INFLUENCE OF CORANNULENE'S CURVED CARBON LATTICE (C_{20}H_{10}) ON LITHIUM INTERCALATION

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ABSTRACT

Ab initio molecular orbital calculations have been used to investigate the influence of corannulene's curved carbon lattice (C_{20}H_{10}) on lithium intercalation. This has been approximated by investigating the reaction of lithium atoms with either the corannulene molecule directly or with a sandwich structure formed from two corannulene molecules. In the first case, one corannulene molecule, three, six and seven lithiums have been used to form Li_{3}(C_{20}H_{10}), Li_{6}(C_{20}H_{10}) and Li_{7}(C_{20}H_{10}). The last complex has a lithium to carbon ratio of 1:2.86 indicative of a high capacity lithium carbon anode versus the 1:6 ratio found in stage 1 lithium intercalated graphite. The change in Gibbs energy for formation of Li_{3}(C_{20}H_{10}) with a multiplicity of 4 (3 unpaired electrons) is -4.75 kcal/mole. However, when a multiplicity of 2 is used (1 unpaired electron), the change in Gibbs energy is -8.49 kcal/mole. The change in Gibbs energy for formation of Li_{6}(C_{20}H_{10}) and Li_{7}(C_{20}H_{10}) (multiplicity of 2) are -26.48 and -26.47 kcal/mole, respectively. In all the lithium corannulene complexes described, each complex has a molecular orbital composed only of lithium orbitals, indicative of lithium cluster formation. However, in the formation of Li_{3}(C_{20}H_{10})_{2} with three lithium atoms intercalated between two corannulene carbon lattices, there are no molecular orbitals indicative of lithium cluster formation. The multiplicity for this chemical system is 4 and the corannulene lattices are stacked one over the other like saucers. The corannulene carbon lattices are separated by approximately 4.5 Å. The separations between lithiums are 3.13, 3.60 and 3.79 Å. These results are in contrast to those found in the Li_{3}C_{60} endohedral complex with a multiplicity of 4. In this complex there is a molecular orbital composed only of lithium orbitals. The calculated results in this investigation suggest that the carbon lattice stacking configuration is important for lithium cluster formation.

For Li_{6}(C_{20}H_{10}), a transition state intermediate complex has been found through the geometry optimization process. Optimization of this structure results in a complex which is 13.42 kcal/mole more stable. These preliminary results indicate that the energy of activation for the removal of one lithium from this complex is on the
order of 13.42 kcal/mole or 0.58 eV.

INTRODUCTION

Ab initio molecular orbital calculations have been used to investigate the influence of corannulene's curved carbon lattice on lithium intercalation. This has been approximated by investigating the reaction of lithium atoms with either the corannulene molecule directly or with a sandwich structure formed from two corannulene molecules. Previous work with the C\(_{60}\) fullerene carbon lattice indicated that for Li\(_3\)C\(_{60}\) and Li\(_5\)C\(_{60}\) endohedral complexes there are molecular orbitals composed only of lithium orbitals, indicative of lithium cluster formation. However, in a sandwich structure formed from two planar coronene carbon lattices in which six lithiums were intercalated, lithium cluster formation was not observed. For Li\(_6\)(C\(_{24}\)H\(_{12}\))\(_2\) the lithiums are located near the carbon edge sites. Electrostatic potential calculations for the dianions of coronene and perylene (C\(_{20}\)H\(_{12}\)) have shown that the highest negative potential is located on the outside edge of the planar carbon lattice. Thus this high negative potential as well as lithium-lithium repulsion influence the bonding sites for the lithium ions. In this investigation, it has been found that with the curved carbon corannulene carbon lattice the highest negative electrostatic potential for the corannulene dianion is on the concave side of the molecule. The influence of this lattice on the nature of lithium bonding and cluster formation will be discussed.

COMPUTATIONAL APPROACH

Gaussian 94 is used for all ab initio calculations. 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 I illustrates the method for calculating the thermodynamic parameters used in this study.

