studies is that we may justifiably include such effects in future ligand-field analyses when the chemistry demands, even though such inclusion may not be analytically supportable by the given data and circumstances. After all, the neglect of the $e_{\pi\sigma}$ parameter in the presence of nearby lone pairs or of bent bonds constitutes an assumption in itself. Far better, surely, to guess—though not refine, perhaps—a nonzero value for it by informed extrapolation from the present studies and so improve estimates of the remaining CLF parameters that are optimized. Of course, we do not expect to find CLF values for misdirected valence to be any more transferable between systems than are diagonal e_λ values.

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Clusters of Ionic Molecules: Octahedral vs. Planar Ring Structures of LiF, LiOH, and $LiNH_2$ Hexamers

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Accurate ab initio calculations have been performed to study the structures and energies of the hexamers of LiF, LiOH, and $LiNH_2$. Large basis sets including diffuse and polarization functions have been used in these calculations. Distorted octahedral structures are found to be significantly more stable than planar hexagonal-type structures for all three hexamers. The results are compared to those from previous studies on the tetramers of these molecules. The energies of hexamerization are calculated to be ≃310 kcal/mol for LiF and LiOH and ≃270 kcal/mol for $LiNH_2$.

Introduction

Lithium compounds are known to associate in solvents, in the crystal, and even in the gas phase.[1-5] Colligative measurements, NMR investigations, mass spectrometric observations, and X-ray crystal structure determinations have shown that aggregation is typical in these compounds. The earliest and the most well known examples are the X-ray structures of ethyllithium[6] and methyllithium,[7] which show the existence of tetramers having an essentially tetrahedral arrangement of lithium atoms with the alkyl groups being attached to the faces of the tetrahedron. Numerous other examples involving dimers, trimers, tetramers, and hexamers have now been observed.[1-5]

The smaller oligomers, viz. dimers, trimers, and tetramers, have formed the object of a large number of theoretical studies.[8-15] However, with the exception of a study on $(LiH)_6$[16] and a small basis set calculation on $(CH_3Li)_6$,[9] hexamers have been described only experimentally.[17-25] On the basis of early experiments involving colligative, infrared, and NMR data, Brown et al.[17-19] proposed a symmetrically bridged octahedral structure for alkyllithium hexamers. This basic structure has since been confirmed by X-ray structural investigations on cyclohexyllithium[22] and (trimethylsilyl)lithium.[23] Molecular weight determinations by Fraenkel et al.[24] established that the state of aggregation of (2-methylbutyl)lithium in hydrocarbon solvents is six. On the basis of NMR line-shape analysis, they have also suggested an octahedral structure for this compound. More recently, Barr et al.[25] have determined the structures of the hexamers of several iminolithium compounds and have seen similar octahedral geometries.

In this study, we have undertaken a detailed investigation of the structures and energies of the hexamers of LiF, LiOH, and $LiNH_2$. The basic structures considered are the distorted octahedral form (D_{3d}) and the hexagonal planar arrangement (D_{6h}) in order to establish the relative energies of the octahedral vs. planar arrangements. In a previous study on the tetramers of these compounds,[14] we found that $(LiF)_4$ and $(LiOH)_4$ prefer tetrahedral structures, whereas $(LiNH_2)_4$ is more stable as a planar D_{4h} framework. The calculated square-planar arrangement of $(LiNH_2)_4$ was in good agreement with the experimental results of Lappert et al.[26] on a larger analogue, $[Li(NCMe_2(CH_2)_3CMe_2)]_4$

