

# Layered carbon lattices and their influence on the nature of lithium bonding in lithium intercalated carbon anodes

L.G. Scanlon<sup>a,\*</sup>, G. Sandi<sup>b</sup>

<sup>a</sup> Air Force Research Laboratory, Power Division, Battery Branch, WPAFB, OH 45433, USA

<sup>b</sup> Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA

## Abstract

Ab initio molecular orbital calculations have been used to investigate the nature of lithium bonding in stage 1 lithium intercalated carbon anodes. This has been approximated by using layered carbon lattices such as coronene, (C<sub>24</sub>H<sub>12</sub>), anthracene, and anthracene substituted with boron. With two coronene carbon lattices forming a sandwich structure and intercalated with either two, three, four or six lithiums, it has been found that the predominant mode of bonding for the lithium is at the carbon edge sites as opposed to bonding at interior carbon hexagon sites. With a single planar coronene molecule approximating a graphene sheet, the bonding of four lithiums with this molecule is near the interior carbon hexagon sites. For anthracene and boron substituted anthracene, lithium bonding takes place within the carbon hexagon sites. The separation between lithiums in a sandwich type structure with two anthracenes in the eclipsed conformation is 5.36 Å. The effect of boron substitution is to increase lattice flexibility by allowing the lattice to twist and lithium to bond at adjacent hexagon sites. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Ab initio; Gaussian; Lithium intercalation; Coronene; Tetraboroanthracene; Carbon anodes

## 1. Introduction

Ab initio molecular orbital calculations have been used to investigate the nature of lithium bonding in stage 1 lithium intercalated carbon anodes. This has been approximated by using layered carbon lattices such as coronene, (C<sub>24</sub>H<sub>12</sub>), anthracene, and anthracene substituted with boron. Coronene and anthracene have been used to form sandwich structures in which lithium is inserted. In addition to the sandwich type structure, a planar coronene molecule has been used to represent a single graphene sheet as a potential site for lithium bonding [1]. The effect of boron in a carbon lattice has been evaluated by comparing the difference in behavior of a single anthracene molecule reacting with a dilithium cluster as compared to a 1,4,5,8-tetraboroanthracene-molecule.

## 2. Computational approach

Gaussian 94 is used for all ab initio calculations [2]. Geometry optimizations and frequency calculations are

performed using the Hartree–Fock method. The restricted open-shell Hartree–Fock (ROHF) method is used for those chemical systems with unpaired electrons in order to avoid spin contamination. All calculations are for chemical species in the gas phase. A Mulliken population analysis is used in determining atomic charge distribution in the molecules and in the composition of the molecular orbitals. Scheme 1 illustrates the method for calculating the thermodynamic parameters used in this study.

## 3. Results and discussion

### 3.1. Li<sub>6</sub>(C<sub>24</sub>H<sub>12</sub>)<sub>2</sub>

Stage 1 lithium intercalated graphite has been approximated by using two planar coronene carbon lattices to form a sandwich structure in which lithiums can be intercalated. In this investigation, two, three, four and six lithiums are intercalated. Table 1 shows the calculated thermodynamic parameters for coronene and lithium–coronene complexes. The calculated change in Gibbs energy for formation of Li<sub>6</sub>(C<sub>24</sub>H<sub>12</sub>)<sub>2</sub> from six lithium atoms and two coronene carbon lattices is –36.50 kcal/mol at 298.15 K and 1 atm. The calculated change in electronic

\* Corresponding author: Tel.: +1-937-255-7770; Fax: +1-937-656-7529; E-mail: scanlog@picard.ml.wpafb.af.mil

$$\begin{aligned}\Delta E^{298} &= \Delta E_e^0 + \Delta E_v^0 + [\Delta(\Delta E_v)^{298} + \Delta E_r^{298} + \Delta E_t^{298}] \text{ Thermal Energy} \\ \Delta H^{298} &= \Delta E^{298} + \Delta(PV) \\ \Delta G^{298} &= \Delta H^{298} - T\Delta S\end{aligned}$$

### Definition of Terms

$\Delta E_e^0$	Electronic energy difference between products and reactants at 0 K.
$\Delta E_v^0$	Difference between the zero-point vibrational energies of the products and reactants (0 K).
$\Delta(\Delta E_v)^{298}$	Change in the vibrational energy difference between 0 K and 298 K.
$\Delta E_r^{298}$	Difference in the rotational energies of products and reactants at 298 K.
$\Delta E_t^{298}$	Difference in the translational energy change between products and reactants at 298 K.
$\Delta(PV)$	PV work term = $\Delta n RT$ where $\Delta n$ is equal to the difference in moles between products and reactants.

