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CNDO/2 Study on Lithium Bonding in Lithium Methoxide—Amine Systems

Z. Latajka[a], **H. Ratajczak**[a, *], **K. Romanowska**[a], and **Z. Tomczak**[b]

[a] Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland
[b] Institute of Physics, Technical University of Warsaw, 00-671 Warsaw, Poland

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A systematic CNDO/2 study has been carried out on the lithium-bonded model systems, CH_3OLi—NR_3, formed between lithium methoxide and aliphatic amines. Significant correlations between calculated molecular properties of the complexes and the ionization potentials of the amines have been found, and these are discussed on the basis of *Mulliken*'s charge transfer theory. Similarities and differencies between the lithium bond and the hydrogen bond are discussed.

CNDO/2 Untersuchungen der Lithium-Bindung in Lithiummethoxid—Amin-Systemen

Es wurde für das Modellsystem CH_3OLi—NR_3 eine systematische CNDO/2 Studie durchgeführt um die Lithium-Bindung zwischen Lithiummethoxid und einer Reihe von aliphatischen Aminen zu untersuchen. Es wurde eine signifikante Korrelation zwischen den berechneten Eigenschaften der Komplexe und den Ionisierungspotentialen der Amine gefunden; das wird auf Basis der Elektronen-Donor-Acceptor Theorie nach *Mulliken* diskutiert. Lithium- und Wasserstoff-Brücken-Bindung werden gegenübergestellt und Analogien bzw. Unterschiede herausgearbeitet.

Introduction

It is often assumed that the hydrogen atom is unique in its ability to form a specific type of bond called the hydrogen bond. From all chemical elements the lithium atom has an electronic structure relatively similar to the hydrogen atom. The first suggestion concerning the lithium bond formation, X-Li ... Y, in analogy to the hydrogen bond, was proposed by *Shigorin*[1] several years ago. However this hypothesis has not been fully verified so far[2, 3]. On the basis of IR matrix isolation studies of some lithium-bonded systems, *Ault* and *Pimentel*[4] have came to the conclusion that the molecular structure of lithium-bonded complexes is similar to that of hydrogen-bonded ones.

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Recently, *ab initio* calculations[5–7] performed in our laboratory show that the lithium bond is considerably stronger than the corresponding hydrogen bond.

In our previous paper[8] systematic CNDO/2 studies on lithium-bonded systems formed by methyllithium with aliphatic amines are discussed. Some correlations between calculated molecular properties of complexes *vs.* ionization potentials of amines have been found.

Now we have investigated the electronic structure of the lithium bond in complexes formed by lithium methoxide with aliphatic amines using the CNDO/2 molecular orbital method. Amines as electron-donor molecules were chosen because of the wide range of ionization potentials covered in this series. This should allow to prove how far the calculated properties of closely related lithium-bonded systems depend upon the properties of the components of the complex. For comparison, the molecular properties for the hydrogen-bonded system $CH_3OH—NH_3$ have been also calculated.

Molecular Orbital Calculations and Results

We have applied the CNDO/2 method[9–11] using the CNINDO program (QCPE 141). Experimental geometries for CH_3OH and amines were used[12]. For the CH_3OLi molecule the O-Li bond length was 1.8 Å and remaining structural parameters were taken from CH_3OH[12].

The calculated dipole moments of CH_3OH and CH_3OLi are 2.38 D and 5.72 D, respectively. The former value is in reasonable agreement with that obtained from the *ab initio* calculation ($\mu = 1.51$ D)[13] as well as with experimental data ($\mu = 1.69$ D)[14]; the dipole moment of CH_3OLi is unknown.

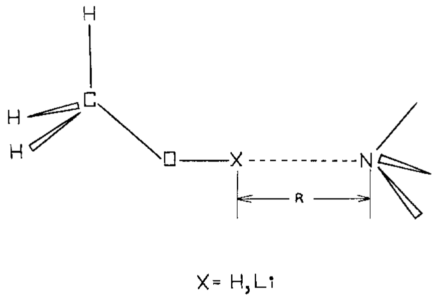

Fig. 1. The geometrical structure of $CH_3OH—NH_3$ and CH_3OLi-amine systems

The structure assumed for the lithium methoxide—amine complexes is shown in Fig. 1. The intermolecular distance, *R*, is measured from the nitrogen atom of the amine to the lithium atom. The interaction energy of the complexes studied (ΔE) represents the difference between the energy of the complex and the sum of the computed energies of the separated molecules.

