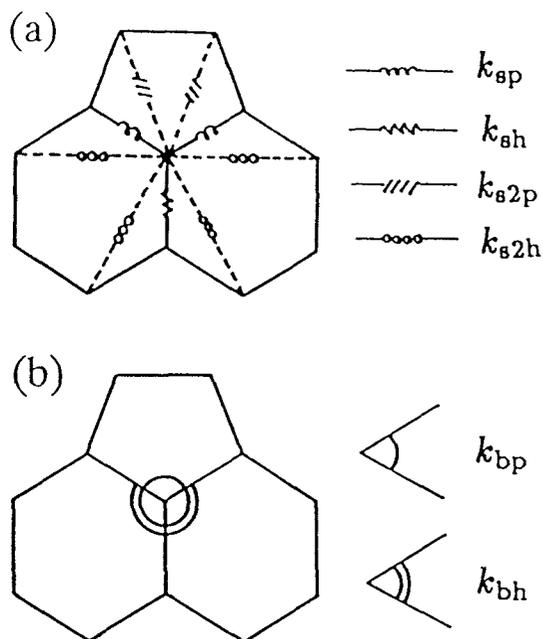


Figure 1. Schematic diagram of the spring model for the C_{60} cluster, (a) the springs for bond-stretching motion and (b) the springs for angle-bending motion.

tively. Furthermore we define k_{bp} and k_{bh} as the spring constants representing angle-bending motion inside a pentagon and a hexagon, respectively (Fig. 1(b)).

We now explain the spring model for CBN, whose point group symmetry is S_6 . That is, the symmetry of CBN is considerably reduced in comparison with I_h of C_{60} . The schematic model of CBN is shown in Fig. 2, in which 6 C-C, 12 C-N, 12 C-B and 60 B-N bonds exist. Therefore many kinds of spring constants must be considered.

We determine the spring constants so as to reproduce the change in binding energy accompanied with the given distortions of cluster structure, assuming the harmonic approximation. Here the binding energy is calculated by using the first principle MO method with Harris approximation. Furthermore, by considering the linear terms in the change in binding energy against the

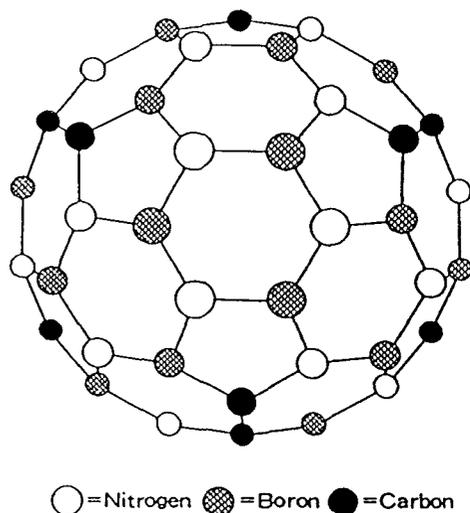


Figure 2. Schematic model of $C_{12}B_{24}N_{24}$ as viewed along the threefold axis.

displacements, it becomes possible to determine the spring constants even if the selected structure is not in equilibrium. Thus in determining the spring constants, it is sufficient to choose the independent distortions at least by the twice of the numbers of the spring constants. Finally, by using determined spring constants, we obtain an equilibrium structures from minimizing the sum of the elastic energy accumulated in each spring and calculate the eigen frequencies of the intramolecular vibrations.

We find that this procedure developed in our study is quite easy in deriving the eigen frequencies of the cluster in comparison with the conventional procedure adopting the first principle calculation. In our procedure, we need only the spring constants and the equilibrium structure in order to calculate the Hess matrix, on the other hand, in the conventional procedure, one must calculate about $3N \times 3N$ matrix elements of the Hessian, where N denotes the total number of the constituent atoms.

3. RESULTS AND DISCUSSION

The calculated spring constants for C_{60} are given in Table 1, where the bond-stretching and the angle-bending spring constants are expressed in $eV/\text{\AA}^2$ and in $eV/(\text{rad})^2$. In order to examine

Table 1
Bond-stretching and angle-bending spring constants in C_{60} .