Scheme 1.

energy for this reaction is  $-88.57$  kcal/mol at 0 K. This strong electrostatic interaction is offset by a large reduction in entropy due to lithium intercalation. The  $T\Delta S$  term has a value of  $-63.33$  kcal/mol. The positive charges on lithium range in value from 0.55 to 0.78. This is consistent with electron transfer to the carbon lattice upon lithium intercalation. The optimized structure for  $\text{Li}_6(\text{C}_{24}\text{H}_{12})_2$  is shown in Fig. 1 showing the top and side views. It gives a reasonable approximation for stage 1 lithium intercalated graphite even though the lithium to carbon ratio is 1:8 vs. 1:6 for stage 1 lithium intercalated graphite. Separation between eclipsed carbon lattices in stage 1 lithium intercalated graphite is  $3.70$  Å [3]. In this investigation the calculated results show that the coronene lattices are eclipsed with a separation of  $4.03$  Å. There is a slight ruffling of the carbon lattice as shown in Fig. 1b. Separation between adjacent lithiums in  $\text{Li}_6(\text{C}_{24}\text{H}_{12})_2$  is either  $3.32$  or  $2.98$  Å. Even though the separations are very small, composition of the highest occupied molecular orbitals suggests that there is no lithium cluster formation as found in  $\text{Li}_3\text{C}_{60}$  and  $\text{Li}_5\text{C}_{60}$  endohedral complexes [4]. The three highest occupied molecular orbitals in

$\text{Li}_6(\text{C}_{24}\text{H}_{12})_2$  are composed of a combination of lithium and carbon orbitals. The calculated energies for these orbitals are  $-4.60$ ,  $-3.91$  and  $-3.67$  eV. In contrast, in the  $\text{C}_{60}$  molecule, with either 3 or 5 endohedral lithiums, there are molecular orbitals composed only of lithiums, indicative of cluster formation. The calculated energies for these orbitals are  $-2.37$  and  $-7.68$  eV, respectively.

As shown in Fig. 1a, the lithiums occupy sites near the edge of the carbon lattice as opposed to the interior of the carbon hexagon sites. Electrostatic potential calculations for the dianions of coronene and perylene ( $\text{C}_{20}\text{H}_{12}$ ) suggest that there are two regions of negative electrostatic potential. Fig. 2a and b show that the highest negative electrostatic potential occurs along the edge of the carbon lattice while the potential inside the carbon hexagon sites is somewhat less. Therefore this difference in potential may influence the bonding site for the lithiums.

### 3.2. $\text{Li}_4(\text{C}_{24}\text{H}_{12})_2$

Fig. 3 shows the optimized structure for  $\text{Li}_4(\text{C}_{24}\text{H}_{12})_2$ . The carbon lattices are staggered with a separation of

Table 1  
Gas phase calculated thermodynamics parameters for coronene and lithium–coronene complexes

Molecule	Method/basis set	$E_e^0$ Hartrees <sup>a</sup>	$E_v^0$ kcal/mol	$E^{298}$ (thermal) kcal/mol	$S^{298}$ cal/mol K
$\text{Li}^0$	UHF/3-21G	$-7.3815131$		$0.889^b$	$33.17^c$
$\text{C}_{24}\text{H}_{12}$	RHF/3-21G	$-910.821002$	$190.031$	$197.858$	$109.666$
$\text{Li}_2(\text{C}_{24}\text{H}_{12})_2$	RHF/3-21G	$-1836.4333039$	$377.742$	$396.711$	$188.493$
$\text{Li}_3(\text{C}_{24}\text{H}_{12})_2$	ROHF/3-21G	$-1843.8500348$			
$\text{Li}_4(\text{C}_{24}\text{H}_{12})_2$	RHF/3-21G	$-1851.2737938$	$375.061$	$396.326$	$202.762$
$\text{Li}_4(\text{C}_{24}\text{H}_{12})$	RHF/3-21G	$-940.3778814$	$188.643$	$200.815$	$136.309$
$\text{Li}_6(\text{C}_{24}\text{H}_{12})_2$	RHF/3-21G	$-1866.0722231$	$375.729$	$398.256$	$205.960$
$(\text{C}_{24}\text{H}_{12})^{2-}$	RHF/6-31G(d)	$-915.7274291$			
$(\text{C}_{20}\text{H}_{12})^{2-}$	RHF/6-31G(d)	$-764.2147366$			