RESULTS & DISCUSSION

Li\(_3\)(C\(_{20}\)H\(_{10}\)) (Multiplicity 4) Table I shows the calculated thermodynamic parameters for corannulene and lithium corannulene complexes. Figure 1 shows the optimized structure for Li\(_3\)(C\(_{20}\)H\(_{10}\)) with three unpaired electrons (multiplicity 4). The lithium separation distances are 3.17, 3.17 and 2.75 Å. Lithium-carbon separations vary from 2.16 to 2.58 Å. The positive charges on the lithiums are 0.46, 0.46 and 0.56. Analysis of the composition of the molecular orbitals shows that there is a molecular orbital at -1.69 eV composed only of lithium orbitals. This is indicative of lithium cluster formation. The total atomic spin densities for the three lithiums are 0.38, 0.38 and 0.30. This suggests that there is an electron shared between the three lithiums which is also consistent with lithium cluster formation.
Scheme I

\[ \Delta E^{298} = \Delta E_e^0 + \Delta E_v^0 + \left[ \Delta \left( \Delta E_e^{298} + \Delta E_r^{298} + \Delta E_t^{298} \right) \right] \text{Thermal Energy} \]

\[ \Delta H^{298} = \Delta E^{298} + \Delta (PV) \]

\[ \Delta G^{298} = \Delta H^{298} - T \Delta S \]

**Definition of Terms**

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

Table I. Gas Phase calculated thermodynamics parameters for corannulene and lithium-corannulene complexes.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Method/ Basis Set</th>
<th>$E_e^0$ Hartrees*</th>
<th>$E_v^0$ kcal/mole</th>
<th>$E^{298}$ (thermal) kcal/mole</th>
<th>$S^{298}$ cal/mole-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^0$</td>
<td>UHF/3-21G</td>
<td>-7.3815131</td>
<td>156.604</td>
<td>163.113</td>
<td>99.658</td>
</tr>
<tr>
<td>C$<em>{20}$H$</em>{10}$</td>
<td>RHF/3-21G</td>
<td>-758.9081759</td>
<td>155.019</td>
<td>164.479</td>
<td>120.541</td>
</tr>
<tr>
<td>Li$<em>3$(C$</em>{20}$H$_{10}$)#</td>
<td>ROHF/3-21G</td>
<td>-781.0902258</td>
<td>156.530</td>
<td>166.280</td>
<td>122.435</td>
</tr>
<tr>
<td>Li$<em>3$(C$</em>{20}$H$_{10}$)##</td>
<td>ROHF/3-21G</td>
<td>-781.100568</td>
<td>156.530</td>
<td>166.280</td>
<td>122.435</td>
</tr>
<tr>
<td>Li$<em>3$(C$</em>{20}$H$_{10}$)$_2$#</td>
<td>ROHF/3-21G</td>
<td>1540.0605329</td>
<td>158.511</td>
<td>171.152</td>
<td>140.070</td>
</tr>
<tr>
<td>Li$<em>6$(C$</em>{20}$H$_{10}$)</td>
<td>RHF/3-21G</td>
<td>-803.3165143</td>
<td>158.511</td>
<td>171.152</td>
<td>140.070</td>
</tr>
<tr>
<td>Li$<em>6$(C$</em>{20}$H$_{10}$)###</td>
<td>RHF/3-21G</td>
<td>-803.2951244</td>
<td>158.158</td>
<td>170.480</td>
<td>138.534</td>
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<tr>
<td>Li$<em>7$(C$</em>{20}$H$_{10}$)</td>
<td>ROHF/3-21G</td>
<td>-810.7112498</td>
<td>159.263</td>
<td>173.040</td>
<td>149.272</td>
</tr>
<tr>
<td>(C$<em>{20}$H$</em>{10}$)$_2$##</td>
<td>RHF/6-31G(d)</td>
<td>-762.9608339</td>
<td>158.511</td>
<td>171.152</td>
<td>140.070</td>
</tr>
</tbody>
</table>

* 1 Hartree=627.5095 kcal/mole
** Translational term, $3/2 \ RT$
*** Experimental Gas Phase Value CRC Handbook of Chemistry & Physics 73rd Edition
# Multiplicity is 4 (three unpaired electrons)
## Multiplicity is 2 (one unpaired electron)
### Transition state complex
The electrostatic potential calculation for the dianion of corannulene shows that the highest negative potential is on the concave side of the ring. This is shown in Figure 2. In view of the positions of the lithium ions, this effect plays a prominent role in determining lithium bonding sites. The change in Gibbs energy for formation of Li₃(C₂₀H₁₀) is -4.75 kcal/mole at 298.15 K and 1 atm.

Li₃(C₂₀H₁₀) (Multiplicity 2) The effect of changing the multiplicity from 4 to 2 (one unpaired electron) was evaluated in order to determine its influence on structure and relative energy. This is illustrated in Figures 3 and 4.

When compared to the previous structure with a multiplicity of 4, the lithium separations are mostly smaller. The values for these separations are 3.02, 3.02 and 2.83 Å. The change in Gibbs energy for formation of Li₃(C₂₀H₁₀), multiplicity of 2, is -8.49 kcal/mole at 298.15 and 1 atm. The greater change in Gibbs energy for this system is primarily due to the increased electrostatic energy which amounts to about 3 kcal/mole. In this system there is a molecular orbital composed only of lithium orbitals. The calculated energy level is -4.22 eV. The total atomic spin densities for the lithiums are zero since there are two electrons in this orbital.

