Extended Abstracts of the 2006 International Conference on Solid State Devices and Materials, Yokohama, 2006, pp. 314-315

D-4-3

Theoretical Investigation of Electrical and Electronic Properties of Carbon Materials

Arunabhiram Chutia[1], Zhigang Zhu [1], Hideyuki Tsuboi[1], Michihisa Koyama [1], Akira Endou[1], Momoji Kubo [1,2], Carlos A. Del Carpio[1], Parasuraman Selvam[3], Akira Miyamoto [1,3,*]

[1]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-11-1302, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[2]PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan
[3]New Industry Creation Hatchery Center, Tohoku University, 6-6-10, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
Tel.: + 81-22-795-7236; Fax: + 81-22-795-7235; E-Mail: miyamoto@aki.che.tohoku.ac.jp

1. Introduction

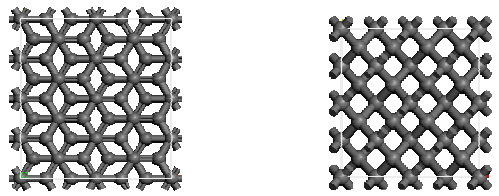
The linear carbon chains with conjugated double bonds are one of the most promising groups of one-dimensional systems whose electronic properties differ from the periodic three-dimensional materials. In recent years, the theoretical investigations on the electronic properties of such materials, a new group of quantum-well structures other than those based on metals, have been in focus [1]. These investigations on the electronic properties of conjugated organic polymers have provided interesting information that has resulted in the understanding of the relationship between structural, electronic and optical properties of the certain polymers. For example, Weimer et al. [1] have shown the effect of chain length and substituents on the energy gap of polymer chains; Briére et al. [2] have treated the polymer as a one dimensional periodic system and they found smaller energy gaps for carbazole and borafluorene as compared to the biphenyl and fluorene. While these studies have dealt with the fundamental aspects of these materials, we, for the first time, focus our attention to investigate theoretically the electrical conductivity of some linear carbon chains. In this work, apart from investigating the energy gap due to the highest occupied and lowest unoccupied molecular orbitals with the increase in chain lengths of the conjugated polyenes, we apply our novel tight-binding quantum chemical molecular dynamics program, "Colors" [3] to estimate the electrical conductivity of the systems under study.

2. Computational Details

In this investigation, the "Colors" code was used to study the electronic properties and estimating the electrical conductivity [3]. The DMol^3 and CASTEP programs were also employed to deduce the electronic properties of these systems. In our studies, fully optimized structures were used and these structures were optimized using DMol^3 at DNP level of basis set with GGA/PW91 exchange and correlation functional. In CASTEP, the cell optimization was carried out using plane wave basis set and GGA/PW91 functional, and that periodic structures were employed.

3. Results and Discussion

In this study, electrical and electronic property investigation was carried on diamond and graphite. The models used for this study is shown in Fig 1.



(a) (b)

Fig. 1 Calculation model for: (a) graphite and (b) Diamond.

Table I presents the estimated values of energy gaps and electrical conductivity of graphite and diamond. From the estimated values of conductivity, it may be noted that, as expected, diamond shows an insulating behavior while graphite display conducting behavior. The estimated conductivity value of graphite is in good agreement with the experimental findings while the observed difference of electrical conductivity of diamond could be attributed to the structural characteristics or difficulty in measuring the electrical conductivity of insulators [3]. Thus, the present investigation validated our proposed methodology for estimation of conductivity and its application to understand the electrical properties of different carbon materials.

Table I Calculated energy gap and electrical conductivity of graphite and diamond.

Species	Energy gap (eV)		Electrical conductivity (S cm^{-1})	
	Calc.	Exp.	Calc.	Exp.
Graphite	0.0	0.0	0.7×10^{5}	$\sim 10^{5}$
Diamond	5.6	5.5	5.6×10^{-32}	$\sim 10^{-13}$

Table II shows the highest occupied and the lowest unoccupied molecular orbital energy gaps obtained from our calculation for the C_nH_{n+2} (n = 2, 4, 8, 10, 14 and 16) systems. All the C_nH_{n+2} systems are *trans*-polyenes. It is clear from this study that the observed energy gap values obtained from Colors program is in good agreement with the experimental findings. On the other hand, DMol^3 have underestimated the energy gap values for the well-known defects of DFT [4], i.e., while the common LDA and GGA exchange-correlation functional yield useful ground state energy and other ground state properties, they usually result in orbital energy spectra which are qualitatively incorrect. This is especially true for the unoccupied orbital manifold. As a result the HOMO-LUMO energy gaps are often

underestimated. Fig.2 shows the partial density of states (PDOS) for C_8H_{10} system obtained from Colors and CASTEP. It is found that the C(2*p*) orbital contributes mainly to the highest occupied and the lowest occupied molecular orbital. Table III summarizes the calculated electrical conductivity data. The conductivity values presented in this table are with reference to the $C_{16}H_{18}$ system, which has been normalized using experimental data. The theoretically estimated values for the electrical conductivity of these systems have shown that there is an increase in the electrical conductivity with the increase in the chain length.

