Table 2. Some Important Results for Apex Bridged Complexes

Complex	μ-CO	μ-SO_2	μ-H	μ-Cl	μ-C_2H_2
HOMO orbital	$2a_1$	$1b_2$	$1b_2$	$3a_1(1a_2)$	$2a_2$
LUMO orbital	$3a_1$	$3a_1$	$1b_1$	$2b_1(4a_1)$	$3a_1$
HOMO-LUMO gap(eV)	1.05	0.81	0.38	0.16	0.47
Electron Counting	d^2-d^2	d^2-d^2	d^3-d^3	d^3-d^3	d^2-d^2
Prediction to Stability	stable	stable	stable	unstable	stable

University for his discussion and encouragement and assistance in most of the calculations.

Appendix

Extended Hückel calculations[19] were performed with the parameters listed in Table 1. The geometry for $Mo_2(OH)_4(\mu\text{-}OH)_2(\mu\text{-}X)$ was taken from the experimental structure of the tert-butyl derivative[20] except Mo-O-H angles of 104.5 were used. Bond lengths for calculations involving $Mo_2(OH)_6Py_2(HCCH)$ were taken from the experimental structure for $Mo_2(O\text{-}i\text{-}Pr)_6(Py)_2(HCCH)$.

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Ab Initio Studies of Lithium Bonded Complexes with H_2O Molecule

Dae Hyun Baik and Mu Shik Jhon*

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-650

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Lithium bonded complexes with H_2O molecule were investigated theoretically by varying the substituent of lithium compound as follows; LiH, LiLi, $LiCH_3$, $LiNH_2$, LiOH, LiF, and LiCl. Some hydrogen bonded complexes with H_2O molecule were also investigated to be compared with lithium bonded analogues. Electron correlation effect on the structures and energies of lithium bond was also investigated through MP2 and MP4 corrections. Unlike hydrogen bond with H_2O molecule, lithium bonded complexes with H_2O molecule were found to be interacting linearly with H_2O molecule. Electron correlation effect was very small for lithium bonded complexes. The lithium bond energies were found to be less affected by the choise of substituent of lithium compound.

Introduction

Hydrogen bonds have long been studied in a great detail by theoreticians and spectroscopists; however, lithium bonds have not been studied so much. Although oligomeric alkyllithium clusters are now believed to be formed by multi-

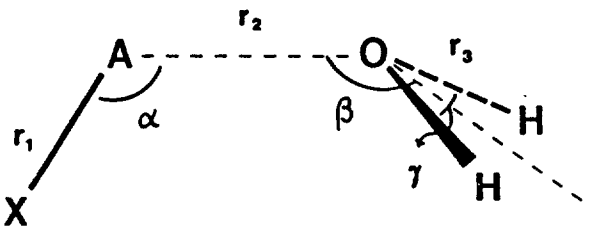

Figure 1. Definition of structural parameters of complexes considered in the geometry optimization (A = Li or H).

center electron deficient bonds, the 'lithium bond' concept have once been suggested for the alkyllithium clusters, -R-Li-R-Li-R-.[1]

The stability of lithium bonded molecular dimers was first investigated theoretically by Kollman *et al.* by using double zeta quality Gaussian lobe functions.[2] The evidence on the existenc of lithium bonding was first demonstrated by Ault and Pimentel in 1975.[3]

Since then, several theoretical investigations have been reported on the lithium bonds. The H_2O molecule as an electron donor, however, has been considered very few and with limited basis sets.[4]

In this work, we have been studied using lithium bonding characteristics with H_2O molecule using *ab initio* SCF theory[5] by varying lithium compounds in order to investigate the substituent effect such as LiH, LiLi, $LiCH_3$, $LiNH_2$, LiOH, LiF, and LiCl. The hydrogen bonded complexes of H_2O with HF and HCl have also been considered to be compared with the lithium bonded analogues. Electron correlation effect was also investigated by using Moller-Plesset's perturbation theory[6] to the second order (MP2) for both fluorine and chlorine compounds and to the fourth order (MP4) for only fluorine compounds only for the reason of computational limitations.

Method of Calculation

All SCF *ab initio* calculations were carried out using the Gaussian 82 package of computer program.[7] The basis set used is polarized split valence 6-31G** Gaussian set[8] of which the exponents used are those included in the Gaussian 82 program. All the structural parameters including intermolecular interaction bond length were optimized at SCF (restricted Hartree-Fock) level with the only assumption that the plane bifurcating water molecule includes lithium atom and the atom in the substituent X directly bonded to the lithium atom (Figure 1).

