The Body-Centered Cubic Structure of Methyllithium Tetramer Crystal: Staggered Methyl Conformation by Electrostatic Stabilization via Intratetramer Multipolarization

Yusuke Ohta, Akimitsu Demura, Takuya Okamoto, Haruko Hitomi, and Masataka Nagaoka*

Graduate School of Information Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

Received: December 2, 2005; In Final Form: April 24, 2006

The methyllithium tetramer $(CH_3Li)_4$ structure in the bcc crystal has been theoretically optimized with the use of density functional theory calculations under the periodic boundary condition. The X-ray structure shows that the methyl-group conformation in tetramer in crystal takes the staggered form rather than the eclipsed form that is taken in the isolated tetramer, i.e., the crystal packing effect, and this has been reproduced for the first time. It is concluded that the staggered form is advantageous in crystal, as a whole, due to the larger electrostatic stabilization via the induced intratetramer multipolarization, although it should cause, simultaneously, smaller destabilization in intratetramer electronic energy.

1. Introduction

Alkyllithiums are organometallic reagents that are not only strong bases but also very useful compounds in organic synthesis, as they form an important group of nucleophilic reagents. However, the native structures of these reagents in solution remain incompletely understood, and there is a strong desire to clarify the aggregation type in which such alkyllithiums as methyllithium, ethyllithium, and buthyllithium exist in solution: dimeric, tetrameric, or hexameric.[1]

There have been a number of studies, especially for methyllithium in aggregation, via NMR,[2] flash vaporization mass spectroscopy,[3] X-ray analysis,[4] neutron powder diffraction,[4] reaction rate analysis,[5] and molecular orbital (MO) calculations.[6-14] There have also been a few reports on crystal methyllithium from X-ray powder diffraction, which showed the body-centered cubic (bcc) unit cell ($a = 7.24$ Å, space group I-4_3m (no. 217)) containing two tetramers with the atomic distances $r(Li-Li) = 2.68$ Å, $r(C-Li) = 2.31$ Å (intratetramer), and $r(C-Li) = 2.36$ Å (intertetramer), respectively.[4b]

Meanwhile, Streitwieser[15a] and Bushby[15b,c] showed that even a simple electrostatic model can reproduce the ratio of $r(C-C)$ and $r(Li-Li)$ distances in tetrameric methyllithium, leading to the recent theoretical viewpoint that organolithium oligomers $(RLi)_n$ can be considered to be aggregates of lithium cations and carbanions, predominantly bound by electrostatic forces.[6] However, Schleyer long opposed this claim of the highly ionic nature of organolithium electrostatic model compounds, and it has been reported that $r(Li-Li) = 2.40$ Å and $r(C-Li) = 2.20$ Å for the isolated methyllithium tetramer by the B3LYP/6-31+G(d) level of theory.[8a]

Although these theoretical values, on the whole, are in quite good agreement with the experimental values for oligomers, it is interesting that the eclipsed conformation of four methyl groups existing in the tetramer (T_d symmetry) is different from that reported experimentally for crystal methyllithium by 60 degrees, since the latter methyl groups each show a staggered conformation with respect to the C−Li bond (Figures 1a and 1b). In relation to the fact that the agostic interaction[16] between

the C−H bond and lithium atom is significantly larger than those in monomers and dimers and leads to a shortening of the $r(Li-H)$ distance in the eclipsed conformation of the C−H and the C−Li bonds,[8a] it was recently suggested that the conformation difference might be due to the interaction among methyl groups of neighboring methyllithium tetramers, giving rise to the "packing effect" that favors the staggered conformation.[1a,8a]

In this article, we (i) report for the first time the theoretically optimized structures of methyllithium tetramers in the unit cell of the bcc crystal, and (ii) clarify the reason for the structural difference in methyllithium tetramer $(CH_3Li)_4$ between the isolated and bcc crystal states. The computational details are first explained in section 2, and the results and discussion are then presented in section 3. Finally, a summary is given in section 4.