<sup>a</sup>1 Hartree =  $627.5095$  kcal/mol.

<sup>b</sup>Translational term,  $3/2 RT$ .

<sup>c</sup>Experimental gas phase value, CRC Handbook of Chemistry and Physics, 73rd edn.

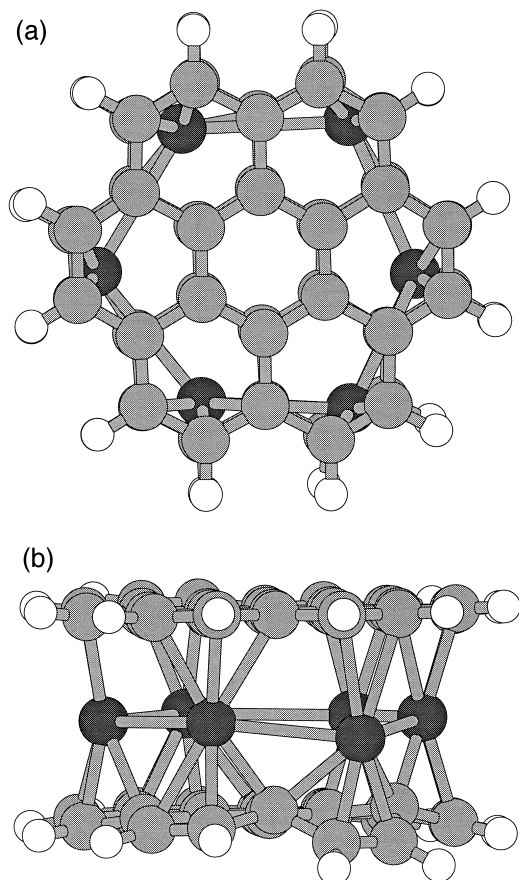


Fig. 1. Optimized structure for  $\text{Li}_6(\text{C}_{24}\text{H}_{12})_2$  showing top (a) and side (b) views.

4.3 Å. The separations between adjacent lithiums are 3.44, 5.01, 4.04 and 4.08 Å. The change in Gibbs energy in the formation of this complex from four lithium atoms and two coronene lattices is  $-32.75$  kcal/mol. The change in electronic energy is  $-66.35$  kcal/mol at 0 K. The value of the  $T\Delta S$  term is  $-44.50$  kcal/mol. As in the case for  $\text{Li}_6(\text{C}_{24}\text{H}_{12})_2$ , the highest occupied molecular orbitals are composed of both lithium and carbon orbitals thus suggesting no lithium cluster formation. The calculated energies for the two highest occupied molecular orbitals are  $-3.86$  and  $-3.45$  eV. The charges on the lithiums vary from 0.74 to 0.78.

### 3.3. $\text{Li}_4(\text{C}_{24}\text{H}_{12})$

Fig. 4 shows the optimized structure for  $\text{Li}_4(\text{C}_{24}\text{H}_{12})$ . The lithiums are arranged in a rectangular fashion approximately 2.3 Å above coronene near the interior carbon hexagon sites. Separation between adjacent lithiums is either 2.99 or 3.31 Å. Initially coronene was planar, but upon complexation with four lithiums, the coronene molecule has become curved. Analysis of the composition of molecular orbitals shows that there is one molecular orbital at  $-4.22$  eV composed only of lithium orbitals.