The geometry optimization of MP2 level of electron correlation was performed for the complexes: H_2O-HF, H_2O-ClH, H_2O-LiF, and H_2O-LiCl with fixed MP2 optimized structure of H_2O molecule. Pulay's gradient method[9] was used in the MP2 optimizations. Higher correlation was investigated for the complexes of H_2O-HF and H_2O-LiF using MP4 level with single, double, and quadruple excitations (MP4-SDQ) with a frozen core approximation. H_2O molecule has been held fixed at MP4-SDQ optimized geometry. Other geometrical constraints in optimization are the same to the SCF optimization with the exception of approximation that and defined in Figure 1 are equal to 180 degrees. This assumption was based upon the results of SCF optimization. Fletcher-Powell's minimization method[10] was used in the MP4 optimizations. Population analyses were based on the Mulliken's method.[11]

Results and Discussion

The SCF 6-31G** optimized structure of H_2O molecule is r(OH) = 0.934Å and < (HOH) = 106.0°. In forming Li bonding complexes, the bond angle of H_2O molecule (α, see Figure 1) were increased by 1.8—2.2 degrees. Corresponding changes in the H bond cases were 1.1 and 0.8 degrees for H_2O-HF and H_2O-HCl, respectively. The structural changes in forming Li bonding complexes were also found to be larger than in H bonding cases for other geometrical parameters. As it can be seen from Table 1 that the elongations of the bond lengths of A-X (Δr_1, A = Li or H) are 0.19 0.53 for Li bonds, 0.010 and 0.012 for H_2O-HF and H_2O-HCl, respectively, in angstroms. The decreased amounts of the total electronic charge density (Mulliken's population) of H_2O molecule were found to be also larger in the Li bond cases (0.0564 — 0.0750Å for lithium bonds, 0.0323 and 0.0342Å for hydrogen bonds). As it has been observed by other authors with NH_3 molecule as an electron donor,[12] the atomic electronic charge densities of bridging atoms (Li and H) have been found to change reversely for the two types of intermolecular bonding except H_2O-LiLi case. Even in the above exceptional case, however, the total electronic charge density of H_2O molecule was decreased. The amounts of changes of the electronic charge density of bridging atoms were found to be also larger by about two times or more in Li bond cases.

The above differences in two types of intermolecular bonding seems to be closely related to the differences in dimerization energies of these two types of intermolecular bonding,

Table 1. 6-31G SCF optimized results for H_2O-AX complexes for A = Li or H[a]**

AX	LiH	LiLi	$LiCH_3$	$LiNH_2$	LiOH	LiF	LiCl	HF	HCl
r_1	1.655	2.860	2.019	1.769	1.610	1.574	2.099	0.911	1.278
Δr_1	0.025	0.053	0.019	0.020	0.020	0.019	0.027	0.010	0.012
r_2	1.915	1.914	1.937	1.930	1.945	1.946	1.897	1.811	1.973
α	179.8	179.2	179.9	179.8	179.3	179.4	179.4	174.3	175.7
β	179.1	179.0	178.1	179.2	179.2	178.8	178.8	138.6	145.4
γ	107.9	108.2	107.8	108.0	107.9	107.8	107.8	107.1	106.8
$\Delta\gamma$[b]	1.9	2.2	1.8	2.0	1.9	1.8	1.8	1.1	0.8
Δq_A^b	.0855	-.0274	.0457	.0878	.0529	.0414	.0830	-.0266	-.0260
ΔE[c]	22.51	17.43	21.04	20.79	20.04	21.47	25.01	9.06	6.11

[a]See Fig. 1 for the definition of structural parameters. Bond lengths are in Å and bond angles are in degrees
[b]$\Delta x = x(complex) - x(monomer)$ [c]In kcal/mol.

Table 2. MP2 and/or MP4 optimized results for H_2O-AX complexes for A=Li or H[a]

	H_2O-LiF[b]		H_2O-HF		H_2O-LiCl[b]	H_2O-HCl
Method	MP2	MP4	MP2	MP4	MP2	MP2
r_1	1.5824	1.5874	0.9345	0.9316	2.0903	1.2867
Δr_1	0.0158	0.0174	0.0135	0.0114	0.0262	0.0185
r_2	1.9293	1.9547	1.7485	1.7704	1.8870	1.8640
α	180.0	180.0	169.4	170.5	180.0	175.3
β	180.0	180.0	120.1	122.3	180.0	126.0
Δq_A	0.0393	0.0386	-0.0296	-0.0234	0.0824	-0.0253
ΔE[c]	23.27	22.53	10.66	10.03	27.32	7.81