2. Computational Details

To estimate the total energy difference depending on the conformation of methyl groups in isolated methyllithium tetramers, 24 successive partial optimizations were executed for the tetramer under 24 different constraints of the dihedral angle χ(H−C−X−Li) (X: a dummy atom (the yellow central sphere in Figure 1), from 0 to 120 degrees in 5-degree increments. Then, 24 calculations were performed using the B3LYP/6-31G-(d)//B3LYP/6-31G(d) level of theory in Gaussian98,[17] i.e., an ab initio MO program package.

Next, to optimize the crystal structure and the total energy in both unit cells of the eclipsed and the staggered conformation, CASTEP,[18a] i.e., an ab initio quantum mechanical program package based on the density functional theory (DFT), was utilized with a total energy plane-wave pseudopotential method.[18b,19,20] The LDA/CA-PZ//LDA/CA-PZ[21] level of theory was then employed. Under the periodic boundary condition (PBC), two tetramers in a unit cell were treated by using the kinetic energy cutoff from 300 to 1300 eV for plane-waves, employing also the ultrasoft pseudopotential (USP) method[22] for the LDA/CA-PZ.

In addition, Gaussian03[23] was utilized with the keyword PBC to study the methyllithium crystal structure. To optimize the

* Corresponding author. URL: http://frontier.ncube.human.nagoya-u.ac.jp/; Tel & Fax: +81-052-789-5623.

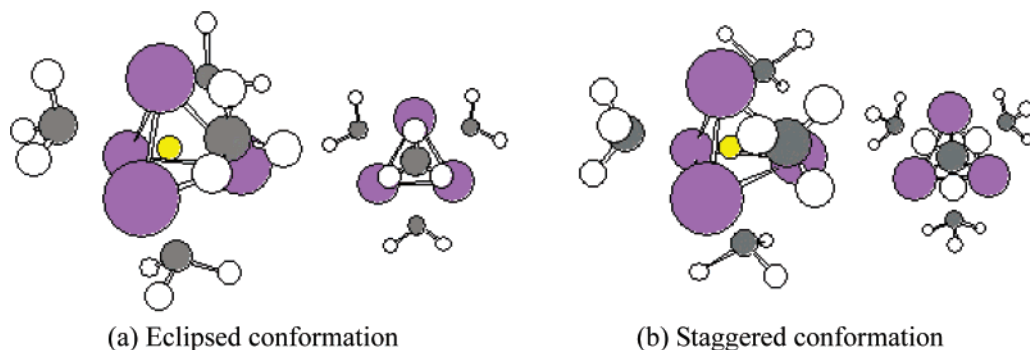(a) Eclipsed conformation (b) Staggered conformation

Figure 1. Optimized structures of methyllithium tetramer $(CH_3Li)_4$ (C, gray; H, white; Li, purple; X (dummy atom), yellow): (a) tetramer in isolation (T_d symmetry, eclipsed conformation) and (b) tetramer in crystal (T_d symmetry, staggered conformation).
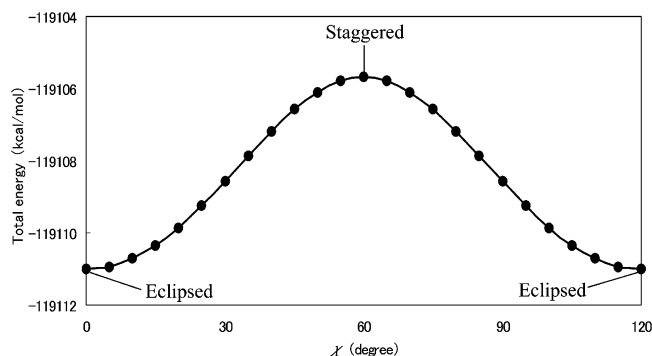

Figure 2. Total energy curve of the isolated methyllithium tetramer $(CH_3Li)_4$ depending on the dihedral angle of methyl group $\chi(H-C-X-Li)$ at the B3LYP/6-31G(d) level of theory (eclipsed conformation: $\chi = 0$ or 120 degrees and staggered conformation: $\chi = 60$ degrees).

structure and the total energy in unit cells of the eclipsed and the staggered conformation, we executed the LSDA/3-21G//LSDA/3-21G calculation on a Fujitsu HPC2500 (64cpu/2node, 32GBmem).