Table I. Optimized Geometries (Å and deg) of the Hexamers

		distorted octahedral (D_{3d})		hexagonal planar (D_{6h})	
struct	param	HF/ STO-3G	HF/ 3-21G	HF/ STO-3G	HF/ 3-21G
$(LiF)_6$	Li–F	1.646,[a] 1.691[b]	1.745,[a] 1.829[b]	1.537	1.629
	Li–Li	2.286, 2.834	2.419, 2.963	3.007	3.108
	F–F	2.431, 2.857	2.631, 3.065	2.924	3.178
	Li–F–Li			156.0	145.2
	F–Li–F			144.0	154.8
$(LiOH)_6$	Li–O	1.758,[a] 1.781[b]	1.836,[a] 1.896[b]	1.659	1.735
	Li–Li	2.290, 2.869	2.375, 2.957	2.986	3.054
	O–O	2.681, 3.162	2.857, 3.320	3.310	3.469
	O–H	0.976	0.964	0.977	0.966
	Li–O–Li			128.2	123.3
	O–Li–O			171.8	176.7
$(LiNH_2)_6$	Li–N	1.903,[a] 2.024[b]	1.989,[a] 2.055[b]	1.844	1.909
	Li–Li	2.272, 3.026	2.323, 3.116	3.185	3.223
	N–N	3.198, 3.255	3.295, 3.452	3.689	3.814
	N–H	1.031, 1.033	1.018, 1.020	1.032	1.020
	H–N–H	100.6	104.9	101.4	105.7
	Li–N–Li			119.4	115.2
	N–Li–N			180.6	184.8

[a] For each Li, there are two equivalent bonds with this length. [b] For each Li, there is only one bond with this length.

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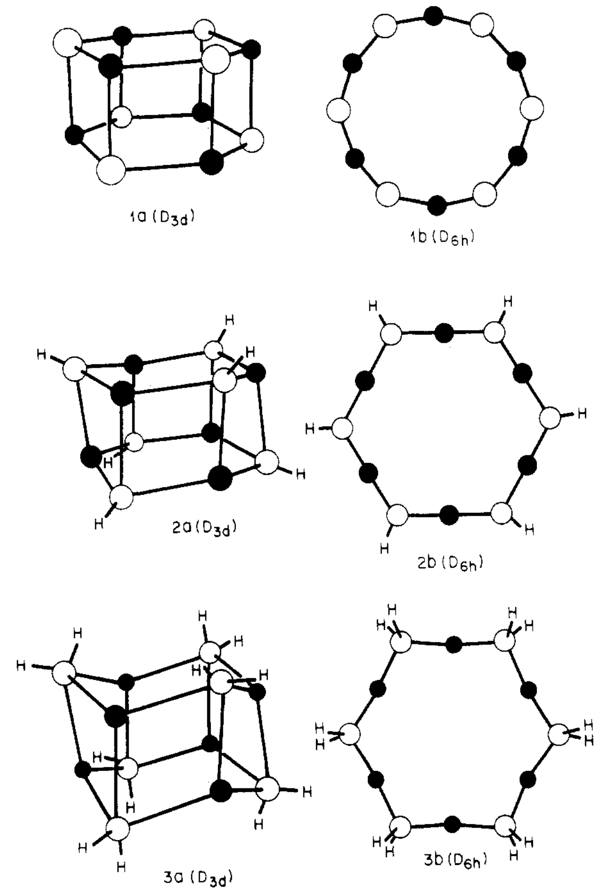

Figure 1. Structures considered in this study. **1a** and **1b** represent $(LiF)_6$, **2a** and **2b** represent $(LiOH)_6$, and **3a** and **3b** represent $(LiNH_2)_6$. In all figures, dark circles represent Li atoms and open circles represent F, O, or N. The figures are computer generated and are true to scale based on the optimized 3-21G geometries.

Table II. Vibrational Frequencies (cm^{-1}) and Zero-Point Energies (kcal/mol) for $(LiF)_6$ Structures Calculated with the STO-3G Basis Set