[a]Bond lengths are in Å and bond angles are in degrees. [b]Linear interactions were assumed according to the results of SCF optimization. [c]In kcal/mol.

which had initiated some research groups to be interested in Li bonds. Lithium bonded complexes were considerably stabilized by up to 25kcal/mole. On the other hand, hydrogen bonded complexes were stabilized by no more than 10 kcal/mole. The interaction energies of lithium bonded complexes were obtained as 17.4-25.0 kcal/mole along with the variation of the substituent of lithium compounds; however, there can be found no systematic trends among them. Moreover, the interaction geometry and the charge transfer was also found to be not systematic with the change of the substituent of lithium compounds. That is, lithium atom is very characteristic in itself and by itself as it serves as an bridging atom The equilibrium geometries of lithium bonded complexes were found to be almost linear; on the other hand, as denoted in footnote a of Table 1, the hydrogen bonded complexes were found to be considerably folded to form cis shape at equilibrium.

We have considered the electron correlation effect on the formation of lithium and hydrogen bonded complexes by MP2 and MP4-SDQ levels of perturbation theory. In Table 3, the results of the electron correlation effect correction considered by both or one of MP2 and MP4-SDQ level of theory are listed in for the complexes of H_2O-LiF, H_2O-HF, H_2O-LiCl, and H_2O-HCl. In this calculation the lithium bonded complexes were approximated to have the linear interaction following the SCF optimization results are listed in Table 1 to save the computing time.

Comparing the geometries optimized with correlation effect with the SCF ones, it can be seen that the correlation effect makes all A-X (A = Li or H) bond of complexes slightly elongated except Li-Cl bond. This fact is also found in the case of monomer calculation. The bond lengths of all monomers considered in the correlation calculation were found to be elongated by the correlation with the exception of LiCl which was somewhat shrinked. The amount of shrinkage is nearly same for both monomer and complex cases (0.08 and 0.09Å, respectively).

The bond length changes of A-X (A = Li or H) in forming complexes with H_2O molecule are listed in $\Delta r1$ row in Table 2. In the case of the lithium bonded H_2O-LiF complex, MP2 and MP4 levels of correlation lessened the amount of lengthening of Li-F bond by 15 and 10%, respectively. On the other hand, in the hydrogen bonded H_2O-HF complex case, the amount of lengthening of H-F bond were increased by 10 and 40% by MP2 and MP4, respectively.

All the intermolecular interaction distances, r_2, were slightly shortened from the SCF results by MP2 correction as shown in Table 2. The order of shortened amount is differ by one in both types of intermolecular interactions. For hydrogen bonded complexes, the amount of shrinkage is 3.4 and 5.5% for H_2O-HF and H_2O-HCl, respectively. For the lithium bonded complexes, the amount of change is negligible. The amounts of MP4 corrections were found to be very small for both complexes of H_2O-LiF and H_2O-HF.

As we can see from Table 2, the electronic charge density difference of hydrogen atoms, H or Li, were not much affected by electron correlation, not only for the signs of differences but also for its magnitude. Nevertheless, the energetics were considerably affected by electron correlation, especially in the cases of hydrogen bonded complexes, by two times or more than in the lithium bond cases. All of the complexes considered were more stabilized by electron correlation. The stabilization energy of H_2O-LiF complex was more increased than SCF value by 10 and 5% by MP2 and MP4, respectively. And the hydrogen bonded H_2O-HF complex was 20 and 12% more stabilized by the two methods of electron correlation, respectively. The difference of the amount of the electron correlation effect on the stabilization energy was found to be larger for the chlorine atom containing complexes such as H_2O-LiCl and H_2O-HCl. The lithium bonded H_2O-LiCl complex was stabilized by 27.3kcal/mol which is 9% more stabilized than the SCF value; on the other hand, the hydrogen bonded H_2O-HCl complex was stabilized by 7.8 kcal/mcl which is 28% more stabilized than the SCF one.

As we have studied so far, lithium bond and hydrogen bond stabilize the intermolecular bonded complexes with H_2O molecule. The interaction structures and the stabilization energies were, however, found to be quite different each other. Unlike the geometries of hydrogen bonded complexes with H_2O molecule, lithium bonded complexes are formed linearly and have more shared structures. As it have been observed in other lithium bond cases, the stabilization energies were considerably larger than hydrogen bonding analogues. The lithium bond energies were found to be less affected by the choise of substituent of lithium compound. Electron correlation effect was very small for lithium bonded complexes with H_2O molecule in geometrics and energetics.