3. Results and Discussion

3.1. Eclipsed Conformation of Methyllithium Tetramer in Isolation. In Figure 1, the isolated tetramer structure (Figure 1a) is compared with one tetramer in a unit cell of the bcc crystal (Figure 1b), because its unit cell consists of two tetramers of methyllithium. It is seen that the relative conformations of three hydrogens in each methyl group with respect to the C–Li bond differ between the tetramers in isolation (Figure 1a) and in crystal (Figure 1b). Namely, the dihedral angles of the C–Li and the C–H bond of each methyl group with respect to the 3-fold axis of the methyl group are 0 degrees in tetramers in isolation and 60 degrees in those in crystal. In the optimized isolated geometry, four methyl groups in the tetramer are all in eclipsed conformations, while those in the bcc crystal are in staggered conformations not only experimentally but also theoretically (see, the following subsection 3.2).

In Figure 2, the total energy curve is shown as a function of the dihedral angle of methyl group $\chi(H-C-X-Li)$, the numerical values being obtained through 24 partial optimizations of the isolated tetramer at the B3LYP/6-31G(d) level of theory. According to Figure 2, the total energy at the eclipsed conformation ($\chi = 0$ or 120 degrees) was found to be the minimum while that at the staggered one ($\chi = 60$ degrees) was the maximum. As a result, since the energy of the eclipsed conformation is lower in isolation by 5.33 kcal/mol than that of the staggered one, the former conformation should be more

plausible in isolation than the latter one. This result is consistent with previous observations that the eclipsed conformation is 5.7 kcal/mol[7] or 6.9 kcal/mol[8a] more stable than the staggered one at B3LYP/6-311+G(2d,p)+ZPC//B3LYP/6-31+G(d) or MP2/6-31G(d)//HF/6-31G+6d(C), where the expression 6-31G+6d-(C) designates such a 6-31G basis set with six additional d-type functions on carbon but not on lithium.[8a]
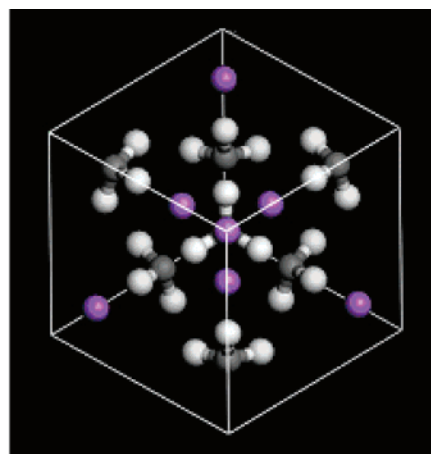
3.2. Staggered Conformation of Methyllithium Tetramer in the bcc Crystal. For the eclipsed and the staggered conformation of two methyllithium tetramers in the unit cell of bcc crystal, we executed structure optimizations by CASTEP under the PBC at the LDA/CA-PZ//LDA/CA-PZ level of theory, with 1300 eV kinetic energy cutoff for plane-waves and 72 Fourier transform grids. The optimized structures are shown in Figures 3a and 3b for the eclipsed and the staggered conformation of two tetramers in the bcc unit cell, respectively. As shown in Table 1, the optimized lattice constants for the eclipsed and the staggered conformation were found to be 6.92 and 6.82 Å, respectively, and which correspond reasonably with the experimental value (7.24 Å).[4a] Figure 4 shows that the convergence of the total energy per bcc unit cell was finally satisfactorily accomplished at the kinetic energy cutoff of 1300 eV for plane waves for both the eclipsed and the staggered conformation. Thus, it has been shown *for the first time* that the total energy per unit cell of the staggered conformation is about 1.57 kcal/mol *lower* than that of the eclipsed one (Figure 4).