sym	vibrational frequencies	zero-point energy
D_{3d}	198 (e_g), 245 (e_u), 288 (a_{2u}), 343 (a_{1g}), 353 (e_g), 374 (a_{1u}), 446 (e_u), 506 (a_{1g}), 639 (a_{2u}), 685 (a_{1g}), 702 (e_u), 735 (e_g), 776 (e_u), 784 (e_g), 798 (a_{1g}), 845 (a_{2u}), 966 (a_{2g}), 987 (e_g), 988 (e_u), 1024 (a_{1u})	27.0
D_{6h}	51 (e_{2g}), 56 (e_{2u}), 121 (b_{2g}), 125 (b_{1u}), 148 (b_{1g}), 153 (b_{2u}), 229 (e_{2u}), 230 (e_{2g}), 247 (a_{1g}), 268 (e_{1u}), 311 (e_{1g}), 350 (a_{2u}), 510 (a_{1g}), 567 (e_{1u}), 739 (e_{2g}), 842 (b_{2u}), 1232 (b_{1u}), 1274 (e_{2g}), 1276 (a_{2g}), 1301 (e_{1u})	21.5

Table III. Total Energies (hartrees) and Relative Energies (kcal/mol) Calculated with Different Basis Sets Using HF/3-21G Geometries

		basis set		
struct	sym	HF/ 3-21G	HF/ 6-31G	HF/ 6-31G+sp+d
$(LiF)_6$	D_{3d}	−638.851 75	−642.115 86	−642.159 72
	D_{6h}	−638.741 14	−642.049 98	−642.108 51
	ΔE^a	69.4	41.3	32.1
$(LiOH)_6$	D_{3d}	−495.371 28	−497.904 39	−497.961 32
	D_{6h}	−495.252 31	−497.815 07	−497.894 50
	ΔE^a	74.7	56.0	41.9
$(LiNH_2)_6$	D_{3d}	−376.717 63	−378.651 33	−378.725 47
	D_{6h}	−376.679 57	−378.614 83	−378.693 31
	ΔE^a	23.9	22.9	20.2

[a] Positive sign indicates that the D_{3d} form is more stable.

Table IV. Binding Energies of Hexamers (kcal/mol) at Different Levels of Theory

		basis set		
struct	sym	HF/ 3-21G	HF/ 6-31G	HF/ 6-31G+sp+d
$(LiF)_6$	D_{3d}	456.0	374.2	312.8
	D_{6h}	386.6	332.8	280.7
$(LiOH)_6$	D_{3d}	409.0	340.1	307.1
	D_{6h}	334.4	284.1	265.1
$(LiNH_2)_6$	D_{3d}	342.9	295.1	272.3
	D_{6h}	319.1	272.2	252.1

Table V. Binding Energies (kcal/mol) of Different Oligomers at the HF/6-31G+sp+d Level of Theory

	binding energy per monomer				
struct	dimer	trimer	tetramer	hexamer	solid[a]
$(LiF)_n$	32.5	42.0	47.0	52.1	65
$(LiOH)_n$	33.6	41.5	47.5	51.2	59
$(LiNH_2)_n$	32.8	40.3	41.8	45.4	

[a] Experimental values from ref 38. These values probably have an uncertainty of ≃3-5 kcal/mol.

(i.e. (2,2,6,6-tetramethylpiperidinato)lithium tetramer). Thus, it is of interest to see if such planar arrangements are feasible for the hexamers also, although no such structure has been reported as yet experimentally.

Computational Methods

The Hartree-Fock method[27] was used in the determination of all molecular geometries. The standard STO-3G basis set[28] and the split-valence 3-21G basis set[29] were used in these optimizations. The 3-21G basis set has been previously shown to be reliable in the calculation of geometries of lithium compounds.[3,5] For each of the three compounds $(LiF)_6$, $(LiOH)_6$, and $(LiNH_2)_6$, the geometrical parameters of the distorted octahedral form (D_{3d}) and the hexagonal planar form (D_{6h}) were completely optimized by using efficient gradient techniques. The optimized structures are represented in Figure 1 and the corresponding geometrical parameters are listed in Table I.