In the hydrogen bonding cases, relative separations of two interacting molecules were reduced from SCF values by about 10% by MP4 correction. In the lithium bonding cases, the separations were found to be decreased by MP2 whereas increased by MP4 corrections; yet, the amount of changes were by far smaller than in the hydrogen bondings.

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Synthesis of Perhydroisoquinoline Ring Systems by *N*-Acyliminium Cyclization*

Joong-Kwon Choi*, Young-Shik Jung, No-Sang Park

Korea Research Institute of Chemical Technology P.O. Box 9, Daedeogdanji, Daejeon 302-343

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The stereochemistry of *N*-acyliminium cyclizations to form decahydropyrrolo[2,1-*a*]isoquinolin-3(2*H*)-ones was studied. Particular attention was paid to the stereocontrol by an acetoxy group present on pyrrolidone ring. Two of the three new chiral centers were formed stereospecifically, and the third was controlled by elimination-hydrogenation seqeunce.

Introduction

As part of a chemical program related to the synthesis of new pharmaceuticals, we became interested in the preparation of fused indolizidine ring systems. *N*-Acyliminium ion initiated olefin cyclizations have been recognized as a potent tool in the synthesis of nitrogen heterocycles mainly due to the effort of Speckamp group.[1] Although a number of stereochemical features of these reactions have been reported, the effect of asymmetric centers on their stereochemical course has received little attention.[2] Few earlier examples are shown in Figure 1. Speckamp has shown that the stereochemistry of cyclizations of *N*-acyliminium ion derived from tartarimide could be controlled.[3] Hart[4] and Chamberlain[5] have shown that the stereochemistry of cyclizations of *N*-acyliminium ions derived from maliimides were well controlled in their syntheses of pyrrolizidine alkaloids. Also it is known by Hart and Chamberlain that the regiochemistry of $NaBH_4$ reduction of maliimides is highly controllable. Herein are reported some results obtained during the course of studies.

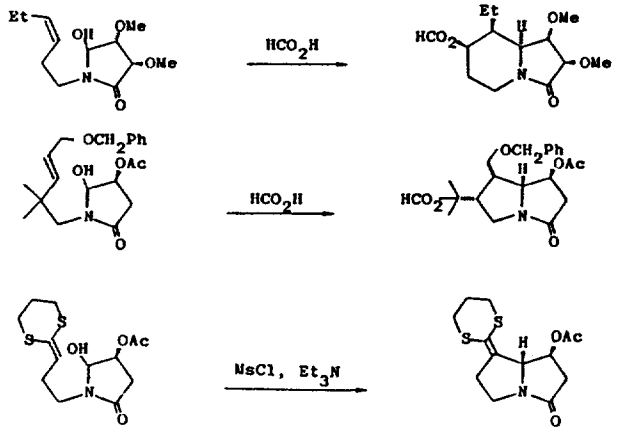
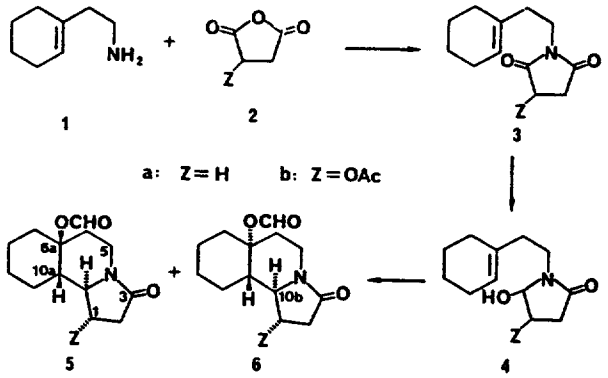


Figure 1. Examples of *N*-Acyliminium Cyclizations

Results and Discussion

The study was begun with *N*-[2-(1-cyclohexenyl)ethyl] succinimide **3a**. The imide **3a** was prepared by reacting 2-(1-cyclohexenyl)ethylamine **1** and succinic anhydride **2a** followed by cyclization of the intermediate amide-acid with acetyl chloride[4] as shown in Scheme 1. This imide could be purified by column chromatography, but satisfactory result was obtained also by using crude product. The imide **3a** was reduced with $NaBH_4$ in methanol to give a hydroxylactam **4a** and it was treated with formic acid to give one major product. Although there were four possible isomers for cyclization product due to three asymmetric centers present in the structure (without considering optical isomers), the NMR spectrum of the major product showed only two formyl protons at δ 8.06 and 8.16. Two minor products were also detected.



Scheme 1

The reaction would proceed via two possible conformers as shown in Scheme 2. The conformer **7B** should proceed through boat form and the amount of the conformer itself