Similarly, the optimized structures by Gaussian03 at the LSDA/3-21G//LSDA/3-21G level of theory, were found to be almost the same as those by CASTEP (Figures 3a and 3b). The total computing time was almost 1 khr each for the eclipsed and the staggered conformation, using 8 CPUs in parallel on a Fujitsu HPC2500 (64cpu/2node, 32GBmem). The optimized lattice constants for the eclipsed and the staggered conformation, i.e., 6.90 and 6.85 Å, also show a good agreement with the experimental values (Table 1). On the other hand, for the total energy per unit cell, the staggered conformation is about 7.69 kcal/mol more stable than the eclipsed one (Table 1), with the former showing a larger stabilization in Gaussian03 calculation. It should be noted again that, as far as we know, the present theoretical calculations are the first to successfully reproduce the previous experimental results for the methyllithium crystal by Weiss et al.[4]

Now, why does the methyllithium tetramer in the bcc crystal exist in the staggered conformation? As was mentioned in the Introduction, it has been suggested that the conformation difference might be due to the interaction among methyl groups of neighboring methyllithium tetramers, giving rise to the "crystal packing effect" which favors the staggered conformation.[1a,8a] While most previous researches claimed that the crystal packing effect with short-range interactions should determine
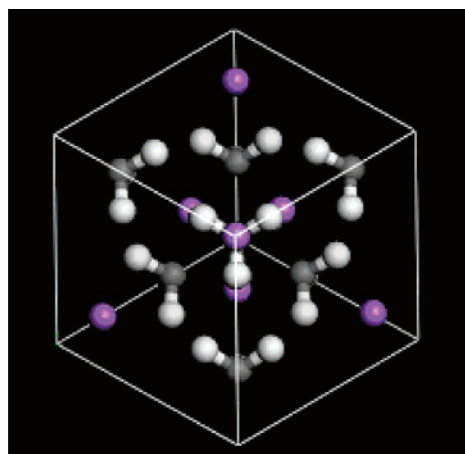
(a) Eclipsed conformation   (b) Staggered conformation

Figure 3. Optimized structures of two methyllithium tetramers $[(CH_3Li)_4]_2$ in the bcc unit cell (C, gray; H, white; Li, purple; space group I-4_3m (no. 217)): (a) eclipsed conformation and (b) staggered conformation.

TABLE 1: Optimized Lattice Constants (experimental value: 7.24 Å) and Relative Energies (eclipsed conformation standard) per bcc Unit Cell for the Optimized Eclipsed and Staggered Conformation of Two Methyllithium Tetramers $[(CH_3Li)_4]_2$ in a bcc Unit Cell

	eclipsed conformation		staggered conformation	
	CASTEP[a]	Gaussian03[b]	CASTEP[a]	Gaussian03[b]
lattice constant (Å)	6.92	6.90	6.82	6.85
relative energy (kcal/mol)	0.00	0.00	−1.57	−7.69

[a] At the LDA/CA-PZ level. [b] At the LSDA/3-21G level.

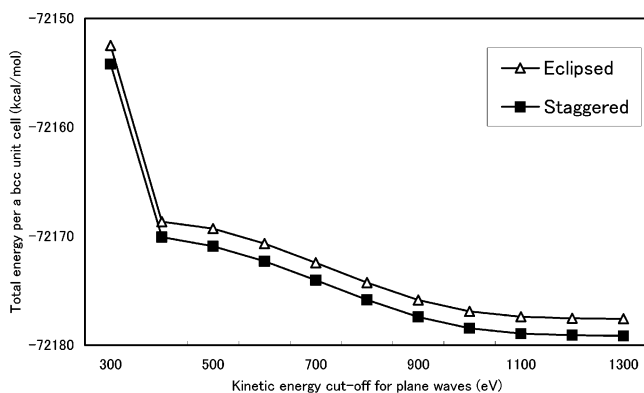**Figure 4.** Total energy per bcc unit cell for the optimized eclipsed and staggered conformation of two methyllithium tetramers $[(CH_3Li)_4]_2$ at the LDA/CA-PZ level of theory using the ultrasoft pseudopotential (USP) method.

the alignment of the methyl groups,[8a] it is our view that the *inclusion of long-range interactions among redistributed charges of tetramers is also important*. We posit that our calculation results are due to the enhancement of charge multipolarization in the intratetramer. In the following subsection, we show that this conjecture is reasonable by using the effective point charge model.