In order to determine if the calculated structures are indeed minima with the symmetries used, the complete harmonic force constants and the associated vibrational frequencies were evaluated[30] for the $(LiF)_6$ struc-

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tures with the STO-3G basis set. All the computed frequencies were positive for both the D_{3d} and the D_{6h} structures, confirming that lower symmetry distortions do not result in energy stabilization. Though similar calculations were not directly carried out for $(LiOH)_6$ and $(LiNH_2)_6$ structures, preliminary calculations with lower symmetries showed that both the D_{3d} and the D_{6h} structures are likely to be minima for these hexamers as well. The calculated vibrational frequencies of the $(LiF)_6$ structures are listed in Table II.

Larger basis sets including diffuse and polarization functions may be important in the reliable calculation of relative energies of these systems.[10,14] To investigate such basis set effects, single-point calculations were carried out at the 3-21G geometries with the standard 6-31G basis set[31] augmented by a set of diffuse sp functions[32] and a set of six d-type functions[33] on F, O, or N. This basis set, denoted as 6-31G+sp+d has been previously used in the accurate calculation of association energies in such systems.[10,14] The calculations with the 6-31G+sp+d basis set for $(LiNH_2)_6$ involved a total of 192 basis functions. The calculated total energies and the associated binding energies for different basis sets are listed in Tables III and IV, respectively. Table V has a comparison between the hexamers and the smaller oligomers such as dimers, trimers, and the tetramers.

In our previous study on the tetramers of LiF, LiOH, and $LiNH_2$, electron correlation effects were included by means of Møller–Plesset perturbation theory through third order.[34,35] However, such effects were found to be completely unimportant in the evaluation of the relative energies of the tetrahedral and planar forms, contributing less than 1 kcal/mol in all cases. This is not surprising since the bonding involved has a high degree of ionic character. Thus the effects of electron correlation were not included in this study.

Results and Discussion

The geometries of the distorted octahedral forms as seen in Figure 1 are rather striking. This structure can be considered as an octahedron of lithium atoms with the electronegative groups being attached to six of the faces of the octahedron. This reduces the overall symmetry to D_{3d}. However, all six lithium atoms as well as six electronegative groups are equivalent to each other in this structure. Thus the structure of $(LiF)_6$, for example, can also be considered as two interpenetrating octahedra formed by Li and F atoms. The overall structure appears to be very close to a hexagonal prism with alternating Li and F atoms. This is very similar to the essentially cubic arrangement of Li and F atoms in the tetramer, $(LiF)_4$.

Our calculated geometries cannot be directly compared to the experimental values since the latter are not available for these molecules. However, there are some derivatives for which accurate geometries have been determined. For example, Barr et al.[25] have recently studied the hexamers of several iminolithium compounds such as $[LiN{=}C(Ph)NMe_2]_6$ and have seen a distorted octahedral framework very similar to our structure **3a**. Our calculated Li–N bond lengths (3-21G) are in remarkable agreement with those of Barr et al. Our calculations indicate the presence of two "short" Li–N bonds at 1.99 Å and one "long" bond at 2.06 Å, essentially in perfect agreement with the corresponding experimental values of 1.98, 2.01, and 2.05 Å. The slight asymmetry seen between the two short bonds in the experiments is probably due to crystal packing effects.

Additional comparisons between our calculated parameters and those of other derivatives are also possible. For example, the Li–Li distances that we have calculated can be compared to the corresponding values found in the hexamer of cyclohexyllithium. Zerger et al.[22] have found experimentally that the six lithium faces to which the cyclohexyl groups are attached each have two short Li–Li distances (2.397 Å) and one long distance (2.968 Å). These are very close to the corresponding calculated values in Table I. The mean value of the Li–Li distances among the three different hexamers is 2.372 Å for the short Li–Li distance and 3.012 Å for the long Li–Li distance.

The vibrational frequencies in Table II show that the more compact D_{3d} structure generally has higher frequencies than the open D_{6h} structure. However, the Li–F bond lengths in the D_{6h} structure are shorter since there are fewer bonds in this structure, and hence the frequencies corresponding to stretching of such bonds are higher in the D_{6h} form. Many of the low frequencies of the D_{6h} structure correspond to out-of-plane bending vibrations, as expected. The total zero-point energy of the D_{3d} structure is about 5 kcal/mol higher than that of the D_{6h} structure and hence inclusion of their contributions will modify the D_{3d}–D_{6h} energy difference by this amount.

