PL, and CT) describe the deviation from this diagonal representation. This is reflected in the greater relative contribution of other terms, especially CT and MIX, denoting the increased amount of multicenter electron delocalization and CT at atoms with low electronegativity Be, B, and C.

Acknowledgment. This work was supported by Research Community of Slovenia and LEK—Pharmaceutical and Chemical Works. We thank Professor P. v. R. Schleyer for pointing out this problem to us and stimulating discussions and Professor K. Morokuma for kindly sending us the energy decomposition routines. Ljubljanska banka–Gospodarska banka is gratefully acknowledged for generous allotment of computer time.

Registry No. Li, 7439-93-2; $LiBH_2$, 64360-74-3; $LiCH_3$, 917-54-4; $LiNH_2$, 7782-89-0; LiOH, 1310-65-2; LiF, 7789-24-4; $(Li_2)_2$, 12596-49-5; $(LiBH_2)_2$, 88656-95-5; $(LiCH_3)_2$, 33825-29-5; $(LiNH_2)_2$, 88656-96-6; $(LiOH)_2$, 54251-08-0; $(LiF)_2$, 12265-82-6.

Supplementary Material Available: 4-31G/4-31G geometries (coordinates and *Z* matrices) for dimers $(LiXH_n)_2$ (9 pages). Ordering information is given on any current masthead page.

Dimerization Energies of Lithium Compounds with First-Row Substituents

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Lithium compounds have a marked tendency to oligomerize;[1] methyllithium is tetrameric in the crystal,[2] in solution,[3] and even in the gas phase.[4] Only a few aggregation energies are known experimentally: the dimerization energies of LiH,[5] LiOH,[6] and the lithium halides[6] and the trimerization energies of LiF and LiCl.[6] The energy of Li_4, the formal dimer of Li_2, has also been reported recently.[7] A number of calculations, some at very high levels of theory, are available for $(Li_2)_2$,[8] $(LiCH_3)_2$,[9] $(LiNH_2)_2$,[10] $(LiOH)_2$,[11] and $(LiF)_2$.[12] To complete the first-row set, we carried out calculations at uniform levels for all the $LiXH_n$ monomers and dimers where XH_{n+1} is the corresponding first-row hydride.[13] This set of data clarifies the essential nature of the interaction and permits detailed interpretations of the dimerization energies.

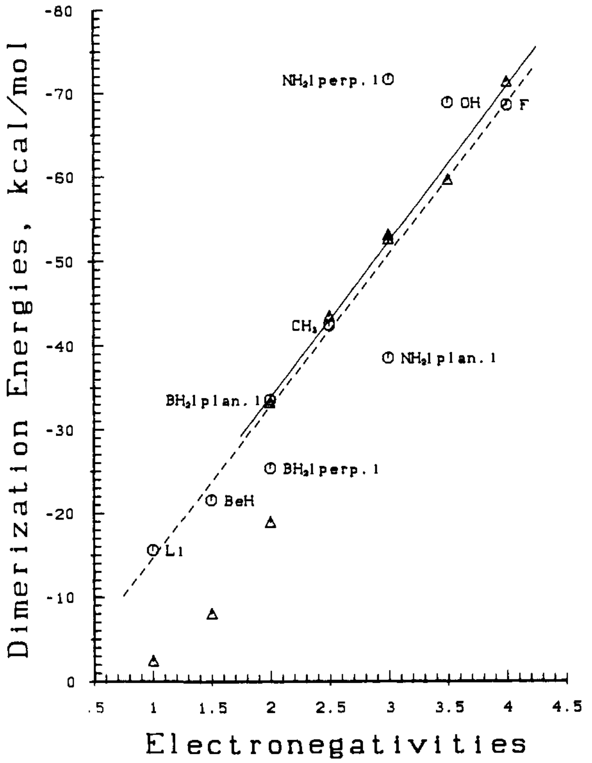
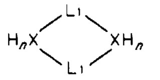


Figure 1. LiX dimerization energies (MP2/6-31G*//3-21G(est)) plotted against the Pauling electronegativities of X (circles and dashed line). Triangular points (and the solid correlation line) are the results of calculations assuming a simple Coulomb model (+ at Li and − at X) using the 3-21G geometries for both LiX monomers and $(LiX)_2$ dimers (see text). At lower theoretical levels similar correlation lines are found but with different slopes.