3.3. Electrostatic Stabilization in Crystal via Intratetramer Multipolarization: The Effective Point Charge Model. For the purpose of understanding why the methyl group conformations differ between the isolated tetramer and the bcc crystal, the *effective lattice energy* $E_{(CH_3Li)_4}^{lattice}$ per unit cell in the bcc lattice crystal was estimated with the use of the *effective point charge model* of lattice energy, where $E_{(CH_3Li)_4}^{lattice}$ is assumed to be the sum of the intratetramer energy of *two* isolated tetramers

$E_{(CH_3Li)_4}^{isolated}$ and the effective lattice potential energy $V_{(CH_3Li)_4}^{lattice}$ as follows:

$$E_{(CH_3Li)_4}^{lattice} = E_{(CH_3Li)_4}^{isolated} + V_{(CH_3Li)_4}^{lattice} \quad (1)$$

where $V_{(CH_3Li)_4}^{lattice}$ can be expressed as the sum of the electrostatic potential energy V_{es} and the van der Waals (vdW) potential energy V_{vdW} as

$$V_{(CH_3Li)_4}^{lattice} = V_{es} + V_{vdW} \quad (2)$$

$$= \sum_{i>j}^{[(CH_3Li)_4]_\infty} \frac{q_i q_j}{4\pi\epsilon_0 R_{ij}} \sum_{m<n}^{[(CH_3Li)_4]_\infty} \left(\frac{A_{mn}}{R_{mn}^{12}} - \frac{B_{mn}}{R_{mn}^{6}} \right) \quad (3)$$

In eq 3, under pairwise approximation, V_{es} and V_{vdW} are treated as Coulomb and Lennard-Jones (L-J) interaction expressions between tetramers in the crystal structure, respectively, ϵ_0 is the dielectric constant of vacuum, $q_{i(\text{or } j)}$, and R_{ij} indicate the effective point charges of the tetramer-constituting CH_3 (as a pseudo atom) and Li, and the interpoint charge separation between the ith and jth effective point charge, respectively, which individually belong to two possible independent tetramers under the PBC. In addition, A_{mn} and B_{mn} are L-J parameters between a pair of mth and nth atoms, 18.705 kcal $Å^{12}$/mol and 2.663 kcal $Å^6$/mol for Li, 1021.313 kcal $Å^{12}$/mol and 25.993 kcal $Å^6$/mol for C, and 86.695 kcal $Å^{12}$/mol and 4.661 kcal $Å^6$/mol for H, respectively, which are obtained from the parameter set PARM94 in the molecular dynamics program suite AMBER7.[24] R_{mn} indicates the interatomic separation. Today, organolithium oligomers are generally considered to be aggregates of lithium cations and carbanions, bound mainly by electrostatic forces.[6] Indeed, an electrostatic description as proposed by Streitwieser[15a] and by Bushby and Steel[15b,c] is well capable of rationalizing the structural features.[6] One could, therefore, regard the present *effective point charge model* as a modern extension of the traditional point charge model originating with Streitwieser.[15a] It enables us to estimate concisely the contributions of the electrostatic and vdW interaction energy and to discuss conceptually the microscopic origin of the crystal packing effect.

Thus, the effective lattice energy $E_{(CH_3Li)_4}^{lattice}$ could be estimated under the PBC only if a set of numerical values of effective point charges suitable for the present purpose were obtained.

