unpublished work on tetramethylcyclobutanedione ketalizations.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compounds 4 – 5 (5 pages). Ordering information is given on any current masthead page.

Nature of Short Li•••H–C Contact Interactions in Organolithium Compounds and Its Implication

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Structures of organolithium compounds seldom follow classical bonding patterns and therefore have been a subject of extensive experimental[1-3] and theoretical[4] studies. One of the striking features of organolithium compounds is short H···Li contacts involving their C–H bonds.[2,3] This is particularly noteworthy in view of the ease of C–H bond activation to remove LiH from organolithium compounds.[2a,c] The H···Li contacts are comparable in length to the Li–H distance [2.043 (1) Å] found in solid lithium hydride.[5a] In gas-phase LiH, the Li–H distance is 1.596 Å.[5b] So far the shortest known D···Li distance is 1.72 (3) Å, which is found in solid CD_2Li_2.[2c] This solid also has a short Li···Li contact, i.e., 2.26 (2) Å, which is the average of the covalent radii sum 2.68 Å and the ionic radii sum 1.80 Å. In solid CD_2Li_2, each CD_2 unit is contained in a distorted cube of Li atoms as shown in the stereodiagram of Figure 1, where the large, medium, and small circles represent C, Li, and D atoms, respectively. The solid lines represent the C–D bonds [C–D(1) = 1.09 (1) Å, C–D(2) = 1.18 (1) Å] and the C–Li bonds [2 × 2.17 (1) Å]. Note that one C–D bond is normal, but the other one is unusually long. The "molecular unit" CD_2Li_2 is neither planar nor tetrahedral in shape, which is not surprising since planar *cis*-CH_2Li_2 is calculated to be only slightly less stable than tetrahedral CH_2Li_2 (by ~8 kcal/mol).[4b] The dashed lines of Figure 1 show the D···Li contacts less than 2.90 Å [i.e., Li···D(1) = 1.72 (3), 2.03 (3), 2.15 (3), 2.28 (1), 2.36 (2) Å; Li···D(2) = 1.99 (3), 2.06 (2), 2.16 (2), 2.38 (2) Å] as well as the Li···Li contact less than 2.70 Å [i.e., Li···Li = 2.26 (2) Å]. As shown in 1, the shortest Li···D and the shortest Li···Li contacts in CD_2Li_2 involve a common Li atom: With a CD_2 unit, one Li makes a monobridged Li···D–C contact and the other Li makes a dibridged Li···D–C contact. The D(1) and D(2) atoms of each CD_2 unit have distorted square-pyramidal and distorted square-planar coordinations of Li atoms, respectively. It is the D(2) atom that is associated with the unusually long C–D bond. In the present work, we examine the two striking structural features of solid CD_2Li_2, i.e., the short D···Li contacts and the long C–D bond, by carrying out ab initio SCF-MO calculations on molecular model systems H–Li···H–CH_nLi_{3-n} (n = 0–3), LiH_2C–Li···H–$CHLi_2$, and $(H\text{–}Li)_3$···H–$CHLi_2$ and consider important implications of our results.

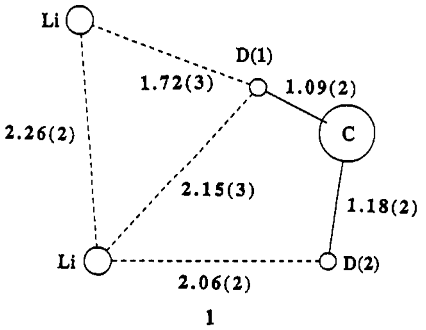

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Table I. Optimum Li•••H Distances r_{opt} and Binding Energies ΔE Calculated for the Li•••H–C Contacts in $(CH_2Li_2)_2$ and $(LiH)(CH_nLi_{4-n})$ (n = 1–4) with the 6-31G Basis Set**

system	symmetry of arrangement	r_{opt}, Å	ΔE, kcal/mol
H_2LiC–Li···H–$CHLi_2$	C_s	1.794	11.4
HLi···H–CLi_3	C_{3v}	1.699	18.6 (19.4)[a]
HLi···H–$CHLi_2$ (θ = 0°, 3)	C_s	1.733	16.8 (16.7)[a]
HLi···H–$CHLi_2$ (θ = 71.8°, 3)	C_s	1.733	25.7
HLi···H–CH_2Li	C_1	1.840	10.4 (8.10)[a]
HLi···H–CH_3	C_{3v}	2.510	0.50 (0.53)[a]

