

**Table 2. Some Important Results for Apex Bridged Complexes**

Complex	$\mu$ -CO	$\mu$ -SO <sub>2</sub>	$\mu$ -H	$\mu$ -Cl	$\mu$ -C <sub>2</sub> H <sub>2</sub>
HOMO orbital	2a <sub>1</sub>	1b <sub>2</sub>	1b <sub>2</sub>	3a <sub>1</sub> (1a <sub>2</sub> )	2a <sub>2</sub>
LUMO orbital	3a <sub>1</sub>	3a <sub>1</sub>	1b <sub>1</sub>	2b <sub>1</sub> (4a <sub>1</sub> )	3a <sub>1</sub>
HOMO-LUMO gap(eV)	1.05	0.81	0.38	0.16	0.47
Electron Counting	d <sup>2</sup> -d <sup>2</sup>	d <sup>2</sup> -d <sup>2</sup>	d <sup>3</sup> -d <sup>3</sup>	d <sup>3</sup> -d <sup>3</sup>	d <sup>2</sup> -d <sup>2</sup>
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<sup>19</sup> were performed with the parameters listed in Table 1. The geometry for Mo<sub>2</sub>(OH)<sub>4</sub>( $\mu$ -OH)<sub>2</sub>( $\mu$ -X) was taken from the experimental structure of the tert-butyl derivative<sup>20</sup> except Mo-O-H angles of 104.5 were used. Bond lengths for calculations involving Mo<sub>2</sub>(OH)<sub>6</sub>Py<sub>2</sub>(HCCH) were taken from the experimental structure for Mo<sub>2</sub>(O-i-Pr)<sub>6</sub>(Py)<sub>2</sub>(HCCH).

### References

1. M. H. Chisholm, Reactivity of Metal-Metal Bonds, ACS Symposium Series 155, *Am. Chem. Soc.*, Washington, DC, 1981.
2. M. H. Chisholm, *Inorganic Chemistry: Toward the 21st Century*, A. C. S., 1983.
3. M. H. Chisholm, J. C. Huffman, J. Leonelli, I. P. Rothwell, *J. Am. Chem. Soc.*, **104**, 7030 (1982).
4. (a) M. H. Chisholm, F. A. Cotton, M. W. Extine, W. W. Reichert, *J. Am. Chem. Soc.*, **100**, 153 (1978); (b) M.

- Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, D. Little, P. E. Fanwick, *Inorg. Chem.*, **18**, 2266 (1979).
5. M. H. Chisholm, J. C. Huffman, I. P. Rothwell, *J. Am. Chem. Soc.*, **103**, 4245 (1981).
6. M. H. Chisholm, K. Folting, J. C. Huffman and J. Ko, *Polyhedron* **4**, 893 (1985).
7. P. J. Blower, M. H. Chisholm, D. L. Clark, and B. W. Eichhorn, *Organometallics*, **5**, 2125 (1986).
8. M. H. Chisholm, D. M. Hoffman, J. C. Huffman, *Organometallics*, **4**, 986 (1985).
9. M. P. Brown, A. N. Keith, Lj Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, K. R. Seddon, *Inorg. Chim. Acta*, **34**, L223 (1979).
10. A. L. Balch, L. S. Benner, M. M. Olmstead, *Inorg. Chem.*, **18**, 2996 (1979).
11. M. Cowie, S. K. Dwight, *Inorg. Chem.*, **19**, 209 (1980).
12. F. A. Cotton, J. D. Jamerson, B. R. Stults, *J. Am. Chem. Soc.*, **98**, 1774 (1976).
13. (a) W. I. Bailey, M. H. Chisholm, F. A. Cotton, L. A. Rankel, *J. Am. Chem. Soc.*, **100**, 5764 (1978); (b) D. S. Ginley, D. R. Bock, M. S. Wrighton, B. Fischer, D. L. Tipton, R. Bau, *J. Organometal. Chem.*, **157**, 41 (1978).
14. E. L. Muetterties, V. M. Day, S. S. Abdel-Meguid, S. Debastini, M. G. Thomas, W. R. Pretzer, *J. Am. Chem. Soc.*, **98**, 8289 (1976).
15. D. M. Hoffman and R. Hoffmann, *Inorg. Chem.*, **20**, 3543 (1981).
16. M. H. Chisholm, J. C. Huffman, I. P. Rothwell, *J. Am. Chem. Soc.*, **103**, 4245 (1981).
17. M. J. Calhorda and R. Hoffmann, *Organometallics*, **5**, 2181 (1986).
18. M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, J. Leonelli, D. Little, *J. Am. Chem. Soc.*, **103**, 779 (1981).
19. R. Hoffmann, W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962).
20. M. H. Chisholm, F. A. Cotton, M. W. Extine, R. L. Kelly, *J. Am. Chem. Soc.*, **101**, 7645 (1979).

