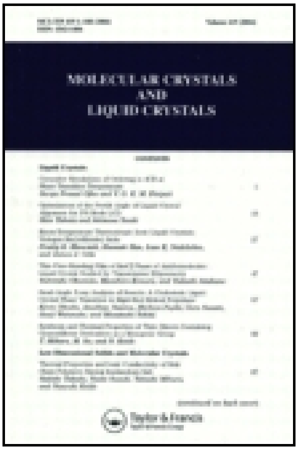

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Molecular Orbital Calculations on Electronic Properties and Lithium Storage of Substituted Disordered Carbons

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Molecular Orbital Calculations on Electronic Properties and Lithium Storage of Substituted Disordered Carbons

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We employed a polyaromatic hydrocarbon $C_{54}H_{18}$ as a model cluster for disordered carbons and investigated the effect of BNB-unit substitutions on the electronic and Li absorption properties of disordered carbons, by using a semiempirical molecular orbital method. BNB substitutions prefer to occur at the periphery of $C_{54}H_{18}$ sheet and create electron acceptor levels in a lower energy region than that for $C_{54}H_{18}$, This level accepts electrons from the absorbed Li atoms more easily, so that the Li absorption energies for these BNB-substituted $C_{54}H_{18}$ are larger than that for $C_{54}H_{18}$. The absorbed Li atoms are stabilized near B atoms to be far from N atoms, and $(BNB)_2$-substituted $C_{54}H_{18}$ has smaller Li absorption energy than $B_2C_{52}H_{18}$. These results indicate that N atoms may have a negative effect for enhancing Li-absorption energy of disordered carbons.

Keywords: molecular orbital calculations; substituted carbons; electronic properties; Li absorptions; Li ion batteries; anode materials

INTRODUCTION

Recently, the application field of rechargeable lithium (Li) ion batteries has been extended rapidly. For improving their capacity, it is important to develop anode materials, which can store a large amount of Li ions. New types of carbon materials have been developed for promising anode materials: disordered carbon-hydrogens[1-3], boron or nitrogen substituted carbons[4-7]. In particular, boron-substituted carbons produced by chemical vapor deposition indicate large Li storage compared to a pristine carbon[4,5]. In our previous study[8], we investigated the change in electronic properties and Li absorption energy of disordered carbons induced by boron or nitrogen substitution, by using a semiempirical molecular orbital (MO) method with model clusters such as $C_{24}H_{12}$, $C_{54}H_{18}$ and $C_{96}H_{24}$. This investigation clarified that boron-substitution into disordered carbons creates an electron acceptor level in a lower energy region than that for the pristine disordered carbons. This lower-lying acceptor-level receives electrons from the absorbed Li atoms more easily, so that the Li absorption energy for the boron-substituted carbon is much larger than that for the pristine carbon.

In the present study, we investigate the effect of substitution of BNB units into $C_{54}H_{18}$, considering the experimental result[9] that BNC ceramic alloys prepared from borane-heterocyclic compounds have BNB units and a large amount of B content: the ratio of B, N and C components is 2:1:4.

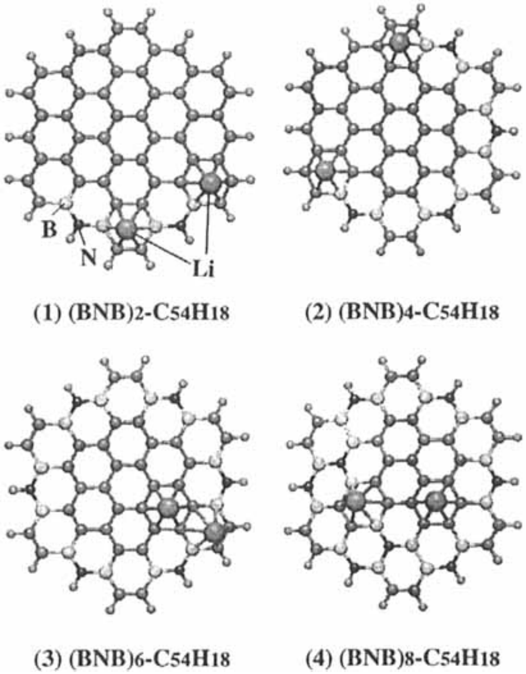
METHOD OF CALCULATION

We perform semiempirical MO calculations based on MNDO (modified neglect of differential overlap)[10] method, by using the semiempirical MO program MOPAC97[11]. The accuracy of the parameters in the MNDO method for C, B, N and Li atoms has been checked by performing ab initio Hartree-Fock calculations for the rather small model clusters $B_2C_{22}H_{12}$, $N_2C_{22}H_{12}$, and their derivatives with two Li absorption[8].