Earlier calculations[8-12] showed that all the dimers $(LiXH_n)_2$ favor the same rhomboid structures with alternating Li and first-row atoms, X, and all Li–X distances equal. Consequently



D_{2h} symmetry was imposed on all dimers except $(LiCH_3)_2$, which has C_{2h} symmetry.[9] For both $LiBH_2$ and $LiNH_2$ two alternative structures were considered, corresponding to perpendicular and planar arrangements of the XH_2 groups.

Table I shows that the final theoretical estimates[14] are not far

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Table I. Dimerization Energies of Lithium First-Row Hydrides at Various Theoretical Levels

dimer		3-21G// 3-21G	6-21G// 3-21G	MP2/6-21G// 3-21G	6-31G*// 3-21G	MP2/6-31G*// 3-21G(est)[a]	exptl or best calcd
$(Li_2)_2$	D_{2h}	−12.4	−11.7	−15.3	−12.0	−15.6 (−16.8)[g]	−26.8,[b] −15.4[c]
$(LiBeH)_2$	D_{2h}	−20.6	−19.4	−21.3	−19.7	−21.6 (−22.2)[g]	
$(LiBH_2)_2$	D_{2h} (perp)	−26.8	−25.2	−26.2	−24.4	−25.4	
	D_{2h} (plan.)	−36.9	−35.3	−34.1	−34.8	−33.6	
$(LiCH_3)_2$	C_{2h}	−46.3	−45.1	−45.1	−42.5	−42.5	
$(LiNH_2)_2$	D_{2h} (perp)	−83.4	−82.5	−81.9	−72.3	−71.7	
	D_{2h} (plan.)	−44.6	−43.6	−38.4	−43.8	−38.6	
$(LiOH)_2$	D_{2h}	−82.5	−81.9	−77.8	−73.0	−68.9	-63.5 ± 8.5[d,f]
$(LiF)_2$	D_{2h}	−87.3	−86.7	−83.9	−71.4	−68.6	-63.3 ± 5.7[e,f]

[a] MP2 correction taken from the 6-21G level. [b] Reference 7. [c] Reference 8. [d] Reference 6b. [e] Reference 6a. [f] The values given include zero point energy corrections. [g] MP2/6-31G*//3-21G.

Table II. Geometrical Parameters (Å) of $LiXH_n$ Monomers and Dimers Used for the Electrostatic Calculations and Resulting Dimerization Energies (kcal/mol)

	monomers[a,b]	dimers[b]			dimerization
X	Li–X	Li–X	Li–Li	X–X	E[c]
Li	2.816	3.164	2.686	5.728	−2.5
Be	2.496	2.774	2.402	5.001	−8.1
B (perp)	2.261	2.482	2.253	4.423	−19.0
(plan.)		2.424	2.325	4.255	−33.3
C	2.001	2.143/2.157	2.174	3.710	−43.6
N (perp)	1.714	1.908	2.236	3.093	−52.7
(plan.)		1.869	2.021	3.145	−53.2
O	1.537	1.730	2.184	2.685	−59.7
F	1.520	1.684	2.235	2.520	−71.4

[a] Reference 19. [b] Calculated with the 3-21G basis set. [c] Calculated by using Coulomb's law; see text and caption, Figure 1.

(about 5 kcal/mol) from the experimentally known dimerization energies for LiOH and LiF.[6] Somewhat better results that more nearly reproduce experimental values can be obtained by adding diffuse functions on the electronegative atoms N, O, and F[10,11] and correcting for zero point energy differences. As can be seen from Table I, the dimerization energies of $LiXH_n$ become more negative with increasing electronegativity of X. The gain in Coulombic energy during dimerization increases with increasing charge separation.

Figure 1 shows a plot of dimerization energies vs. the Pauling electronegativity of X. A remarkably linear relationship results. Only $(LiOH)_2$ and $(LiNH_2)_2$ deviate from the correlation line. The perpendicular conformation of the latter allows the nitrogen lone pairs to enhance stability via multicenter bonding. The same is true for $(LiOH)_2$ but to a lesser extent. $(LiF)_2$ is totally ionic and thus lies on the correlation line.

In the planar $(LiNH_2)_2$ conformation, the nitrogen lone pairs participate in a destabilizing 4π-electron interaction. Steric effects are not responsible for the downward deviation of the planar form, since $(LiBH_2)_2$, which prefers a planar rather than a diborane-like structure, correlates well.

