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CNDO/2 MOLECULAR ORBITAL CALCULATIONS ON THE COMPLEXES FORMED BETWEEN METHYLLITHIUM AND TRIMETHYLALUMINIUM WITH ALIPHATIC AMINES

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Summary

A systematic CNDO/2 study has been carried out on the lithium-bonded model systems, $CH_3Li—NR_3$, formed between methyllithium and aliphatic amines. The molecular complexes of trimethylaluminium with aliphatic amines have also been studied. 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 differences between the lithium bond and the hydrogen bond are discussed.

Introduction

It is well established that organolithium [1—4] as well as organoaluminium [5—11] compounds exist as strongly associated species and form molecular complexes with Lewis bases.

Shigorin [12] has suggested that the organolithium association phenomena can be explained by assuming that the lithium atom forms a lithium bond, X—Li···Y, analogous to a hydrogen bond, but this hypothesis has not been fully verified [13,14]. Recently Ault and Pimentel [15], on the basis of IR matrix isolation studies of some lithium-bonded systems, concluded that the structure of lithium-bonded complexes is very similar to that of hydrogen-bonded species, but with the lithium bond stronger than the hydrogen bond. It thus seemed of interest to study the electronic structure and properties of the lithium bond in model systems by using the quantum chemical method.

One approach in the study of interactions in molecular complexes is to examine the relationship between the properties of the complexes and the electron donor—acceptor (EDA) properties of their isolated components. Such correlations can be further discussed in terms of Mulliken's charge transfer theory [16].

It seemed to us that the complexes formed between methyllithium and aliphatic amines might provide good model systems for studying the dependence of the properties of the lithium bond on the ionization potential of the amine, while a similar study of the complexes formed between trimethylaluminium with amines might throw more light on the electronic structure of EDA complexes. For comparison the molecular parameters for the hydrogen-bonded system, $H_3CH\cdots NH_3$, have also been calculated.

Molecular orbital calculations and results

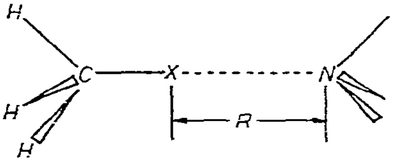
The CNDO/2 method, with the usual parameters, was used [17—19]. Experimental geometries for the amines and CH_4 were taken from the literature [20]. For the CH_3Li molecule the C—Li bond length is 2.188 Å [21]. Experimental structural parameters for the $Al(CH_3)_3$ molecule are taken from the paper by Anderson et al. [22].

The structure assumed for the methyllithium—amine complex is shown in Fig. 1. The intermolecular distance, R, is measured from the nitrogen atom of amine to the lithium atom.

The following model for the trimethylaluminium—amine molecular system was chosen, on the basis of the gas phase electron diffraction study carried out for the trimethylaluminium—trimethylamine complexes [22]: the bond of the electron-acceptor ($Al(CH_3)_3$) was taken to be colinear with the symmetry axis of the N lone pair charge cloud of amine. All the methyl groups have C_{3v} symmetry and the C—Al—N angle is 102.3° (see Fig. 2). The intermolecular distance, R, is measured from the nitrogen atom of the amine to the aluminium atom. The interaction energy of the complexes studied, ΔE, represents the difference between the energy of the complex and sums the computed energies of the separated molecules.

The calculated dipole moment of CH_3Li is 5.34 D. This value agrees well with that obtained by ab initio calculation (μ 5.85 D) [23] as well with the value of 6 D estimated by Andrews [24] from electronegativity and IR spectral data.

Table 1 lists the calculated properties of the systems studied, viz. the inter-



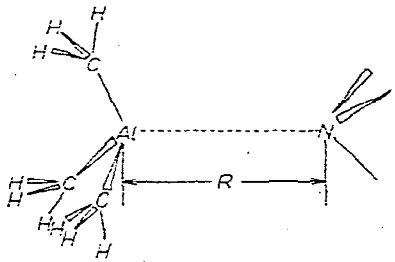


Fig. 1. The geometrical structure of CH_3Li—amine systems.

Fig. 2. The geometrical structure of $Al(CH_3)_3$—amine systems.