Li₃(C₂₀H₁₀)₂ So far, for the lithium-corannulene complexes described, there has been a molecular orbital composed only of lithium orbitals indicative of lithium cluster formation. The influence of a second corannulene lattice stacked on the first lattice, like stacking saucers, is investigated here. The optimized structure is shown in Figure 5. The multiplicity for this system is 4. The separations between lithiums are 3.13, 3.60 and 3.79 Å. The total atomic spin densities for lithiums are nearly zero. The calculated values are 0.04, 0.05 and 0.07. Analysis of the composition of the molecular orbitals shows that there are no orbitals composed only of lithium orbitals.
Fig. 5. Optimized structure for Li$_3$(C$_{20}$H$_{10}$)$_2$.

It therefore appears that in this structure there is no lithium cluster formation. The lithiums are ionic. For this structure, the change in electronic energy at 0 K is -62.53 kcal/mole. The frequency calculation is still in progress.

Li$_6$(C$_{20}$H$_{10}$) Figure 6 shows the optimized structure for Li$_6$(C$_{20}$H$_{10}$).

Fig. 6 Optimized structure for Li$_6$(C$_{20}$H$_{10}$).

Four of the lithiums near the corannulene carbon lattice form a diamond pattern. The lithium carbon separations are on the order of 2.2 to 2.5 Å. The lithium separations along the diamond edge are either 2.79 or 3.37 Å. There is a fifth lithium located in the center and above the diamond pattern which gives the appearance of a distorted square pyramidal structure. This lithium is approximately 2.68 Å above an axis formed from the two lithiums bonded to the corannulene ring and separated by 3.1 Å. A sixth lithium forms a triangular pattern with the apical lithium and one of the lithiums forming the diamond pattern. The separations of this lithium from the apical lithium and the lithium forming the diamond pattern are 3.21 and 3.1 Å, respectively. The change in Gibbs energy for formation of this complex is -26.48 kcal/mole at 298.15 K and 1 atm. There are two molecular orbitals composed only of lithium orbitals indicative of cluster formation. The calculated energies for these orbitals are -4.46 and -6.11 eV.

Li$_6$(C$_{20}$H$_{10}$) (Transition State Complex) Figure 7 shows the optimized structure for Li$_6$(C$_{20}$H$_{10}$). The results of the frequency calculation suggest that this structure is representative of a transition state complex.

Fig. 7. Optimized structure for Li$_6$(C$_{20}$H$_{10}$) (Transition State Complex).

There is an imaginary frequency at -61.8 cm$^{-1}$. The difference in energy between this structure and for the optimized structure Li$_6$(C$_{20}$H$_{10}$) with no imaginary frequency is 13.42 kcal/mole. The transition state complex is less stable by this amount. These results suggest that the energy of activation for the dissociation of Li$_6$(C$_{20}$H$_{10}$) to form Li$_5$(C$_{20}$H$_{10}$) and a lithium atom is on the order of 13.42 kcal/mole or 0.58 eV.

Li$_7$(C$_{20}$H$_{10}$) The optimized structure for Li$_7$(C$_{20}$H$_{10}$) is shown in Figure 8.
There are five lithium ions directly bonding with the corannulene lattice as for the transition state complex. The separations between the lithiums are on the order of 3.0 Å. In this complex, there are three molecular orbitals that are composed only of lithium orbitals. The calculated energies for these orbitals are -0.54, -4.62 and -6.47 eV. The lithium to carbon ratio in this complex is 1:2.86. This ratio is indicative of a high capacity lithium intercalated carbon anode. The change in Gibbs energy for the formation of this complex is -26.47 kcal/mole. This value is very similar to that found for Li₆(C₂₀H₁₀) which is -26.48 kcal/mole. For Li₇(C₂₀H₁₀), the change in enthalpy at 298.15 K is about 7 kcal/greater than that calculated for Li₆(C₂₀H₁₀). However, the greater enthalpy for Li₇(C₂₀H₁₀) is offset by a greater reduction in entropy which amounts to 7.15 kcal/mole for the TΔS term. Therefore the change in Gibbs energy for formation of these complexes is very similar.

CONCLUSIONS

The calculated results suggest that both lattice curvature and stacking configuration are important for lithium cluster formation. In the first case lithium cluster formation is enhanced while in the latter case it is not.

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REFERENCES