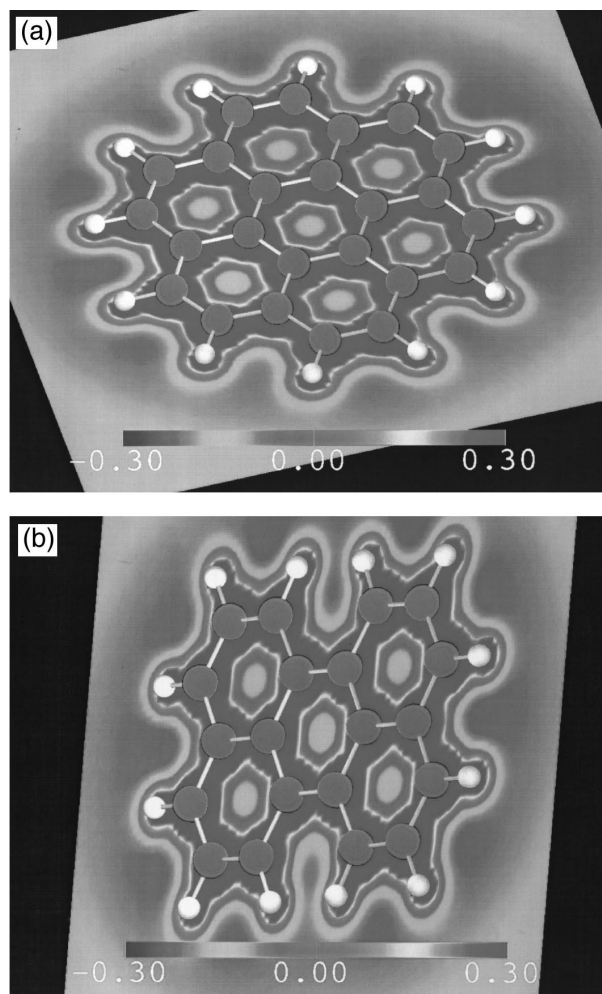


Fig. 2. (a) Electrostatic potential plot for dianion of  $\text{C}_{24}\text{H}_{12}$ . (b) Electrostatic potential plot for dianion of  $\text{C}_{20}\text{H}_{12}$ .

The magnitude of the coefficients for each lithium in this orbital varies from 0.08 to 0.1, while the coefficients for the carbons are on the order of 0.02 or less, except for two