RESULTS AND DISCUSSION

Structures and electronic properties of BNB substituted C54H18

At first, three carbon atoms in $C_{54}H_{18}$ were replaced by a BNB unit, and the relative stability among isomers were investigated for all possible substituted sites: the total number of isomers is 12 for BNB-substitution. For the most stable isomer, we continued BNB-substitution and obtained the most stable isomer for the $(BNB)_2$-substituted $C_{54}H_{18}$. In the same way, the most stable isomers for the $(BNB)_4$, $(BNB)_6$ and $(BNB)_8$-$C_{54}H_{18}$ were obtained. As shown in Fig. 1, the substitutions on the periphery of the $C_{54}H_{18}$ sheet prefer to occur. At the $(BNB)_6$-substitution, all possible sites for BNB-substitutions on the periphery are occupied by BNB, so that some inner carbons are substituted at the $(BNB)_8$-substitution. The ratio of B, N and C contents is 2:1:3.75 for $(BNB)_8$-$C_{54}H_{18}$, which is similar to the experimentally obtained content[9]. The reason why the substitution on the periphery is more preferred is the same as that for boron or nitrogen substitution[8]: the substitution of inner carbon atoms of $C_{54}H_{18}$ affects the three bonds around the substituted atom, while the substitution of edge carbon atoms weakens only two bonds.



(1) $(BNB)_2$-$C_{54}H_{18}$ (2) $(BNB)_4$-$C_{54}H_{18}$

(3) $(BNB)_6$-$C_{54}H_{18}$ (4) $(BNB)_8$-$C_{54}H_{18}$

FIGURE 1 Most stable isomers and two Li-absorption sites for $(BNB)_2$-, $(BNB)_4$-, $(BNB)_6$- and $(BNB)_8$-substituted $C_{54}H_{18}$ sheets. Both sides of N atoms (black circles) are B atoms (light colored). Li atoms are indicated by large circles.

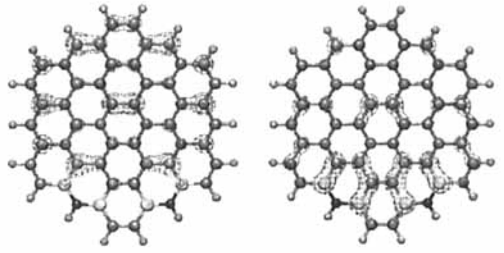
For the four types of BNB-substituted $C_{54}H_{18}$, distributions of highest-occupied MO (HOMO) and lowest-unoccupied MO (LUMO) are compared in Fig. 2, and their energy levels are listed in Table I. LUMO shifts more downward by larger B-substitutions[8], while the larger BNB-substitutions do not cause the larger shift of LUMO: $(BNB)_6$-$C_{54}H_{18}$ with D_{6h} symmetry has a similar LUMO to $C_{54}H_{18}$ and the largest HOMO-LUMO energy gap. As shown in Fig. 2, the HOMO of (BNB)x-substituted $C_{54}H_{18}$ is distributed on C atoms, while the LUMO, which accepts the electrons of the absorbed Li, is mainly distributed on B and its nearest C atoms, avoiding N atoms.

TABLE I HOMO and LUMO energy levels, Li-absorption energies for $C_{54}H_{18}$, B_2 and (BNB)x-substituted $C_{54}H_{18}$.