## Ab Initio Studies of Lithium Bonded Complexes with H<sub>2</sub>O Molecule

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Lithium bonded complexes with H<sub>2</sub>O molecule were investigated theoretically by varying the substituent of lithium compound as follows; LiH, LiLi, LiCH<sub>3</sub>, LiNH<sub>2</sub>, LiOH, LiF, and LiCl. Some hydrogen bonded complexes with H<sub>2</sub>O 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<sub>2</sub>O molecule, lithium bonded complexes with H<sub>2</sub>O molecule were found to be interacting linearly with H<sub>2</sub>O molecule. Electron correlation effect was very small for lithium bonded complexes. The lithium bond energies were found to be less affected by the choice 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 alkyl lithium clusters are now believed to be formed by multi-

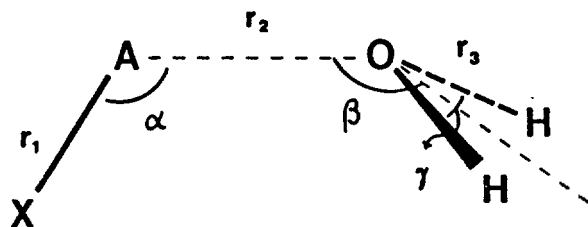


Figure 1. Definition of structural parameters of complexes considered in the geometry optimization (A = Li or H).

center electron deficient bonds, the 'lithium bond' concept have once been suggested for the alkyl lithium clusters,  $-R-Li-R-Li-R$ .<sup>1</sup>

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

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.<sup>4</sup>

In this work, we have been studied using lithium bonding characteristics with  $H_2O$  molecule using *ab initio* SCF theory<sup>5</sup> 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<sup>6</sup> 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.<sup>7</sup> The basis set used is polarized split valence 6-31G\*\* Gaussian set<sup>8</sup> 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:  $H_2O-HF$ ,  $H_2O-CHI$ ,  $H_2O-LiF$ , and  $H_2O-LiCl$  with fixed MP2 optimized structure of  $H_2O$  molecule. Pulay's gradient method<sup>9</sup> 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<sup>10</sup> was used in the MP4 optimizations. Population analyses were based on the Mulliken's method.<sup>11</sup>

### Results and Discussion

The SCF 6-31G\*\* optimized structure of  $H_2O$  molecule is  $r(OH) = 0.934 \text{ \AA}$  and  $\angle(OH) = 106.0^\circ$ . In forming Li bonding complexes, the bond angle of  $H_2O$  molecule ( $\alpha$ , 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 ( $\Delta r_1$ , 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 (0.0564–0.0750 for lithium bonds, 0.0323 and 0.0342 for hydrogen bonds). As it has been observed by other authors with  $NH_3$  molecule as an electron donor,<sup>12</sup> 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\*

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
$\Delta r_1$	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
$\alpha$	179.8	179.2	179.9	179.8	179.3	179.4	179.4	174.3	175.7
$\beta$	179.1	179.0	178.1	179.2	179.2	178.8	178.8	138.6	145.4
$\gamma$	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
$\Delta q_A^c$	.0855	-.0274	.0457	.0878	.0529	.0414	.0830	-.0266	-.0260
$\Delta E^c$	22.51	17.43	21.04	20.79	20.04	21.47	25.01	9.06	6.11

\*See Fig. 1 for the definition of structural parameters. Bond lengths are in  $\text{\AA}$  and bond angles are in degrees

<sup>b</sup> $\Delta \gamma = \gamma(\text{complex}) - \gamma(\text{monomer})$  <sup>c</sup>In kcal/mol.

**Table 2.** MP2 and/or MP4 optimized results for H<sub>2</sub>O-AX complexes for A=Li or H<sup>a</sup>

Method	H <sub>2</sub> O-LiF <sup>b</sup>		H <sub>2</sub> O-HF		H <sub>2</sub> O-LiCl <sup>b</sup>		H <sub>2</sub> O-HCl	
	MP2	MP4	MP2	MP4	MP2	MP4	MP2	MP4
r <sub>1</sub>	1.5824	1.5874	0.9345	0.9316	2.0903	2.0903	1.2867	1.2867
Δr <sub>1</sub>	0.0158	0.0174	0.0135	0.0114	0.0262	0.0262	0.0185	0.0185
r <sub>2</sub>	1.9293	1.9547	1.7485	1.7704	1.8870	1.8870	1.8640	1.8640
α	180.0	180.0	169.4	170.5	180.0	180.0	175.3	175.3
β	180.0	180.0	120.1	122.3	180.0	180.0	126.0	126.0
Δq <sub>A</sub>	0.0393	0.0386	-0.0296	-0.0234	0.0824	0.0824	-0.0253	-0.0253
ΔE <sup>c</sup>	23.27	22.53	10.66	10.03	27.32	27.32	7.81	7.81