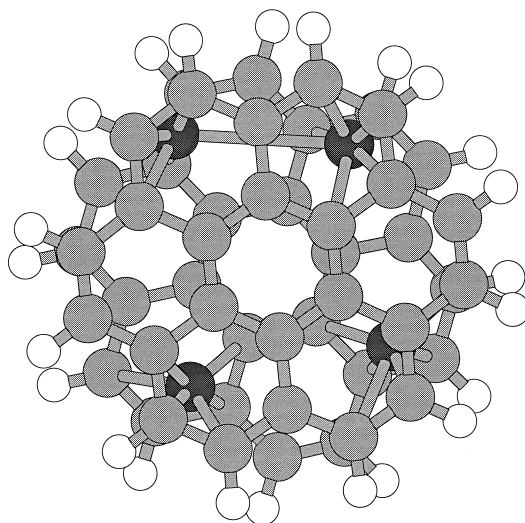
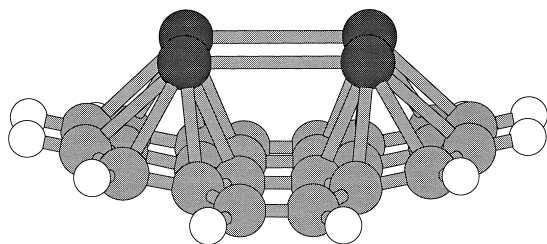
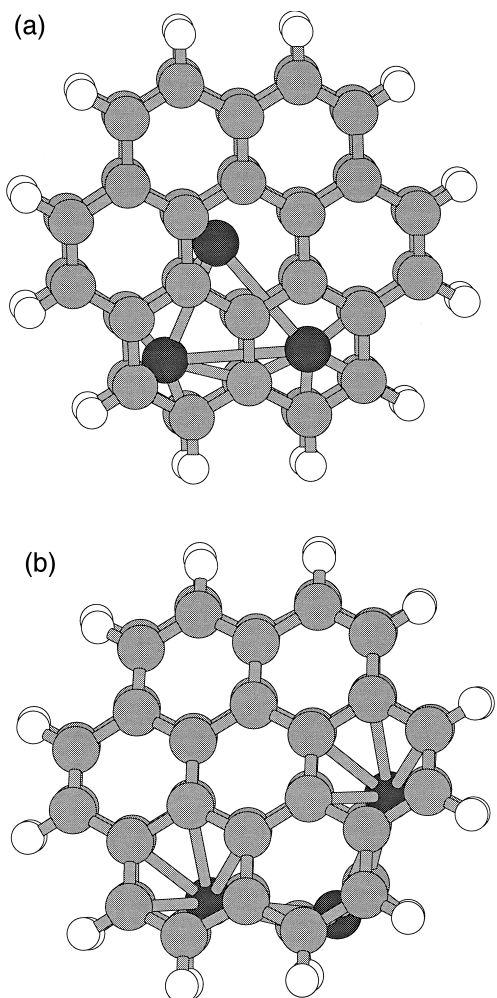
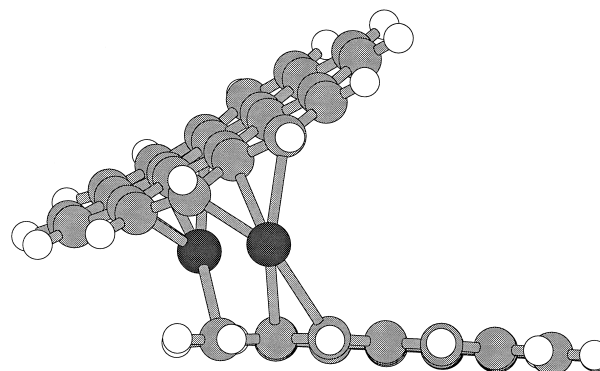


Fig. 3. Optimized structure for  $\text{Li}_4(\text{C}_{24}\text{H}_{12})_2$ .

Fig. 4. Optimized structure for  $\text{Li}_4(\text{C}_{24}\text{H}_{12})$ 

carbons which have values as high as 0.037. The partial positive charge on each lithium is approximately 0.37 which is about one half the magnitude of the charge on lithiums in  $\text{Li}_4(\text{C}_{24}\text{H}_{12})_2$ . The lower charge of 0.37 correlates with two electrons in a molecular orbital composed only of lithium orbitals. The most significant difference for this complex compared to the sandwich structure is that the change in Gibbs energy for formation of  $\text{Li}_4(\text{C}_{24}\text{H}_{12})$  is +7.92 kcal/mol, whereas the change in Gibbs energy for formation of  $\text{Li}_4(\text{C}_{24}\text{H}_{12})_2$  is -32.75 kcal/mol.

Fig. 5. (a) Initial structure prior to optimization for  $\text{Li}_3(\text{C}_{24}\text{H}_{12})_2$ . (b) Optimized structure for  $\text{Li}_3(\text{C}_{24}\text{H}_{12})_2$ .Fig. 6. Optimized structure for  $\text{Li}_2(\text{C}_{24}\text{H}_{12})_2$ .

### 3.4. $\text{Li}_3(\text{C}_{24}\text{H}_{12})_2$

So far the influence of the planar coronene lattice has been to promote lithium ion bonding at the edge sites of the carbon lattice. To test if this was a function of the initial starting conditions for the geometry optimization, it was decided to place three lithiums in a tight cluster near the center of the lattice. This is shown in Fig. 5a. The lithium–lithium separations are 2.72, 2.97 and 3.04 Å. Fig. 5b shows the optimized structure for  $\text{Li}_3(\text{C}_{24}\text{H}_{12})_2$ . The separation between adjacent lithiums is 2.70 Å and separation of the carbon lattices is 4.6 Å. The calculated change in the electronic energy is -39.84 kcal/mol at 0 K. The frequency calculation is still in progress, therefore the change in Gibbs energy has not been calculated. These results for the three lithium case again support the notion that the planar lattice promotes edge site bonding for the lithium ions.