	MO level (eV)		Absorption energy (kcal/mol)				
	HOMO	LUMO	2 Li	4 Li	6 Li	8 Li	10 Li
$C_{54}H_{18}$	-7.46	-1.74	28.6	59.8	83.2	106.6	62.0
$B_2C_{52}H_{18}$	-7.35	-2.51	77.4	102.3	120.9	151.5	124.9
$(BNB)_2$-$C_{54}H_{18}$	-7.47	-2.31	63.7	95.2	118.9	118.9	106.7
$(BNB)_4$-$C_{54}H_{18}$	-7.66	-2.26	72.1	119.0	136.5	140.2	136.9
$(BNB)_6$-$C_{54}H_{18}$	-7.87	-1.77	48.6	97.30	148.4	161.4	150.9
$(BNB)_8$-$C_{54}H_{18}$	-7.90	-1.94	58.3	120.6	150.4	163.3	156.2

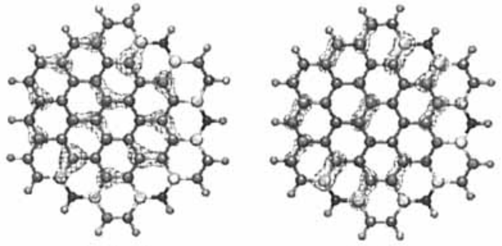
Li-absorption on BNB substituted $C_{54}H_{18}$ sheets

In order to elucidate the effect of BNB-substitutions on Li absorption of $C_{54}H_{18}$, we put two Li atoms above the center of hexagonal rings of the sheets and determined the most stable sites from the comparison of heat of formation for the optimized structures. As expected from the LUMO distribution, two Li atoms are almost stabilized above the hexagonal rings containing B atom (Fig. 1). Moreover, we optimized Li sites for 4, 6 and 8 Li absorptions and found that Li atoms avoid staying near N atoms. Li absorption energies estimated from the change in heat of formation induced by Li absorptions are listed in Table I, which shows the absorption energy is maximum at 8 Li absorption for all but $(BNB)_2$-substituted sheets. This result seems to come from the fact that some Li atoms could not avoid staying near N atoms for the 10 Li absorption.



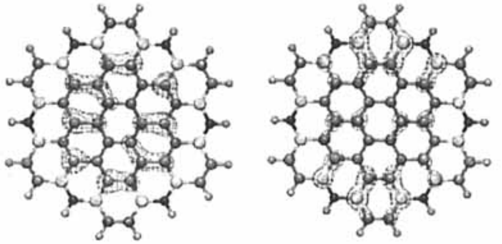
HOMO LUMO

(1) $(BNB)_2$-substituted $C_{54}H_{18}$



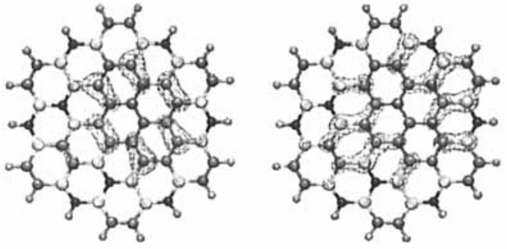
HOMO LUMO

(2) $(BNB)_4$-substituted $C_{54}H_{18}$



HOMO LUMO

(3) $(BNB)_6$-substituted $C_{54}H_{18}$



HOMO LUMO

(4) $(BNB)_8$-substituted $C_{54}H_{18}$

FIGURE 2 Distributions of HOMO and LUMO for $(BNB)_x$-$C_{54}H_{18}$.

Compared with $C_{54}H_{18}$, BNB-substituted sheets have larger absorption energies, although the comparison between $B_2C_{52}H_{18}$ and $(BNB)_2$-$C_{54}H_{18}$ clarifies that N has a negative effect for enhancing Li absorption energy.

CONCLUSIONS

The effect of BNB-unit substitutions on both the electronic and Li absorption properties of disordered carbons was investigated by the semiempirical MO calculations for $C_{54}H_{18}$ and its substituted sheets. BNB substitutions prefer to occur at the periphery of $C_{54}H_{18}$ sheet, and Li atoms are stabilized to avoid the N atoms on the substituted sheets. The Li absorption energies of BNB-substituted sheets are much larger than that of $C_{54}H_{18}$, although $(BNB)_2$-$C_{54}H_{18}$ has smaller Li-absorption energy than $B_2C_{54}H_{18}$, indicating that the inclusion of N atoms as a substituted atom may not increase the Li storage of disordered carbons.

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