The relative energies shown in Table III are basis set dependent and the smaller basis sets overestimate the stability of the more compact D_{3d} structure considerably. This is due, in part, to the basis set superposition error,[36] which results from the inadequacy of small basis sets to describe the bonding in such aggregates. The HF/6-31G+sp+d basis set results are, however, expected to be reliable on the basis of previous experience.[10,14] The individual contributions of the diffuse sp and the d functions (not listed) are roughly additive, with the former decreasing the energy difference and the latter increasing it slightly. For $(LiNH_2)_6$, the 3-21G basis set appears to be adequate in describing the energy difference between the isomers. Similar behavior has been seen previously for the tetramers.[14]

The results from Table III reveal that for all three hexamers the octahedral form is significantly more stable than the planar form. This is very different from the corresponding situation for the tetramers[14] where the planar form was found to be more stable for $(LiNH_2)_4$. Inspection of the octahedral–planar energy differences for the hexamers of LiF, LiOH, and $LiNH_2$ (32.1, 41.9, and 20.2 kcal/mol) with the corresponding tetrahedral–planar energy differences for the tetramers (8.6, 16.2, and −8.9 kcal/mol) reveals that there is a uniform shift of about 25 kcal/mol favoring the compact (D_{3d}) structure on going from the tetramer to the hexamer.

In our previous work on the tetramers,[14] electrostatic models were found to be inadequate in describing the energy differences between the isomers. In these models, the 3-21G geometries were used with unit positive charges to represent Li and unit negative charges to represent F, OH, or NH_2. The electrostatic energies were evaluated by using Coulomb's law for both the oligomers and the monomers. The aggregation energy (for the tetramers, for example) was then calculated as the increase in the electrostatic energy on going from four monomers to the tetramer. Though such models do not reproduce the isomer energy differences correctly, they may be useful in describing the *changes* on going from the tetramer to the hexamer. This can be illustrated for the oligomers of LiF, which most closely resemble an ionic system. For the tetramer, the electrostatic model predicts (incorrectly) that the planar form is more stable by 34 kcal/mol. For the hexamer, the same model predicts (again incorrectly) that the planar form is more stable by only 18 kcal/mol. However, the change on going from the tetramer to the hexamer, being 16 kcal/mol favoring the D_{3d} form, is consistent with the results of the detailed calculations. If this interpretation is correct, this suggests that electrostatic factors contribute significantly to the stability of the compact form on going from the tetramer to the hexamer. Of course, the formation of a 12-membered ring with the necessary angle strain may also be responsible for decreasing the stability of the planar form. It should be remembered that inclusion of zero-point corrections will reduce the D_{3d}–D_{6h} energy difference by $\simeq 5$ kcal/mol as pointed out earlier.

The calculated total binding energies of the hexamers can be seen from Table IV. The binding energies of $(LiF)_6$ and $(LiOH)_6$ are roughly comparable, being $\simeq 310$ kcal/mol, whereas $(LiNH_2)_6$ has a smaller binding energy of $\simeq 270$ kcal/mol. Inclusion of zero-point corrections will reduce these estimates by $\simeq 5$–10 kcal/mol. The comparable binding energies of the hexamers of

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LiF and LiOH are very similar to the corresponding values seen for the tetramers. Purely electrostatic estimates indicate a large decrease in the binding energy on going from $(LiF)_6$ to $(LiOH)_6$. The inadequacy of electrostatic considerations suggests that multicenter covalent bonding may be important for the oligomers of LiOH and $LiNH_2$.

For the planar structure of $(LiNH_2)_6$, an asymmetric structure was investigated, where six alternate Li–N bonds were optimized separately from the other six. The geometry optimization led to the equalization of all the Li–N bonds, ruling out the possibility of a "lithium bond"[37] between lithium and the nitrogen of the next monomer, different from the intramolecular lithium–nitrogen bond.