[a] Calculated with the 6-31++G* basis set using the geometries obtained with the 6-31G** basis set.

Computational Details

Our SCF-MO calculations are carried out by using the GAUSSIAN 86 program.[6] The geometries of CH_nLi_{4-n} (n = 0–4) and LiH are optimized by SCF-MO calculations using the 6-31G** basis set.[7] In our calculations on H–Li···H–CH_nLi_{3-n} (n = 0–3), LiH_2C–Li···H–$CHLi_2$, and $(H\text{–}Li)_3$···H–$CHLi_2$, all fragment geometries are taken to be frozen unless mentioned otherwise. The global minimum energy structures of those systems are not examined, because our objective is to examine the short Li···D–C contacts and the unusually long C–D bond present in solid CD_2Li_2. The global minimum energy structures of stoichiometry CH_2Li_4 and CH_5Li have been reported in the literature.[8]

In our SCF-MO calculations on H–Li···H–CH_nLi_{3-n} (n = 0–3) with a collinear H–Li···H–C arrangement, the interaction energies

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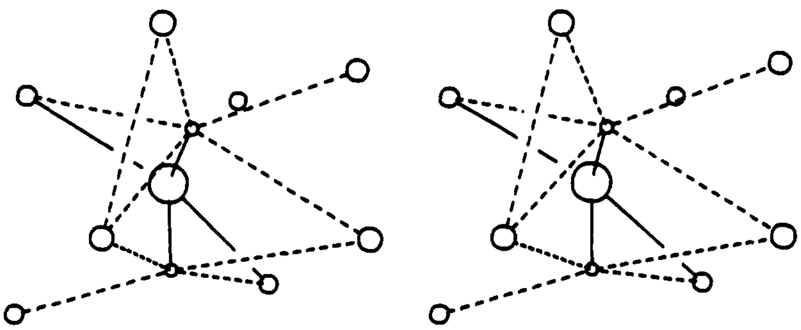
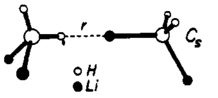


Figure 1. Stereodiagram of a CD_2 unit enclosed in a distorted cube of Li atoms in solid CD_2Li_2.

(ΔE) obtained with the 6-31G** and 6-31++G* basis sets are very similar (See Table I). Unless mentioned otherwise, computational results we refer to are based on the 6-31G** basis set. Triplet CH_2Li_2 is found to be more stable than the singlet.[4b] For all $H-Li\cdots H-CH_nLi_{3-n}$ (n = 0–3), however, our calculations reveal that the singlet state is more stable than the triplet by at least 19 kcal/mol. Thus we consider only singlet-state calculations in the following. At the SCF-MO level, the ΔE of $H-Li\cdots H-CHLi_2$ is calculated to be 16.8 kcal/mol without basis set superposition error (BSSE) correction, and 16.1 kcal/mol when the BSSE is corrected by the counterpoise method.[9] At the correlation level of CISD[10] calculations, the ΔE of $H-Li\cdots H-CHLi_2$ is calculated to be 13.9 kcal/mol without BSSE correction, and 12.7 kcal/mol with the BSSE corrected by the counterpoise method. Namely, the interaction energy ΔE is not significantly affected either by correlation energy or by BSSE correction. In the following, therefore, our discussion is based upon singlet-state SCF-MO calculations with the 6-31G** basis set and without BSSE correction.