A remarkably simple electrostatic model[22] can, however, account well for the calculated dimerization energies. The electrostatic dimerization energy (triangular points in Figure 1) was calculated by treating Li and XH_n as point positive and negative charges at the 3-21G calculated heavy-atom positions for monomer and dimer (see Table II). The dimerization energy is then the increase in electrostatic energy on going from two monomers to a dimer. With the exception of $LiNH_2$ the agreement from $LiBH_2$ to LiF is remarkable. The "covalent" dimers Li_4, $(LiBeH)_2$, and $(LiBH_2)_2$ (perpendicular) are more stable than would be predicted by the electrostatic model, indicating the preference of these elements for multicenter bonding. The deviations for perpendicular NH_2 and for OH indicate the extra involvement of the lone pair electrons in the dimer, compared with the monomer (i.e., σ interactions involving these electrons in the dimer are more favorable than π interactions in the monomer). The planar form of $(LiNH_2)_2$ lies well below the "electrostatic" line, an indirect indication of some π-stabilization in $LiNH_2$ (any π-acceptor character of lithium is decreased in the 4π-electron dimer relative to the monomer). The large (8.2 kcal mol^{-1}) energy difference between planar and perpendicular $(LiBH_2)_2$ is at first sight surprising but reflects the favorable interaction between the inplane π_{BH_2} orbitals and the unsymmetrical combination of the lithium 2s atomic orbitals. This leads to shorter B–Li and B–B but a longer Li–Li distance and hence an increase in electrostatic attraction.

Our conclusion that dimerization energies of LiX compounds are dominated by electrostatic interactions has been confirmed by a Morokuma analysis.[12a,23] The results have wider implications and provide insights into quantitative aspects of lithium chemistry. An increasing number of $LiXR_n$ dimers are being observed experimentally, e.g., by X-ray crystallography.[24] The R substituents are indicated by our further calculations to influence dimerization energies minimally.[25] The factors controlling higher aggregation[9,10] as well as solvation energies[25] will be reported subsequently.

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Registry No. Li, 7439-93-2; $LiBH_2$, 64360-74-3; $LiCH_3$, 917-54-4; $LiNH_2$, 7782-89-0; LiOH, 1310-65-2; LiF, 7789-24-4; $(Li_2)_2$, 12596-49-5; $(LiBH_2)_2$, 88656-95-5; $(LiCH_3)_2$, 33825-29-5; $(LiNH_2)_2$, 88656-96-6; $(LiOH)_2$, 54251-08-0; $(LiF)_2$, 12265-82-6.

Studies of Inclusion Complexes of Cycloamyloses in the Solid State by NMR Methods

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Although previous studies[1,2] of inclusion complexes of the Schardinger dextrins (otherwise known as cyclodextrins or cycloamyloses) using NMR methods have provided valuable insight, those studies have been confined to soluble complexes. Prompted by the rapidly growing interest in the use of modified cycloamyloses as model enzymes,[3-6] and also by commercial use of solid cycloamyloses to sequester a variety of organic substances,[7] we have evaluated two NMR methods for studying these substances in the solid state. We now demonstrate that ^{13}C NMR using the cross polarization–magic angle spinning (CP/MAS) method[8] provides a direct measure of the extent of complexation and that the deuterium quadrupolar echo method[9] gives insight concerning the motion of the guest–substrate within the annulus of the cycloamylose ring.

The ^{13}C CP/MAS spectrum of the solid complex formed by benzene with heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (2,6-di-*O*-Me-β-CD) is shown in Figure 1. Measurement of the relative magnitudes of the ^{13}C resonances indicates that the complex contains 1.0 m equiv of benzene, in good agreement with the value obtained by UV measurement. A series of aromatic molecules such as monosubstituted and symmetrical disubstituted benzenes were studied; their combining ratios of "guest" to "host" are 1:1 with the exception (of ratio 1:2) for larger molecules such as biphenyl. The deuterium solid echo spectrum (Figure 2) of the equivalent complex of benzene-d_6 gave a quadrupole splitting of 48 kHz. For rigidly bound benzene, we would expect[10] a splitting of 144 kHz; rapid rotation of the benzene about its 6-fold axis within the cavity would give a splitting of 70 kHz, and about a 2-fold axis a 16-kHz splitting. Thus it is clear that rapid rotation occurs about the 6-fold axis and that the axis itself undergoes additional angular fluctuations (rms angle approximately 20°).