Methyllithium Tetramer Crystal bcc Structure

J. Phys. Chem. B, Vol. 110, No. 25, 2006 **12643**

TABLE 2: Effective Point Charges (MPA and NPA) at B3LYP/6-311G(d,p) of CH_3 and Li of Methyllithium Tetramer, with Electrostatic, van der Waals and MO Energy at B3LYP/6-311G(d,p) Per Unit Cell (two tetramers) of the bcc Crystal for the Eclipsed and the Staggered Conformation

	eclipsed		staggered	
	MPA	NPA	MPA	NPA
CH_3 charge (*e*)	−0.4776	−0.8505	−0.4871	−0.8647
Li charge (*e*)	0.4776	0.8505	0.4871	0.8647
V_{es} (kcal/mol)	−813.5	−2617.5	−847.8	−2701.3
V_{vdW} (kcal/mol)	−579.7		−579.7	
$E^{isolated}_{(CH_3Li)_4}$ (kcal/mol)	−238306.8		−238292.4	
$E^{lattice}_{(CH_3Li)_4}$ (kcal/mol)	−239700.0	−241504.0	−239719.9	−241573.4

In Table 2, those of CH_3 and Li are shown for both Mulliken population analysis (MPA)[25] and the natural population analysis (NPA)[26] for the reasons explained in the next paragraph. With respect to the geometrical structures, the positions of C and Li in unit cells of the eclipsed and the staggered conformations were both assumed to be fixed to those determined by the experimental data of the crystal structure in X-ray analysis.[4] On the other hand, those positions of H were determined from the structures optimized at the B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory both for the eclipsed and staggered conformations. It should be noted that in calculating the effective lattice potential energy $V^{lattice}_{(CH_3Li)_4}$ (eq 2), we made use of the particle mesh Ewald (PME) method,[27] i.e., the standard treatment for estimating the long-range interaction.

In Table 2, it is noticed that the charge polarization between CH_3 groups and Li atoms at the staggered conformation is larger than that at the eclipsed one in both population analyses. According to the electrostatic description proposed by Streitwieser and by Bushby and Steel, which is well capable of rationalizing the structural features of organolithium oligomers,[15] it is also verified presently that the results of NPA are in line with the view of a predominantly ionic character of the C−Li bond. Thus, it is reasonable that the NPA charges of CH_3 groups and Li atoms show absolute values 0.8505*e* (eclipsed) and 0.8647*e* (staggered) (Table 2) that are larger than the MPA charges 0.4776*e* (eclipsed) and 0.4871*e* (staggered), respectively, since the NPA method indicates a significantly stronger ionic character.[6] Actually, those NPA values are consistent with 0.85*e* to 0.88*e* reported previously by Bickelhaupt et al., who also mentioned that inclusion of correlation has very little influence on the NPA distribution.[6] In addition, the results obtained in the present study also lend support to the contention of Collins et al. that the ionicity of molecules involving a large electronegativity difference is substantially underestimated by the MPA procedure.[25,26]

Further, in Table 2, the *effective point charge model* provides the energetic contributions of Coulomb and vdW potential interaction, V_{es} and V_{vdW}, which are two main interactions among unit cells in the bcc crystal. In addition, $E^{isolated}_{(CH_3Li)_4}$, twice the total energy of a tetramer in isolation, obtained by the B3LYP/6-311G(d,p) level of theory, is also shown and is summed with V_{es} and V_{vdW} to provide the total lattice energy $E^{lattice}_{(CH_3Li)_4}$ (eq 1). Although the eclipsed conformation is 14.4 kcal/mol more stable than the staggered one in isolation, it is recognized that the staggered conformation is more stable by 19.9 kcal/mol in MPA and by 69.4 kcal/mol in NPA than the eclipsed one in the bcc crystal. This is brought about by the larger charge multipolarizations between the rotatory methyl groups and lithium atoms in staggered-methyl tetramers (Table 2), which induce the larger stabilization for the whole electrostatic interaction V_{es} in the staggered conformation so as to surpass the relative destabilization for $E^{isolated}_{(CH_3Li)_4}$ in isolation. This understanding is consistent

with both the previous experimental evidence[4] and the present DFT results (Table 1).