Short Li···H–C Contacts. We first simulate the aforementioned Li···H–C contact interactions in terms of a collinear C–Li···H–C contact between two CH_2Li_2 molecules (see 2). Our calculations on 2 are carried out as a function of the Li···H distance with the geometries of the CH_2Li_2 fragments kept constant.[7] The binding energy ΔE (kcal/mol) and the optimum Li···H distance r_{opt} (Å) calculated for 2 are listed in Table I. The r_{opt} value is close to the shortest Li···D contact found for the monobridged Li···D–C configuration in CD_2Li_2 [1.79 vs 1.73 (3) Å], and the corresponding stabilization energy ΔE is substantial. When the Li···H–C interactions are simulated in terms of a collinear H–Li···H–C contact between LiH[7] and CH_2Li_2 (i.e., $\theta = 0°$ in 3), the r_{opt} value becomes closer to the experimental one [1.73 vs 1.72 (3) Å] as listed in Table I, and the associated stabilization energy becomes greater. Thus our model calculations reproduce the short Li···H contacts of organolithium compounds and also show that these short Li···H–C contacts are substantially stabilizing in nature. The stabilization energy ΔE associated with the Li···H contact of $H-Li\cdots H-CHLi_2$ is about half the binding energy (i.e., 32.5 kcal/mol) calculated for an isolated LiH.



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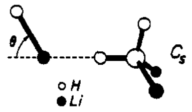

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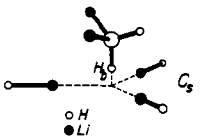

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To understand why the Li···H distances of the Li···H–C contacts in organolithium compounds can become so short as 1.72 (3) Å, we calculate the r_{opt} and ΔE values for collinear H–Li···H–C contacts between LiH and CH_nLi_{4-n} (n = 1–4).[7] These values are listed in Table I, which shows that the Li···H–C contact gives rise to a short Li···H distance only when the carbon atom has at least one Li atom, and the Li···H distances decreases with increasing number of Li atoms on the carbon atom. In ethyllithium[2d] and cyclohexyllithium,[2a] which exist as tetrameric and hexameric units, respectively, the Li···H contacts between alkyllithium units involving the α-hydrogen atoms are shorter than those involving the β-hydrogen atoms. This is consistent with our finding that a strong Li···H–C interaction requires the presence of at least one Li atom on the carbon atom associated with the Li···H–C interaction. Calculations of the ΔE values for 3 as a function of the angle θ (with the Li···H distance fixed at the r_{opt} value for $\theta = 0°$) show that the stabilization energy increases as θ increases from 0°, and the optimum θ value is close to 70° (see Table I). Given a collinear Li···H–C configuration, the H–Li bond of the H–Li···H–C contact or, generally, the C–Li bond of the C–Li···H–C contact should tilt away from the Li···H–C axis as found in solid CD_2Li_2.

C–H Bond Lengthening. We now examine why solid CD_2Li_2 possesses an unusually long C–D bond. For convenience, the H atom in contact with Li in the H–Li···H–C arrangement of $H-Li\cdots H-CH_nLi_{3-n}$ (n = 0–3) will be represented by H_b. The optimum $C-H_b$ bond lengths of $H-Li\cdots H_b-CH_nLi_{3-n}$, obtained with all other geometrical parameters fixed, are calculated to be 1.086, 1.093, 1.095, and 1.102 Å for n = 3, 2, 1, and 0, respectively. These $C-H_b$ bond lengths are normal, and in addition, the $C-H_b$ bonds for n = 0 and 1 are not longer but shorter than the corresponding values[7] of the $H-CH_nLi_{3-n}$ fragments. We note from Figure 1 and 1 that the C–D(1) bond length is normal, and this bond has one Li atom in an almost linear Li···D(1)–C arrangement. Full geometry optimization of $H-Li\cdots H_b-CHLi_2$ with a linear $H-Li\cdots H_b-C$ arrangement also leads to a normal $C-H_b$ distance (i.e., $C-H_b$ = 1.097 Å and $Li\cdots H_b$ = 1.728 Å). However, when the C···Li distance of the linear $C-H_b\cdots Li$ contact is increased from the equilibrium value significantly, the optimum $C-H_b$ distance is calculated to be slightly longer than the normal value (e.g., $C-H_b$ = 1.118 Å when the C···Li contact is increased by 0.7 Å).