TABLE 1

MOLECULAR ORBITAL STUDIES OF CH_3Li—AMINE AND $Al(CH_3)_3$—AMINE COMPLEXES USING THE CNDO/2 METHOD

Complex	ΔE (kcal/mol)	R_{eq} (Å)	Δq (e)	μ (D)	$\Delta\mu$ (D)	I_D^V [c] (eV)
H_3CH—NH_3	1.49	1.90	0.0090	2.28	0.16	10.15
	1.77 [a]	1.893 [a]	0.0092 [a]	2.35 [a]		
	0.76 [b]	2.42 [b]				
CH_3Li—NH_3	73.99	2.20	0.2403	8.82	1.38	10.15
CH_3Li—CH_3NH_2	93.09	2.15	0.2715	9.05	1.66	8.97
CH_3Li—$C_2H_5NH_2$	94.91	2.15	0.2745	9.21	1.84	8.86
CH_3Li—$(CH_3)_2NH$	109.35	2.10	0.2942	9.03	1.89	8.24
CH_3Li—$(CH_3)_3N$	127.56	2.05	0.3266	9.17	2.13	7.82
$Al(CH_3)_3$—NH_3	93.52	2.20	0.3043	6.43	4.29	10.15
$Al(CH_3)_3$—CH_3NH_2	105.60	2.15	0.3366	6.61	4.53	8.97
$Al(CH_3)_3$—$C_2H_5NH_2$	106.57	2.15	0.3400	6.70	4.63	8.86
$Al(CH_3)_3$—$(CH_3)_2NH$	114.69	2.15	0.3438	6.59	4.75	8.24
$Al(CH_3)_3$—$(CH_3)_3N$	125.50	2.10	0.3712	6.64	4.90	7.82
	125.0 [d]	2.12 [d]	0.38 [d]	6.52 [d]		
	31.0 [e]					

[a] From ref. 29, CNDO/2 calculations. [b] From ref. 30, ab initio calculations. [c] From ref. 31, experimental values. [d] From ref. 25, CNDO/2 calculations. [e] From ref. 26, experimental value.

action energy, (ΔE), the equilibrium intermolecular distance ($R(N\cdots Y)$), the amount of charge transferred from 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 potential of amines are also given.

Discussion

Our results for the trimethylaluminium—trimethylamine complex agree well with those obtained by Gropen and Haaland [25] using the CNDO/2 method (see Table 1). However, comparison with the experimental data of Henrickson et al. [26] (31 kcal/mol) shows that the calculated interaction energy is too high by a factor of 4, but the equilibrium intermolecular distance (R 2.10 Å) is in very good agreement with the experimental value (R 2.099 Å) [22]. It is of interest to note that the difference between the calculated intermolecular distances for complexes of $Al(CH_3)_3$ with ammonia and those with trimethylamine (ΔR 0.10 Å; the intermolecular bond distances for $Al(CH_3)_3$—NH_3 and $Al(CH_3)_3$—$N(CH_3)_3$ are 2.20 Å and 2.10 Å, respectively) agrees well with that revealed by experiments on similar complexes with $AlCl_3$ (ΔR 0.051 Å; for $AlCl_3$—NH_3 and $AlCl_3$—$N(CH_3)_3$ the value of R is 1.996 Å [27] and 1.945 Å [28], respectively).

Unfortunately, there are no experimental or ab initio data available for the complexes of alkylamine with methyllithium. However, some indication of the expected reliability of these calculated results may be obtained from the comparison of data obtained for the methane—ammonia system by using the ab initio and CNDO/2 methods. Our results for this system agree well with those obtained by Bonchev and Cremashi [29] using the CNDO/2 method. However comparison with the ab initio data of Pople et al. [30] indicates that the interaction energy is overestimated by a factor of 2 and the calculated equilibrium distance is underestimated by 0.5 Å. (A similar observation was made for molecular complexes studied by ab initio and CNDO/2 methods [32]). Thus it is better 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 the absolute values.

Table 1 shows that the calculated molecular properties for the CH_3Li—amine and $(CH_3)_3Al$—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 amines. The calculated quantities are inversely proportional to the ionization potential of the amines, as predicted by Mullikens's resonance structure theory [16].