Table 1. *Molecular orbital studies of hydrogen bonding in* $CH_3OH—NH_3$ *complex and lithium bonding in* CH_3OLi*—amine complexes using the CNDO/2 method*

Complex	$-\Delta E$ [kcal/mol]	R_{eq} [Å]	Δq [e]	μ [D]	$\Delta\mu$ [D]	I_D^v [eV]
$CH_3OH—NH_3$	7.36 6.48[a]	1.63 1.88[a]	0.0353 0.046[a]	4.28	0.58	10.15[b]
$CH_3OLi—NH_3$	63.60	2.20	0.2341	9.06	1.25	10.15[b]
$CH_3OLi—CH_3NH_2$	87.87	2.15	0.2611	9.28	1.53	8.97[b]
$CH_3OLi—C_2H_5NH_2$	89.69	2.15	0.2640	9.41	1.66	8.86[b]
$CH_3OLi—(CH_3)_2NH$	107.05	2.10	0.2854	9.25	1.74	8.24[b]
$CH_3OLi—(CH_3)_3N$	120.51	2.10	0.3025	9.42	1.99	7.82[b]

[a] From ref. 18, *ab initio* calculations.
[b] From ref. 19, experimental values.

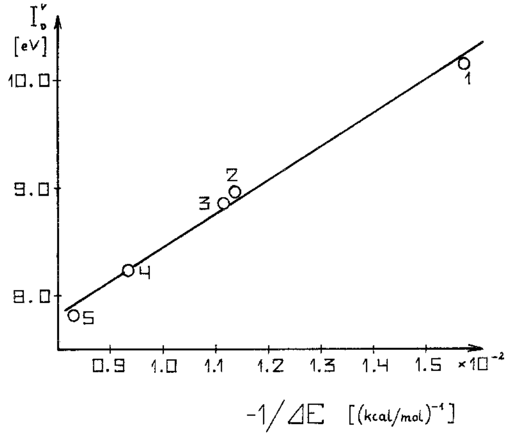

Fig. 2. Correlations between the ionization potentials of the amine and the interaction energy in lithium methoxide-amine complexes. The numbers correspond as follows: (1) NH_3, (2) CH_3NH_2, (3) $C_2H_5NH_2$, (4) $(CH_3)_2NH$, (5) $(CH_3)_3N$

Table 1 lists the calculated properties of the systems studied, *viz.* interaction energy (ΔE), the equilibrium intermolecular distance [R(N ... Y)], the amount of charge transferred from the amine to the electron-acceptor molecule (Δq), the dipole moment of the complex (μ), and the enhancement of the dipole moment due to complex formation ($\Delta\mu$). The experimental values for the ionization potentials of the amines are also given.

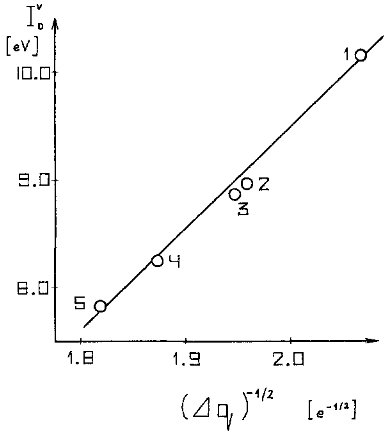

Fig. 3. Correlations between the ionization potentials of the amine and the amount of charge transferred in lithium methoxide-amine complexes. Numbers like Fig. 2

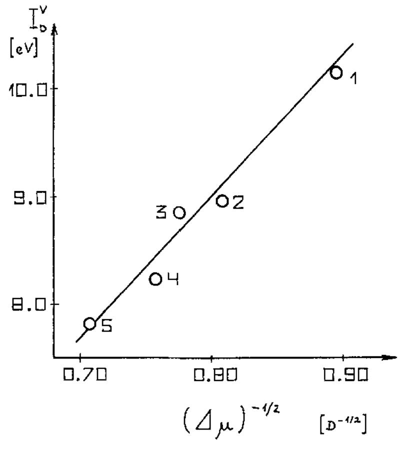

Fig. 4. Correlations between the ionization potentials of the amine and the enhancement of dipole moment in lithium methoxide-amine complexes. Numbers like Fig. 2