### 3.5. $\text{Li}_2(\text{C}_{24}\text{H}_{12})_2$

In the discussion above, the calculated results suggest that formation of the intercalated lithium carbon complexes are thermodynamically allowed. However, for  $\text{Li}_2(\text{C}_{24}\text{H}_{12})_2$ , the calculated change in Gibbs energy for formation of this complex is +6.36 kcal/mol. Fig. 6

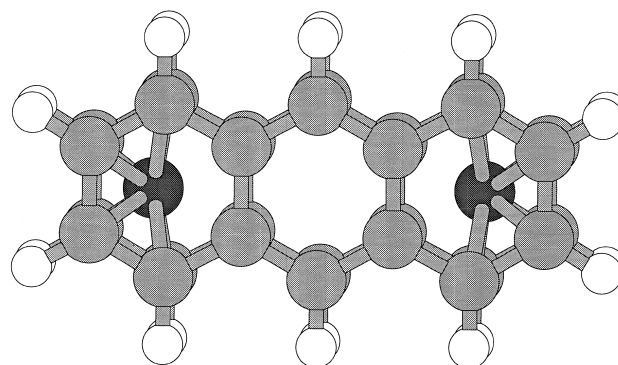
Fig. 7. Optimized structure for  $\text{Li}_2(\text{C}_{14}\text{H}_{10})_2$ .

Table 2

Gas phase calculated thermodynamics parameters for anthracene, boron-substituted anthracene and their lithium complexes

Molecule	Method/basis set	$E_e^0$ Hartrees <sup>a</sup>	$E_v^0$ kcal/mol	$E^{298}$ (thermal) kcal/mol	$S^{298}$ cal/mol K
$\text{Li}^0$	UHF/6-31G(d)	-7.4313723		0.889 <sup>b</sup>	33.17 <sup>c</sup>
$\text{Li}^0$	UHF/6-31 + G(d,p)	-7.4315628		0.889 <sup>b</sup>	33.17 <sup>c</sup>
$\text{C}_{14}\text{H}_{10}$	UHF/6-31 + G(d,p)	-536.0309267	129.890	135.424	92.840
$\text{Li}_2(\text{C}_{14}\text{H}_{10})_2$	ROHF/6-31 + G(d,p)	-1086.9641703			
$\text{Li}_2$ -cluster	UHF/6-31G(d)	-14.866925	0.486	2.201	47.268
$\text{C}_{14}\text{H}_{10}$	RHF/6-31G(d)	-535.9987697	130.671	136.149	91.131
$\text{B}_4\text{C}_{10}\text{H}_6$	UHF/6-31G(d)	-480.620691	89.119	96.054	104.963
$\text{Li}_2(\text{C}_{14}\text{H}_{10})$	UHF/6-31G(d)	-550.8756734	131.814	138.698	101.269
$\text{Li}_2(\text{B}_4\text{C}_{10}\text{H}_6)$	UHF/6-31G(d)	-495.5090539	91.237	99.243	108.431

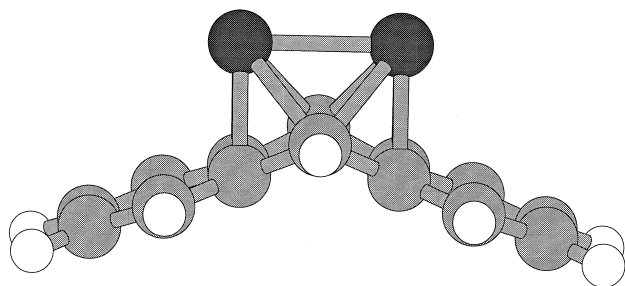
<sup>a</sup>1 Hartree = 627.5095 kcal/mol.<sup>b</sup>Translational term,  $3/2 RT$ .<sup>c</sup>Experimental gas phase value, CRC Handbook of Chemistry and Physics, 73rd edn.<sup>d</sup>1,4,5,8-Tetraboroanthracene.

shows the optimized structure for this complex. The separation of the carbon lattices may be due to repulsion between the lattices. Although the calculated changes in electronic energy at 0 K and enthalpy at 298.15 K are -20.84 and -22.61 kcal/mol, respectively, the reduction in entropy determines the thermodynamic feasibility of the reaction as the magnitude of the  $T\Delta S$  term is -28.97 kcal/mol.