Previously, Kaufmann et al. stated that the staggered conformation of the $(CH_3Li)_4$ units found in the crystal is due to a packing effect, since each lithium is "solvated" by a neighboring cluster and the Li−H interactions in the eclipsed conformation are overcome by the sterically more favorable staggered orientation.[1a] Recently, Kwon et al. reconfirmed the favorability of the eclipsed conformation in isolation from the viewpoint of the hyperconjugation effect, and further mentioned as well that "the staggered orientation found in the solid state may be due to the interaction of methyl groups of neighboring methyllithium tetramers giving rise to a crystal packing effect which favors a staggered conformation".[7] However, as far as we know, neither these two research groups nor any others have ever explained the packing effect in microscopic terms in detail. Since the so-called "crystal packing effect" can be said as an inclination of molecular aggregates to take the most closely packed structure, it should appear originally as a result of the vdW interactions. However, for the present $(CH_3Li)_4$ crystal, since there is no difference in V_{vdW} between the eclipsed and the staggered conformation (Table 2), the favorability of staggered conformation is probably not due simply to the "crystal packing effect" in its original meaning. In such a case, it is plausible that the conformation might be stabilized by the electrostatic interaction V_{es} rather than by the vdW interaction V_{vdW} itself, and is realized, as presently, by the multipolarization of charge distribution in the staggered conformation. This suggests to us in general that such additional contribution should also be included in the "crystal packing effect".

4. Summary

In this article, to understand the origin of the "crystal packing effect" that brings about the difference in the methyllithium tetramer $(CH_3Li)_4$ structures with respect to the conformations of methyl groups between tetramers in isolation and in the bcc crystal, the tetramer structure in the crystal has been theoretically optimized quantum mechanically by the DFT calculations under the PBC using both CASTEP and Gaussian03. An X-ray structure has been reproduced, for the first time, in which the conformation of methyl groups in the tetramer in the crystal preferably takes the staggered form in distinction to the eclipsed form in the isolated tetramer, which was previously confirmed both experimentally and theoretically.

In addition, the proposed stabilization mechanism is such that the staggered conformation is advantageous, as a whole, in crystal, due to the larger electrostatic stabilization via the induced intratetramer multipolarization, although it should cause, at the same time, smaller destabilization in intratetramer electronic energy. Our molecular mechanical calculations using the *effective point charge model* also verified that predictions by the

stabilization mechanism lead consistently to the previous experimental evidence of the staggered favorability in the solid state.

Finally, it is concluded that the "crystal packing effect" arises in the crystal structure due to enhancement of the charge multipolarizations between the rotatory methyl groups and the lithium atoms in staggered-methyl tetramers and, therefore, the whole crystal structure is determined to be the most stable geometry by taking into consideration both the electrostatic and vdW energy contribution among tetramers in the bcc crystal, in addition to the amount of electronic energies of all the individual tetramers.

Supporting Information Available: The full reference for Gaussian98,[17] Gaussian03,[23] and AMBER7,[24] is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Sapse, A. M.; Jain, D. C.; Raghavachari, K. In *Lithium Chemistry*; Sapse, A. M.; Schleyer, P. v. R., Eds.; John Wiley & Sons: New York, 1995; p 45 and references therein. (b) Yamataka, H.; Yamada, K.; Tomioka, K. In *Chemistry of Functional Groups*; Rappoport, Z., Marek, I., Eds.; John Wiley & Sons: New York, 2004; p 901.

(2) (a) Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 2174. (b) McKeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1969**, *91*, 1057.

(3) Landro, F. J.; Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Organomet. Chem.* **1983**, *249*, 1.