Figure 1 and 1 show that the axis of the unusally long C–D(2) bond is nearly perpendicular to the "plane" of the four Li atoms surrounding D(2) in a square-planar manner. To test if such right-angle $Li\cdots H_b-C$ arrangements cause the $C-H_b$ bond lengthening, we carry out SCF-MO calculations for $(HLi)_3\cdots H_b-CHLi_2$, 4: The three HLi molecules are arranged trigonally (D_{3h} symmetry) with the Li atoms placed at 2.16 Å (i.e., the average of the four Li···D(2) distances) from the center of the Li_3 equilateral triangle. The H_b-CHLi_2 fragment is arranged with the H_b-C bond aligned along the 3-fold rotational axis of $(HLi)_3$ and with the C atom located at 1.18 Å above the plane of $(HLi)_3$. Hence in 4, the H_b atom is located above the plane of $(HLi)_3$. Optimization of the $C-H_b$ distance in 4 (with all other geometrical parameters kept constant) is found to increase the $C-H_b$ bond length to 1.140 Å, so that H_b comes closer to the plane of the Li atoms. This is consistent with our hypothesis that the nearly four right-angle

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[10] Configuration interactions with all the single and double excitations generated from the Hartree–Fock wave function.

Li$\cdots$D(2)–C contacts are primarily responsible for the unusually long C–D(2) bond.

Discussion

All organolithium compounds are believed to be predominantly ionic with small but nonnegligible covalent contributions.[11] Our results are consistent with this conclusion, since the binding energy of HLi$\cdots$H–CH$_n$Li$_{3-n}$ (n = 0–3) is substantial only when the carbon atom has at least one Li atom. A C–Li bond possesses a substantial carbanion character,[11a] so that the carbanion character of H–CH$_n$Li$_{3-n}$ should increase with decreasing n. This explains why the binding energy of HLi$\cdots$H–CH$_n$Li$_{3-n}$ increases with decreasing n (see Table I).

As described above, the main features of bonding in HLi$\cdots$HCH$_n$Li$_{3-n}$ can be understood in terms of ionic bonding. However, some of our findings are not explained by ionic bonding alone. When H–Li is tilted in the H–C–H plane of CH$_2$Li$_2$ as shown in **3**, the binding energy of HLi$\cdots$H–CHLi$_2$ increases by about 50% (at θ = 72°) with respect to that of linear H–Li$\cdots$H–CHLi$_2$ (θ = 0°). An energy lowering of nearly the same magnitude is also obtained when H–Li tilts in any of the two H–C–Li planes of CH$_2$Li$_2$. Thus the energy lowering of HLi$\cdots$H–CHLi$_2$ is caused primarily by the bending in the H–Li$\cdots$H arrangement and is not much affected by the relative orientations of the dipoles of the HLi and CH$_2$Li$_2$ fragments. In terms of dipole–dipole electrostatic stabilization alone, the H–Li tilting in the H–C–H plane would have been preferred. An additional factor to consider in explaining the r_{opt} and ΔE values of HLi$\cdots$H–CH$_n$Li$_{3-n}$ (n = 0–3) is that the Li atomic orbitals of HLi interact appreciably with the lone-pair orbitals of the carbon center and with the σ orbital of the C–H bond (σ_{C-H}). This is reasonable because the Li 2s and 2p orbitals, being diffuse, have their amplitude maxima at a distance quite removed from the atomic center.[12] In the HLi$\cdots$H–CHLi$_2$ compound (**3**), the Li sp hybrid orbital of HLi points to the carbon when θ = 0° while the Li p orbital does when θ = 90°. The Li p orbital has an amplitude maximum farther away from the Li center than does the Li sp hybrid orbital. Thus the overlap of the Li orbitals with the carbon lone pair or the σ_{C-H} orbital would be greater for θ = 90° than for θ = 0°, which accounts for why the energy minimum of **3** occurs when θ is closer to 90°. When the Li$\cdots$C distance of linear HLi$\cdots$H–CHLi$_2$ (θ = 0°) is increased, it is possible to reach a point where the Li orbitals overlap negligibly with the carbon lone-pair orbital but appreciably with the σ_{C-H} orbital. Thus, it is not surprising that the C–H bond of linear HLi$\cdots$H–CHLi$_2$ is stretched slightly only when the Li$\cdots$C distance is increased substantially from its optimum value. The lengthening of the C–H$_b$ bond in (HLi)$_3\cdots$H$_b$–CHLi$_2$ (**4**) is also easily understood in terms of the overlap interactions of the Li orbitals of (HLi)$_3$ with the σ_{C-H} orbital of the C–H$_b$ bond. This bond is lengthened significantly because it makes several short C–H$\cdots$Li contacts.