<sup>a</sup>Bond lengths are in Å and bond angles are in degrees. <sup>b</sup>Linear interactions were assumed according to the results of SCF optimization. <sup>c</sup>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 a 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<sub>2</sub>O-LiF, H<sub>2</sub>O-HF, H<sub>2</sub>O-LiCl, and H<sub>2</sub>O-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 shrunked. 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<sub>2</sub>O molecule are listed in Δr<sub>1</sub> row in Table 2. In the case of the lithium bonded H<sub>2</sub>O-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<sub>2</sub>O-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<sub>2</sub>, 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<sub>2</sub>O-HF and H<sub>2</sub>O-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<sub>2</sub>O-LiF and H<sub>2</sub>O-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<sub>2</sub>O-LiF complex was more increased than SCF value by 10 and 5% by MP2 and MP4, respectively. And the hydrogen bonded H<sub>2</sub>O-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<sub>2</sub>O-LiCl and H<sub>2</sub>O-HCl. The lithium bonded H<sub>2</sub>O-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<sub>2</sub>O-HCl complex was stabilized by 7.8 kcal/mol 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<sub>2</sub>O 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<sub>2</sub>O 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 choice of substituent of lithium compound. Electron correlation effect was very small for lithium bonded complexes with H<sub>2</sub>O 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.

## References

1. For example, see A. N. Rodionov, G. V. Kazennikova, T. V. Talalaeva, D. N. Shigorin, and K. A. Kocheshkov, *Doklady Akad. Nauk. SSSR*, **129**, 951(1959).
2. P. A. Kollman, J. F. Liebman, and L. C. Allen, *J. Am. Chem. Soc.*, **92**, 1142 (1970).
3. B. S. Ault, and G. C. Pimentel, *J. Phys. Chem.*, **79**, 621 (1975).
4. G. V. Kulkarni, and C. N. R. Rao, *J. Mol. Struct.*, **100**, 531 (1983).
5. C. C. N. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

6. C. Moller, and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).
7. J. S. Binkley, M. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, G. Flueter, and J. A. Pople, Carnegie-Mellon Chem Pub Unit, Pittsburgh, PA, 1983.
8. (a) P. C. Hariharan, and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973); (b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, *J. Chem. Phys.*, **77**, 3654 (1982).
9. P. Pulay, *Mol. Phys.*, **17**, 197 (1969).
10. R. Fletcher, and M. J. D. Powell, *Comput. J.*, **6**, 163 (1963).
11. R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1963).
12. M. M. Szczesniak, and H. Ratajczak, *Chem. Phys. Lett.*, **44**, 465 (1976).

## Synthesis of Perhydroisoquinoline Ring Systems by *N*-Acylium Cyclization\*

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The stereochemistry of *N*-acylium 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 sequence.

### 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*-Acylium 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.<sup>1</sup> 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.<sup>2</sup> Few earlier examples are shown in Figure 1. Speckamp has shown that the stereochemistry of cyclizations of *N*-acylium ion derived from tartramide could be controlled.<sup>3</sup> Hart<sup>4</sup> and Chamberlain<sup>5</sup> have shown that the stereochemistry of cyclizations of *N*-acylium ions derived from malimides were well controlled in their syntheses of pyrrolizidine alkaloids. Also it is known by Hart and Chamberlain that the regiochemistry of NaBH<sub>4</sub> reduction of malimides is highly controllable. Herein are reported some results obtained during the course of studies.

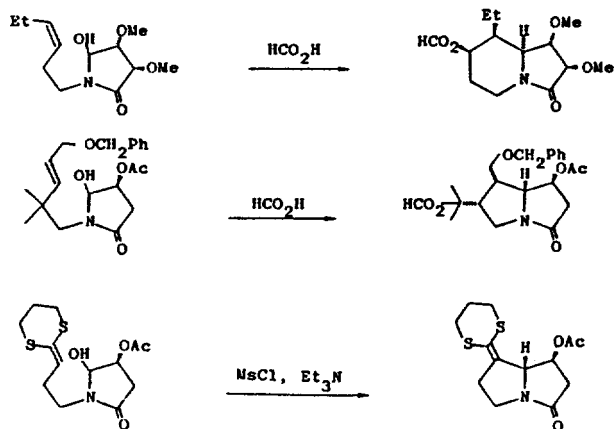
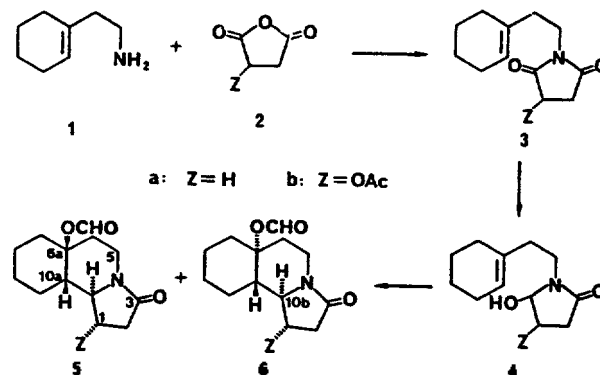


Figure 1. Examples of *N*-Acylium Cyclizations

### 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<sup>4</sup> 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<sub>4</sub> 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  $\delta$  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