Discussion

Since the calculated results are obtained by means of the CNDO/2 method, one should expect that the intermolecular distances are too small and the binding energies too great in comparison with experimental values as well as with those obtained by employing more advanced quantum chemical methods[15–17]. Comparison of our results for the methanol-ammonia system with those obtained by the *ab initio* STO-3 G calculations carried out by *Del Bene*[18] indicates that the interaction energy is slightly overestimated and the calculated equilibrium distance is underestimated by 0.2 Å. Thus it is more reasonable to consider changes in the calculated properties of the series of closely related complexes *e.g.* as a function of electron-donor properties of amines rather than absolute values.

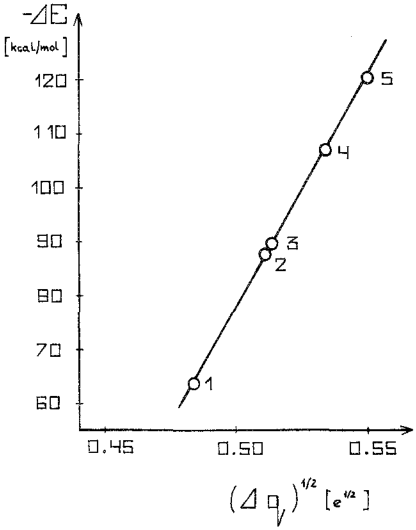

Fig. 5. Correlations between the interaction energy and the amount of charge transferred in lithium methoxide-amine complexes. Numbers like Fig. 2

Table 2. *Average molecular orbital energy shifts upon complex formation (in a. u.)*

Complex	$(\Delta E)_{av}$ Electron donor	$(\Delta E)_{av}$ Electron acceptor
$CH_3OH—NH_3$	—0.0240	0.0244
$CH_3OLi—NH_3$	—0.1204	0.0236
$CH_3OLi—CH_3NH_2$	—0.0974	0.0326
$CH_3OLi—C_2H_5NH_2$	—0.0763	0.0315
$CH_3OLi—(CH_3)_2NH$	—0.0825	0.0326
$CH_3OLi—(CH_3)_3N$	—0.0726	0.0356

From Table 1 one can see that the calculated molecular properties for CH_3OLi—amine systems, *viz.* the interaction energy (ΔE), equilibrium distance (R), amount of charge transferred (Δq), enhancement of dipole moment ($\Delta \mu$), depend upon the ionization potential of the electron lone pair of amines. These values are inversely proportional to the ionization potential of amines, as predicted by *Mulliken*'s theory[20]. The correlations found between the ionization potential of the amine and the interaction energies, the amount of charge transferred, the enhancement of dipole moment as well as the correlation between the interaction energies and the amount of charge transferred are presented in Figs. 2-5. Similar relations have been found by *Ratajczak* and *Orville-Thomas*[21-24] for iodine-amine charge-transfer complexes[21] and hydrogen-bonded ones[22-24] as well as for methyllithium—and trimethylaluminium—amine systems[8]. Thus the CH_3OLi—amine complexes behave as electron-donor-acceptor systems.