The above discussion suggests that, although the primary reason for the short C–H$\cdots$Li contacts found for organolithium compounds is ionic,[11] the overlap interactions of the Li orbitals with the carbon lone pair and those with the σ_{C-H} orbitals play a nonnegligible role. As pointed out by Kaufman et al.,[11a] the latter are the organolithium analogue of the agostic interactions of transition-metal complexes of hydrocarbons.[13]

Concluding Remarks

Our study shows that short Li$\cdots$H distances of intermolecular Li$\cdots$H–C contacts occur when the carbon atom bears at least one Li atom. Such an Li$\cdots$H–C contact interaction is strongly stabilizing, and the associated interaction energy is nearly half the binding energy of an isolated LiH. This finding provides a natural explanation for the observation that solid alkyllithium exists as oligomeric units containing lithium atom clusters,[1a,2a,d] because formation of the lithium atom clusters leads to a large number of strongly stabilizing intermolecular Li$\cdots$H–C contacts involving the Li-bearing carbon atoms. The present work shows that a C–H bond can be lengthened significantly when it makes several Li$\cdots$H–C contacts close to right-angle arrangements.

Acknowledgment. Work at North Carolina State University is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science, under Grant DE-FG05-86ER45259. J.J.N. thanks DGICYT (Project PB89-0268) and the NATO and Ministerio de Educacion y Ciencia (Spain) for fellowships that made it possible to visit North Carolina State University. G.D.S. gratefully acknowledges the support of the Office of Naval Research and the National Science Foundation.

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[12] According to our atomic orbital calculations of Li and C using the 6-31G** basis set, the amplitude maxima of the Li 2s and 2p orbitals occur at ~1.0 and 2.0 Å away from the atomic center, respectively, and those of the C 2s and 2p orbitals both at ~0.5 Å away from the atomic center.

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Novel Conversion of a 3-(1-Hydroxyethyl)azetidinone to a 3-(Hydroxymethyl)azetidinone: A Synthesis of 6-(Hydroxymethyl)-1β-methylcarbapenem[1]

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The 6-(1-hydroxyethyl)carbapenem, thienamycin (**1a**),[2] is a potent, broad-spectrum antibiotic first isolated from cultures of the soil microorganism *Streptomyces cattleya*. Its discovery has prompted an intense and widespread research effort directed toward the synthesis of a host of structural analogues. One such analogue, the 6-(1-hydroxyethyl)-1β-methylcarbapenem (**2**) has recently been reported[3] to retain the excellent antibiotic activity of **1a** and its more stable *N*-formimidoyl derivative **1b**, while displaying superior chemical and enzymatic stability. Although 9-northienamycin[4] (**1c**) has also been isolated as

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