(4) (a) Weiss, E.; Lucken, E. A. C. *J. Organomet. Chem.* **1964**, *2*, 197. (b) Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265. (c) Köster, H.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1978**, *160*, 1. (d) Weiss, E.; Lambertsen, T.; Schubert, B.; Cockcroft, J. K.; Wiedenmann, A. *Chem. Ber.* **1990**, *123*, 79. (e) Weiss, E. *Angew. Chem.* **1993**, *105*, 1565. (f) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501 and references therein. (g) Walfort, B.; Lameyer, L.; Weiss, W.; Irmer, R. H.; Bertermann, R.; Rocha, J.; Stalke, D. *Chem. Eur. J.* **2001**, *7*, 1417. (h) Klumpp, G. W.; Geurink, P. J. A.; Spek, A. L.; Duisenberg, A. J. N. *J. Chem. Soc., Chem. Commun.* **1983**, *15*, 814.

(5) (a) Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 2456. (b) West, P.; Waack, R.; Purvort, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 840. (c) Mackin, K. M.; Richey, H. G., Jr. *J. Org. Chem.* **2002**, *67*, 4370. (d) Yamataka, H.; Sasaki, D.; Kuwatani, Y.; Mishima, M.; Shimizu, M.; Tsuno, Y. *J. Org. Chem.* **2001**, *66*, 2131. (e) Sun, X.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 2452. (f) Sun, X.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 2459.

(6) Bickelhaupt, F. M.; Hommes, N. J. R. v. E.; Guerra, C. F.; Baerends, E. J. *Organometallics* **1996**, *15*, 2923.

(7) Kwon, O.; Sevin, F.; McKee, M. L. *J. Phys. Chem. A* **2001**, *105*, 913.

(8) (a) Kaufmann, E.; Raghavachari, K.; Reed, A. E.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, 1597. (b) Hommes, N. J. R. v. E.; Schleyer, P. v. R.; Wu, Y. D. *J. Am. Chem. Soc.* **1992**, *114*, 1146.

(9) Herzig, L.; Howell, J. M.; Sapse, A. M.; Singman, E.; Snyder, G. *J. Chem. Phys.* **1982**, *77*, 429.

(10) Graham, G.; Richtsmeiser, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 5759.

(11) Koizumi, T.; Kikuchi, O. *Organometallics* **1995**, *14*, 987.

(12) Nakamura, M.; Nakamura, E.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 11016.

(13) Mori, S.; Kim, B. H.; Nakamura, M.; Nakamura, E. *Chem. Lett.* **1997**, *10*, 1079.

(14) Haffner, F.; Sun, C.; Williard, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 12542.

(15) (a) Streitwieser, A., Jr. *J. Organomet. Chem.* **1978**, *156*, 1. (b) Bushby, R. J.; Steel, H. L. *J. Organomet. Chem.* **1987**, *336*, C25. (c) Bushby, R. J.; Steel, H. L. *J. Chem. Soc., Perkin Trans.* **1990**, *2*, 1143.

(16) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

(17) Frisch, M. J., et al. *Gaussian98*, Revision A.3; Gaussian, Inc.; Pittsburgh, PA, 1998.

(18) (a) *Material Studio CASTEP*; Accelrys Inc.; San Diego, 2001. (b) Milman, V.; Winkler, B.; White, J. A.; Pickard, C. J.; Payne, M. C.; Akhmatskaya, E. V.; Nobes, R. H. *Int. J. Quantum Chem.* **2000**, *77*, 895.

(19) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64*, 1045.

(20) Segall, M. D.; Lindan, P. J. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; M. C. Payne, M. C. *J. Phys.: Condens. Matter* **2002**, *14*, 2717.

(21) Nagy, Á.; Andrejkovics, I. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 233.

(22) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.

(23) Frisch, M. J., et al. *Gaussian03*, Revision B.03; Gaussian, Inc.; Pittsburgh, PA, 2003.

(24) Case, D. A., et al. *AMBER7*; University of California, San Francisco, 2002.

(25) Collins, J. B.; Streitwieser, A. *J. Comput. Chem.* **1980**, *1*, 81.

(26) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(27) Darden, T.; York, D.; Pederson, L. *J. Chem. Phys.* **1993**, *98*, 10089.