In previous studies,[10-14] the smaller oligomers of LiF, LiOH, and $LiNH_2$ have been studied in detail. It is of interest to see how the binding energy per monomer increases as the cluster size increases. Table V lists the binding energies (per monomer) of the dimers, trimers, tetramers, and hexamers of these compounds. These values were all calculated at a uniform level of theory by using the 6-31G+sp+d basis set. It should be remembered that zero-point vibrational effects would decrease these binding energies (per monomer) by $\simeq$1–2 kcal/mol. Comparison of the tetramers with the hexamers in Table V shows that the binding energy per monomer in the hexamer is about 3–5 kcal/mol higher than that in the tetramer. In addition, the binding energy per monomer in the solid is known experimentally[38] for LiF and LiOH, and these values are also listed in the last column of Table V. Comparison between the hexamers and the solid shows that there is still a significant difference, not unexpected for these predominantly ionic molecules.

Other Isomeric Structures

In addition to the octahedral and planar ring arrangements considered above, other geometries are also possible for these hexamers. In particular, we have performed preliminary explorations of two such geometrical arrangements, viz. (1) a geometry based on the NaCl lattice, i.e. a 3 × 2 × 2 rectangular solid (D_{2h} symmetry) closely related to the geometry expected in the solid state, and (2) a similar geometry but only in 2-dimensions, i.e. a 6 × 2 planar framework (C_{2h} symmetry). Analogous structures for the hexamer of LiH have been considered previously by Kato et al.[16] who referred to these two structures as "fence dimer" and "fence" geometries, respectively. Our preliminary results indicate that both these geometrical arrangements represent local minima on the potential surface but that neither of these structures is as stable as the octahedral arrangement considered in detail in this study. In fact, these additional calculations strongly suggest that the octahedral structures **1a**, **2a**, and **3a** are probably the global minima for the hexamers of LiF, LiOH, and $LiNH_2$, respectively.

Conclusions

The structures and energies of the hexamers of LiF, LiOH, and $LiNH_2$ have been investigated with accurate ab initio molecular orbital techniques. Large basis sets including diffuse and polarization functions have been used in these calculations. For all three systems, distorted octahedral forms (D_{3d}) are found to be considerably more stable than planar (D_{6h}) forms. These results are quite different from the corresponding results involving the tetramers. Electrostatic factors appear to contribute significantly to these differences. The binding energies of $(LiF)_6$ and $(LiOH)_6$ are about 310 kcal/mol and that of $(LiNH_2)_6$ is about 270 kcal/mol.

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UV Photoelectron Spectrum and Electronic Structure of $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$: An Interpretation by means of ab Initio CI Calculations

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The He I photoelectron spectrum of $\{Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)\}_2$ is reported and interpreted by means of ab initio SCF and CI calculations. An original quantum-chemical treatment accounts for the relaxation and the relocalization of the metal 3d and ligand outer valence electrons. Part of the correlation effects are also included. The calculations yield four well-separated clusters of levels that can be consistently correlated with the four resolved band systems (A′, A″, B, and C) of the experimental spectrum. The degree of matching between the groups of computed levels and the experimental bands appears excellent, especially for this class of molecules. The analysis of the SCF wave function obtained for the neutral complex confirms the existence of two molecular orbitals (MO's) delocalized over the $[FeNO]_2$ fragment responsible for the stabilization of the system. A considerable charge transfer from the Cp ring (Cp = C_5H_5) toward the NO ligands through the metal atoms is noticed from the Mulliken population analysis. The very labile character of the Cp π electrons is confirmed by an analysis of the 12 computed ionized states. More specifically, the positive hole created in Fe by the ionization of a localized metal 3d electron is almost quantitatively compensated by a transfer of charge originating in the Cp rings.

Introduction

Binuclear clusters with two π-acceptor bridging ligands such as CO or NO have recently been the subject of several experimental[2-5] and theoretical[2-10] studies that have brought to light the unexpected character of their metal–metal interaction. It now appears that the low-lying π^* orbitals of the bridging ligands

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