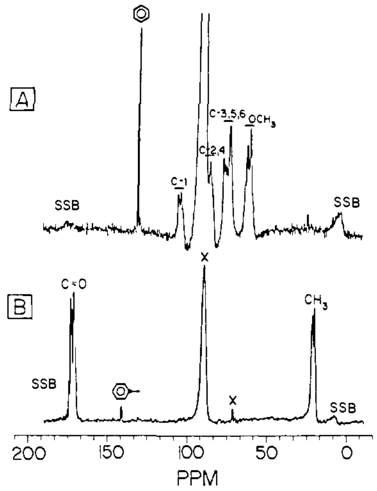

Figure 1. ^{13}C NMR of polycrystalline inclusion complexes of cycloamyloses. The experiments were performed at room temperature on a Bruker CXP-200 FT NMR spectrometer operating at 200 MHz for ^1H with an rf field of 15 G. A Delrin spinner was used, with a spinning frequency of 4.3 kHz. The spectra were plotted on the same scale. (A) Normal CP/MAS spectrum of benzene with 2,6-di-*O*-Me-β-CD. (B) Nonprotonated carbon spectrum of toluene with 2,3,6-tri-*O*-Ac-β-CD, obtained by setting a 40-μs period without proton decoupling prior to ^{13}C data acquisition (carbonyl, 172.18, 171.37, 170.36; aromatic 140.33; Delrin, 88.86; methyl, 22.12, 21.31, 20-30). Assignments are based on solution spectra, and chemical shifts are relative to external tetramethylsilane. The Delrin signals and spinning side-bands are indicated as X and SSB respectively.

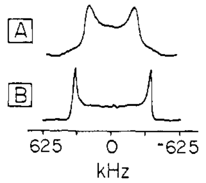

Figure 2. Deuterium NMR spectra of benzene-d_6: (A) within the cavity of 2,6-di-*O*-Me-β-CD; (B) of 2,3,6-tri-*O*-Ac-β-CD. 90° pulse length was 2.5 μs, with a τ delay of 100 μs. A recycle delay of 1.0 s was used.

Combined use of both of the above methods, but particularly the latter, enables direct evaluation to be made of various factors that influence the mobility of the guest molecule within the annulus of the host. The quadrupole splittings (40.0 kHz) for $(CD_3)_2SO$ in the α-CD complex at 20 °C is substantially larger than that of the β-CD complex (7.4 kHz) at the same temperature; cooling the β-CD sample to -23 °C increases the splitting to 38.8 kHz. Both these observations reflect the decreased mobility of Me_2SO in the smaller annulus of the α-CD (4.7–5.2 Å) vs. that of the β-CD (6.0–6.4 Å). It is also possible to vary the mobility of the guest by changing the substituents attached to the host. Thus benzene-d_6 gives a splitting of 48 kHz when sequested in the 2,6-di-*O*-Me-β-CD, which increases to 68.5 kHz for the complex with 2,3,6-tri-*O*-Ac-β-CD, close to the theoretical value for pure C_6 rotation. A similar differential is found for $C_6H_5CH_2D$, the respective values being 30 and 40 kHz; the latter is close to the value (45 kHz) expected[11] for fast rotation of a methyl group about its 3-fold axis. Additional fast motion of the long molecular axis may be the source of the smaller splitting observed. Intuitively it is reasonable to expect an increase in motion due to decreased barriers to aliphatic conformational changes with increase in distance of the pendant group from the annulus; this is nicely illustrated by the decreases in the magnitude of the quadrupole splitting of $C_6H_5CH_2D$ (29 kHz) compared to $C_6H_5CH_2CH_2D$ (<5 kHz) at 20 °C. On cooling to -90 °C, the latter splitting increases to 37 kHz. This latter observation indicates that the molecular motion is almost completely confined to the methyl group, with some additional motion of the aliphatic chain being responsible for the slight reduction of the quadrupole splitting from the 44 kHz value expected for a pure methyl rotation.

Supportive evidence that is indicative of differential motion of various functional groups in the solid complexes stems from the ^{13}C CP/MAS measurements used to differentiate between the resonances of carbons that are protonated from those that are not. From the elegant concept of dipolar dephasing,[12] a delay time of ca 40–100 μs is introduced between the end of the cross-polari-

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