To illustrate the correlations, plots of the ionization potential of the amine against the interaction energies in methyllithium— and trimethylaluminium—amine complexes are shown in Fig. 3. They are similar to those found recently by Ratajczak and Orville-Thomas for iodine—amine charge-transfer complexes

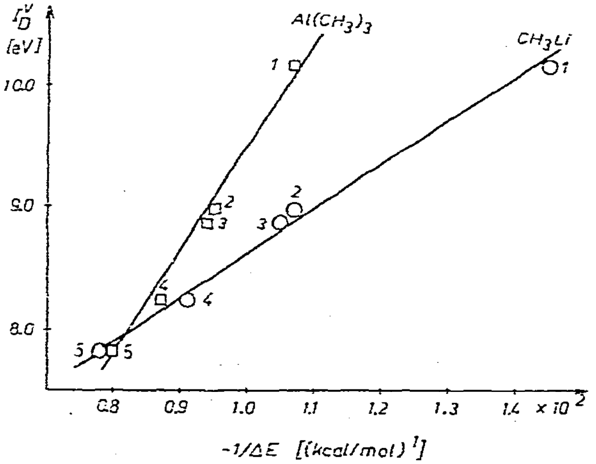


Fig. 3. Correlations between the ionization potential of the amine and the interaction energy in trimethylaluminium— and methyllithium—amine complexes. The numbering is as follows: 1, NH_3; 2, CH_3NH_2; 3, $C_2H_5NH_2$; 4, $(CH_3)_2NH$; 5, $(CH_3)_3N$.

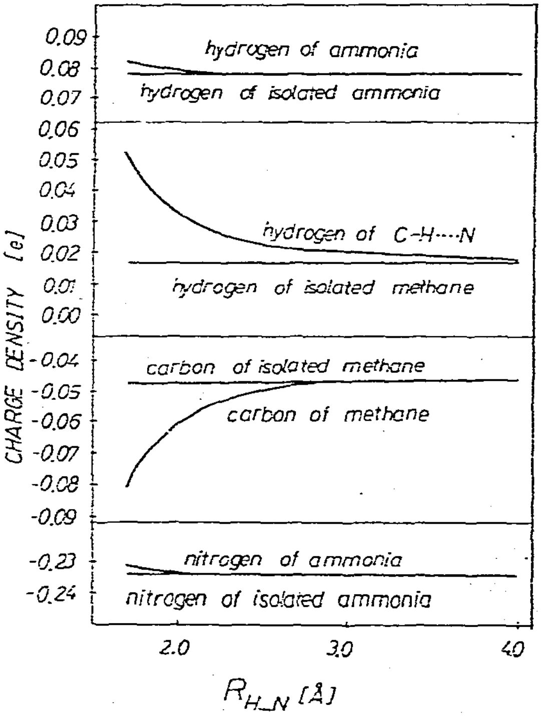


Fig. 4. Dependence of charge densities in H_3CH—ammonia system on H···N distance. Calculated equilibrium distance H···N is equal to 1.90 Å.

TABLE 2

AVERAGE MOLECULAR ORBITAL ENERGY SHIFTS UPON COMPLEX FORMATION (in a.u.)

Complex	$(\Delta E)_{av}$ Electron donor	$(\Delta E)_{av}$ Electron acceptor
H_3CH-NH_3	−0.0192	0.0164
CH_3Li-NH_3	−0.1191	0.0356
$CH_3Li-CH_3NH_2$	−0.0914	0.0256
$CH_3Li-C_2H_5NH_2$	−0.0733	0.0266
$CH_3Li-(CH_3)_2NH$	−0.0788	0.0265
$CH_3Li-(CH_3)_3N$	−0.0713	0.0310
$Al(CH_3)_3-NH_3$	−0.1359	0.0305
$Al(CH_3)_3-CH_3NH_2$	−0.0972	0.0320
$Al(CH_3)_3-C_2H_5NH_2$	−0.0742	0.0314
$Al(CH_3)_3-(CH_3)_2NH$	−0.0800	0.0339
$Al(CH_3)_3-(CH_3)_3N$	−0.0677	0.0384

[33] and hydrogen-bonded complexes [34,35]. Thus the CH_3Li- and $(CH_3)_3Al-$ amine complexes behave as electron donor—acceptor systems.

An analysis of the molecular orbital energy shifts upon complex formation for the systems studied has been carried out, and the results are given in Table