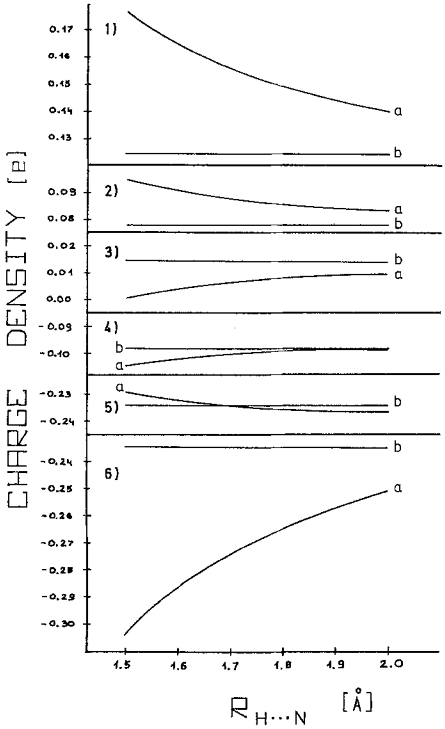

Fig. 6. Dependence of charge densities in the CH_3OH—NH_3 system on H - - - N distances (calculated equilibrium distance of H - - - N 1,63 Å): (1) H of the OH; (2) H of NH_3; (3) H of CH_3; (4) C; (5) N; (6) O.—(a) Densities in the complex; (b) densities in the isolated components

We have also performed an analysis of the molecular energy shifts upon complex formation for the systems studied, and the results are given in Table 2. One observes an increase of all molecular orbital energies of the electron-acceptor and the decrease of all molecular energies of the electron-donor. A similar behaviour was observed for CH_3Li- and $Al(CH_3)_3$-amine systems[8] as well as for other electron-acceptor systems[8, 25, 26]. According to *Kollman* and *Allen*[15] molecular energy shifts of this type are a characteristic feature of electron-donor-acceptor interactions.

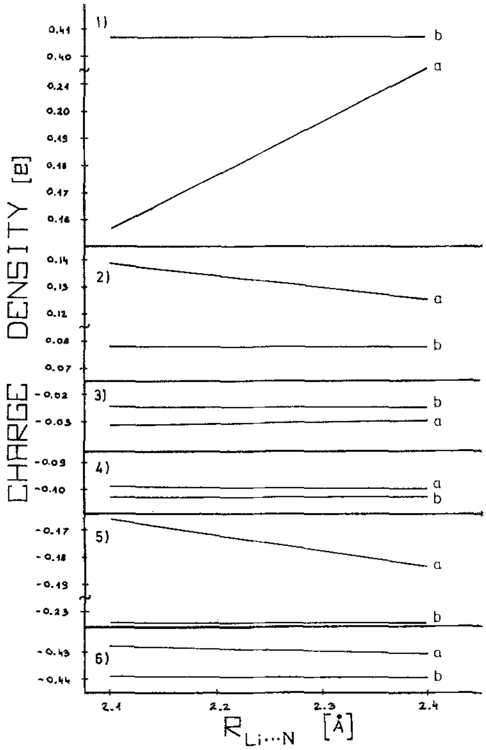

Fig. 7. Dependence of charge densities in the CH_3OLi—NH_3 system on Li - - - N distances (calculated equilibrium distance of Li - - - N 2,20 Å): (1) Li; (2) H of NH_3; (3) H of CH_3; (4) C; (5) N; (6) O.—(a) Densities in the complex; (b) densities in the isolated components

It is interesting to compare the lithium-bonded system CH_3OLi—NH_3 with the corresponding hydrogen-bonded system CH_3OH—NH_3. Our results indicate that the lithium bond will be considerable stronger than the hydrogen bond. This is in agreement with recent CNDO/2[5,8] and *ab initio*[5–7] predictions for hydrogen- and lithium-bonded systems.

Further, it is interesting to examine the changes in the charge distribution upon the lithium- as well as hydrogen-bond formation. Relations between the charge density as a function of intermolecular distance for the $CH_3OH—NH_3$ and $CH_3OLi—NH_3$ complexes are presented in Figs 6, and 7. The relations obtained for the $CH_3OH—NH_3$ system are typical to those found for other hydrogen-bonded complexes. It is of interest to note that a considerable loss of electron density of the bridge hydrogen is observed which is a general feature[15]. However, in the case of lithium bond formation, presented in Fig. 7, one observes a decreased density for the nitrogen and hydrogen atoms of ammonia as well as a slight decrease of electronic density for the oxygen and carbon atoms of lithium methoxide and a remarkable increase of the charge density of lithium (comparable to the $CH_3Li—NH_3$ complex[8]). This behaviour is very sensitive to intermolecular distances. In this respect the lithium bond shows a behaviour different from that of the hydrogen bond.

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