Stretching	Value ^a	Bending	Value ^b
k_{sp}	22.1	k_{bp}	6.93
k_{sh}	34.6	k_{bh}	4.57
k_{s2p}	3.56		
k_{s2h}	2.47		

^a in $eV/\text{\AA}^2$.

^b in $eV/(\text{rad})^2$.

the accuracy of our spring model, we compare the calculated Raman- and IR-active mode frequencies in C_{60} with the experimental results by Bethune *et al.* [5] and find that they agree within 9% difference on the average. It is noticed that the magnitude of k_{sp} and k_{sh} are the same order as that of the nearest-neighbor spring constant for bond-stretching motion in graphite, whose value is about $23 eV/\text{\AA}^2$ [4]. Furthermore we find that k_{sp} is smaller than k_{sh} and that k_{s2p} is larger than k_{s2h} . This seems reasonable because it is most likely that the spring constant becomes smaller as the distance between atoms becomes larger, i.e., the distances between two atoms connected by the spring k_{sp} , k_{sh} , k_{s2p} and k_{s2h} are 1.47, 1.42, 2.37 and 2.50 \AA , respectively. In addition to this relation, the directional dependence of the interatomic forces due to the covalency appears in the noticeable difference between the spring constants of the nearest neighbor bonds and of the second nearest neighbor bonds.

Next, we show the spring constants of CBN in Table 2. As the first step of studies on the dynamics of CBN, we here assume the same type of 6 spring constants for CBN as those for C_{60} , neglecting the difference among C-C, C-B, C-N and B-N bonds. That is, the calculated spring con-

Table 2
Bond-stretching and angle-bending spring constants in $C_{12}B_{24}N_{24}$.

Stretching	Value ^a	Bending	Value ^b
k_{sp}	9.3	k_{bp}	-0.17
k_{sh}	5.7	k_{bh}	14.0
k_{s2p}	4.2		
k_{s2h}	3.7		

^a in $eV/\text{\AA}^2$.

^b in $eV/(\text{rad})^2$.

stants are the averages of the spring constants of each bond which should be taken into account under the S_6 symmetry; for example, k_{sp} is the average of 12 C-B, 12 C-N and 36 B-N bonds and also k_{sh} is the average of 6 C-C and 24 B-N bonds. Here we restrict ourselves to the analysis of qualitative properties emerged from the averaged description mentioned above. We find that k_{sp} and k_{sh} are much smaller than those for C_{60} . On the other hand, k_{s2p} and k_{s2h} are almost the same as those of C_{60} . This tendency indicates that the directional dependence of the interatomic forces in CBN is smaller than that in C_{60} . This feature reflects the ionic character of CBN due to the charge transfer from boron to nitrogen and contrasts sharply with the covalent character of C_{60} .

We now discuss the relative stability of CBN to C_{60} by the difference in the magnitude of the evaluated spring constants between them. As shown above, the nearest neighbor bonds in CBN are remarkably weakened. Moreover, since Kobayashi and Kurita showed the variation of bond orders, i.e., 0.57 (C-C), 0.45 (C-B), 0.30 (C-N) and 0.37-0.42 (B-N), respectively [3], we expect that a particular bond like C-B or C-N has a smaller spring constant than the averaged one in Table 2. The magnitude of the weak spring constant in CBN is roughly estimated less than one fifth of that of C_{60} or graphite. Although it is hard to tell the temperature at which the network of C_{60} is broken, it is presumed to be about 4000 K from the melting temperature of graphite [7]. Therefore, CBN is expected to collapse below 1000 K. It is reported that the circumstance of synthesis

of fullerene prefers high temperature more than 1500 K [8, 9]. Consequently, we conclude that CBN can't be obtained in the present condition of the fullerene synthesis. In order to confirm this expectation, we will show the spring constants for the nonequivalent bonds in CBN somewhere.

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