The discussion so far has focused on the influence of the planar coronene carbon lattice on the nature of bonding in lithium intercalated carbon. In the discussion that follows, anthracene was used to form a sandwich structure in which two lithiums are placed. The influence of boron substitution in anthracene has been investigated by comparing the calculated change in Gibbs energy for the reaction of a dilithium cluster with anthracene and boron-substituted anthracene.

### 3.6. $\text{Li}_2(\text{C}_{24}\text{H}_{10})_2$

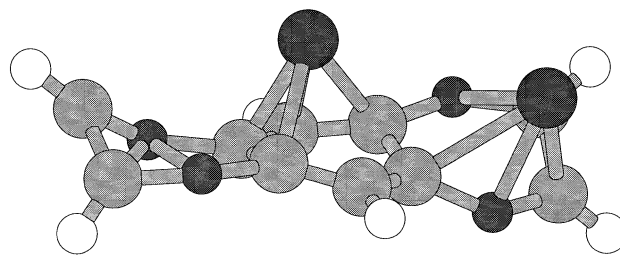
The optimized structure for  $\text{Li}_2(\text{C}_{24}\text{H}_{10})_2$  is shown in Fig. 7. The lithiums are separated by 5.36 Å. Carbon lattice separation is 4.25 Å. Table 2 shows the calculated parameters for anthracene, boron-substituted anthracene, and the lithium complexes. The calculated change in electronic energy for formation of this complex at 0 K is -24.59 kcal/mol. Although this structure may be thermodynamically allowed, the large separation between lithiums

Fig. 8. Optimized structure for  $\text{Li}_2(\text{C}_{14}\text{H}_{10})$ .

is not very representative of the spacing required in stage 1 lithium intercalated graphite.

### 3.7. $\text{Li}_2(\text{C}_{24}\text{H}_{10})$ and $\text{Li}_2(\text{B}_4\text{C}_{10}\text{H}_6)$

In the formation of  $\text{Li}_2(\text{C}_{14}\text{H}_{10})$ , a dilithium cluster was initially positioned over the center ring of anthracene about 1.2 Å above the ring. Fig. 8 shows the optimized structure resulting from the reaction between these two chemical species. The lithiums are ionic with a separation of 2.46 Å. The calculated change in Gibbs energy for this reaction is +5.23 kcal/mol. Fig. 9 shows the optimized structure for  $\text{Li}_2(\text{B}_4\text{C}_{10}\text{H}_6)$ . The initial position of the dilithium cluster was again over the center ring of anthracene. The calculated change in Gibbs energy for formation of  $\text{Li}_2(\text{B}_4\text{C}_{10}\text{H}_6)$  is +1.64 kcal/mol. Although both structures are not thermodynamically allowed, the effect of boron is to enhance the thermodynamic feasibility of the reaction. The enhancement is primarily from the increase in the electrostatic interaction between the lithium ions and the 1,4,5,8-tetraboroanthracene-dianion. This is reflected in the calculated electronic energy which is -13.45 kcal/mol. For  $\text{Li}_2(\text{C}_{14}\text{H}_{10})$ , the calculated electronic energy is -6.26 kcal/mol. The  $T\Delta S$  values are very similar for these two structures. For  $\text{Li}_2(\text{B}_4\text{C}_{10}\text{H}_6)$  and  $\text{Li}_2(\text{C}_{14}\text{H}_{10})$ , the values are -13.06 and -11.58 kcal/mol, respectively.

Fig. 9. Optimized structure for  $\text{Li}_2(\text{B}_4\text{C}_{10}\text{H}_6)$ .

#### 4. Conclusions

Planar carbon lattices may be important for promoting carbon edge site bonding for lithium ions in lithium intercalated graphite where the graphite is highly ordered. However, for very a disordered graphite, which is approximated by a single graphene plane, bonding of lithium ions on one or both sides of the graphene plane may not be thermodynamically favorable. Boron substitution in the carbon lattice may be important for increased lithium capacity.

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