Table II Theoretical and experimental [4] energy gaps of certain polyenes.

System	Energy gap (eV)		
	Colors	DMol^3	Exp.
C_2H_4	7.59	5.75	7.6
C_4H_6	5.88	3.92	5.9
C_8H_{10}	4.47	2.41	4.4
$C_{10}H_{12}$	3.72	2.03	3.7
$C_{14}H_{16}$	2.86	1.56	3.2
$C_{16}H_{18}$	2.59	1.39	3.02

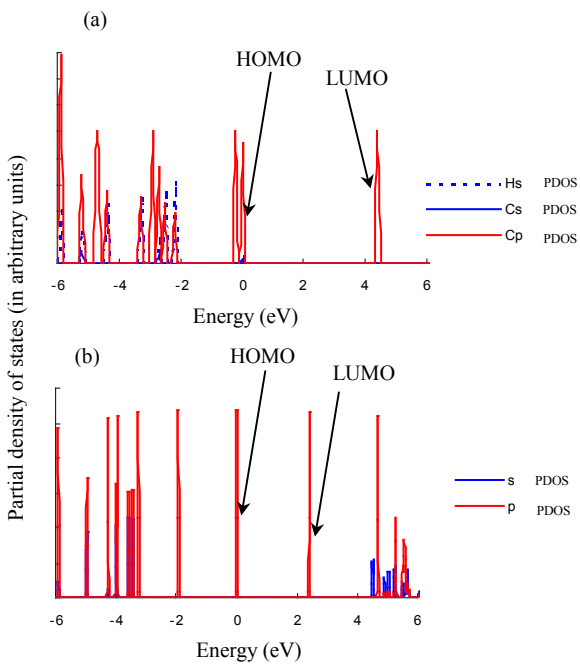


Fig. 2 PDOS of C_8H_{10} obtained from: (a) Colors and (b) CASTEP.

Table III Estimated electrical conductivity of C_nH_{n+2} (n = 4, 8, 10, 14 and 16) .

Systems	Electrical conductivity (S cm^{-1})
C_4H_6	1.3×10^{-33}
C_8H_{10}	8.7×10^{-22}
$C_{10}H_{12}$	4.5×10^{-15}
$C_{14}H_{16}$	7.4×10^{-8}
$C_{16}H_{18}$	1.1×10^{-5}

In order to study the effect of doping on these systems, we considered two different models. In one of the models, Fig. 3(b), a hydrogen atom was replaced by bromine atom in C_8H_{10} system, while in the other, bromine molecule (Br_2), Fig. 3 (c), was placed near the C_8H_{10} system. With the bromination and placing the bromine molecule near the polyacetylene molecule reduced the HOMO-LUMO energy gap considerably. The calculated values for HOMO-LUMO energy gaps are listed in Table IV. The electrical conductivity of these systems is then estimated. During this process, we observed that with doping the electrical conductivity of the system increases by an order of 10^9. This observation is in agreement with the experimental findings.

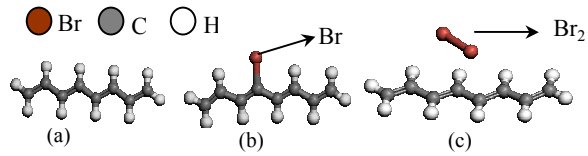


Fig. 3 Optimized structures of: (a) C_8H_{10}, (b) C_8H_9Br and (c) $C_8H_{10}Br_2$.

Table IV Estimated energy gap and electrical conductivity of undoped and doped C_8H_{10} system.

System	HOMO-LUMO energy gap (eV)		Electrical conductivity† (S cm^{-1})
	Calc.	Exp.	Calc.
C_8H_{10}	4.57	4.4	8.7×10^{-22}
C_8H_9Br	3.39	-	7.6×10^{-13}
$C_8H_{10}Br_2$	3.48	-	2.7×10^{-13}

† Normalized with experimental data [5].

4. Conclusions

The energy gap and electrical conductivity of diamond and graphite were successfully estimated and validating our methodology for its use in studying carbon polymers. The electrical conductivity of undoped and doped polyacetylene was then carried out which revealed that the doped polyacetylenes have conductivity of 10^9 more than the former. These findings agree well with the experimental data.

References

[1] M. Weimer, W. Hieringer, F. D. Sala, A. Gorling, *Chem. Phys.* 309 (2005) 77-87

[2] J. Briére and M. Côté, *J. Phys. Chem. B* 108 (2004) 3123-3129

[3] H. Tsuboi, H. Setogawa, M. Koyama, A. Endou, M. Kubo, C. A. Del Carpio, E. Brochlawick, A. Miyamoto; *Jpn. J. Appl. Phys.* 45 (2006) 3137-3143

[4] U. Salzner, J. B. Lagowski, P.G. Pickup and R. A. Poirier, *J. Comp. Chem.* 18 (1997) 1943-1953.

[5] C. K. Chiang, *Phyica A* 321 (2003) 139-151.