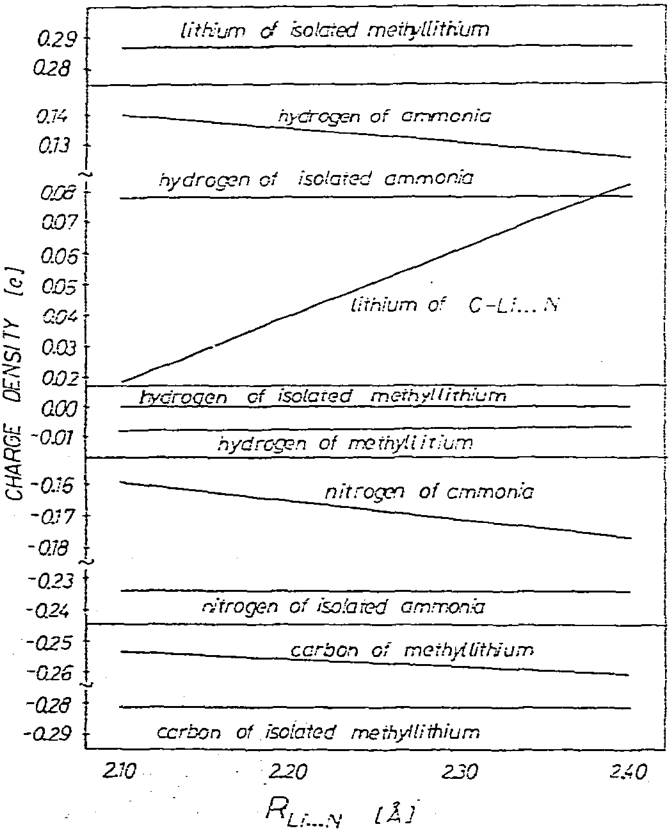


Fig. 5. Dependence of charge densities in CH_3Li—ammonia system on Li···N distance. Calculated equilibrium distance Li···N is equal to 2.20 Å.

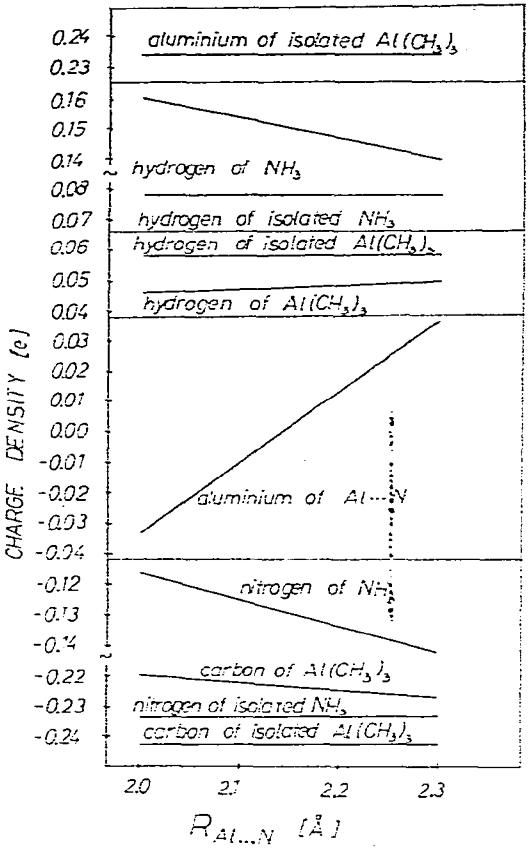


Fig. 6. Dependence of charge densities in trimethylaluminium—ammonia system on Al···N distance. Calculated equilibrium distance Al···N is equal to 2.20 Å.

2. The increase in all the molecular orbital energies of the electron acceptor and the decrease in all the molecular energies of the electron donor are apparent. Similar behaviour was noted for other electron donor—acceptor systems [36]. According to Kollman and Allen [32] such molecular energy shifts are characteristic of electron donor—aceptor interactions.

It is interesting to compare the lithium-bonded system in the CH_3Li—NH_3 complex with the analogous hydrogen-bonded system in the H_3CH—NH_3 complex. Our results indicate that the lithium bond is considerably stronger than the hydrogen bond. This is in agreement with other recent CNDO/2 [38] and ab initio [38,39] calculations.

The change in charge distribution upon complex formation is of interest. Plots of the charge density as a function of intermolecular distance (R) for the molecular systems of methane-, methyllithium- and trimethylaluminium with ammonia are presented in Figs. 4—6, respectively. The plots for the $H_3CH\cdots NH_3$ system are typical of those found for other hydrogen-bonded complexes, which means that the hydrogen bridge provides a path for the flow of charge from the ammonia to the CH_3 group of methane. The considerable loss of electron density at the bridged hydrogen is a general feature of the hydrogen bond.

However, Fig. 5 shows that upon lithium bond formation there is a decrease of charge density at the nitrogen and hydrogen atoms, a slight decrease at the carbon and hydrogen atoms of methyllithium, and a marked increase at the lithium atom; the increase at the lithium atom is very sensitive to the intermolecular distance. In this respect the lithium bond behaves differently from the hydrogen bond, but similar behaviour is shown by the $(CH_3)_3Al{-}NH_3$ complex (see Fig. 6).

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