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CNDO/2 MOLECULAR ORBITAL CALCULATIONS ON THE COMPLEXES FORMED BETWEEN DIMETHYLBERYLLIUM AND ALIPHATIC AMINES

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Summary

A systematic CNDO/2 study has been carried out on the molecular complexes formed between dimethylberyllium and aliphatic amines. It has shown that the calculated molecular properties of these complexes, viz. the interaction energy, amount of charge transferred and the enhancement of the dipole moment are related to the ionization potential of the amine. The results are discussed in terms of the Mulliken's charge transfer theory.

Introduction

The organoberyllium compounds are electron deficient in the sense that they form polymeric species in the crystalline state. However, in the vapour they exist largely as the monomers, along with small amounts of dimers and trimers the proportions of which depend on the conditions of temperature and pressure [1]. Abundant experimental data indicate that they form complexes with Lewis bases [1—3]. The bases trimethylamine [4—6,8], trimethylphosphine [3], dimethyl sulfide [7], dimethyl and diethyl ether [8,9] form 1 : 1 and 2 : 1 complexes with dimethylberyllium. The metal in these complexes is three- and four-coordinate, respectively.

There have been no systematic theoretical studies of the interaction of $Be(CH_3)_2$ with base, and we thought it would be of interest to study the electronic structure and properties of 1 : 1 model systems formed between dimethylberyllium and aliphatic amines by the quantum chemical method. These complexes are especially appropriate for studies of the relationships between the properties of the complexes and the electron-donor—acceptor (EDA) properties of their isolated components since the ionization potential of amine varies over a relatively large range. Such studies might throw more light on the electronic structure of EDA complexes.

Molecular orbital calculations and results

The CNDO/2 method, with the usual parameters, was used [10—12]. The experimental structural parameters were used (i) for $Be(CH_3)_2$ from paper by Alemnningen et al. [13], and for (ii) aliphatic amines from Sutton's tables [14].

The structure assumed for dimethylberyllium—amine complexes is shown in Fig. 1. On the basis of our previous calculations [15] the C—Be—C angle in complexes was taken as 180°. The intermolecular distance, R, is measured from nitrogen atom of the amine to the beryllium atom.

The energy of formation of the complex (ΔE) was obtained as the difference between the computed energy of the complex and the sums of the computed energies of the isolated components. Other calculated properties for the complexes studied in this paper are (a) the equilibrium intermolecular distance (R_{eq}), (b) the amount of charge transferred from amine to the dimethylberyllium molecule (Δq), (c) the dipole moment of the complex (μ_{compl}), and (d) the enhancement of the dipole moment due to the complex formation ($\Delta\mu$), calculated as:

$$\Delta\vec{\mu} = \vec{\mu}_{compl} - \Sigma\vec{\mu}_{components}$$

The results obtained are given in Table 1, as well as the experimental values for the ionization potential of the amines.

Discussion

Our results for the dimethylberyllium—amine complexes in all the cases studied showed that strong complexes are formed. Unfortunately, there are no accurate experimental data available. A comparison with the estimation of heat of coordination of trimethylamine to the $Be(CH_3)_2$ (equal to about 26 kcal mol^{-1}) [4] indicates that the computed complex energy is an overestimate. However, one can expect this fault to be systematic throughout the series of similar systems, and so the general conclusions from the calculated results should be valid.

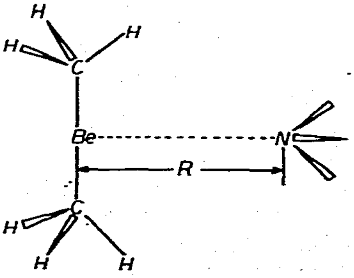

Fig. 1. The geometrical structure of $Be(CH_3)_2$—amine systems.

TABLE 1

MOLECULAR ORBITAL STUDIES OF $Be(CH_3)_2$—AMINE COMPLEXES CALCULATED BY THE CNDO/2 METHOD

Amine	$-\Delta E$ (kcal mol^{-1})	R_{eq} (Å)	Δq (e)	μ_{compl} (D)	$\Delta\mu$ (D)	I_D^v [a] (eV)
NH_3	71.93	1.95	0.2512	4.34	2.24	10.15
CH_3NH_2	82.64	1.90	0.2795	4.52	2.48	8.97
$C_2H_5NH_2$	82.54	1.90	0.2835	4.67	2.64	8.86
$(CH_3)_2NH$	93.46	1.90	0.3012	4.45	2.65	8.24
$(CH_3)_3N$	99.01	1.85	0.3107	4.46	2.76	7.82

[a] From ref. 16, experimental values.

The results given in Table 1 show that all the calculated molecular properties, ΔE, R_{eq}, Δq, and $\Delta\mu$, depend upon the ionization potential of the amines lone pair. The calculated quantities are inversely proportional to the ionization potential of the amines, as predicted by Mullikem's resonance structure theory [17].

To illustrate the correlations, plots of the ionization potentials of the amines against the enhancement of the dipole moment in dimethylberyllium—amine complexes are shown in Fig. 2. They are similar to those found recently for iodine—amine charge transfer complexes [18], and for hydrogen-bonded complexes [19,20], and also for trimethylaluminium—, methyllithium— [21] and lithium methoxide—amine [22] systems. Thus the $Be(CH_3)_2$—amine complexes act as electron-donor—acceptor systems.

An analysis of the molecular orbital energy shifts due to complex formation in the systems studies has been made, and the results are given in Table 2. The increase in all the molecular energies of the electron acceptor and the decrease

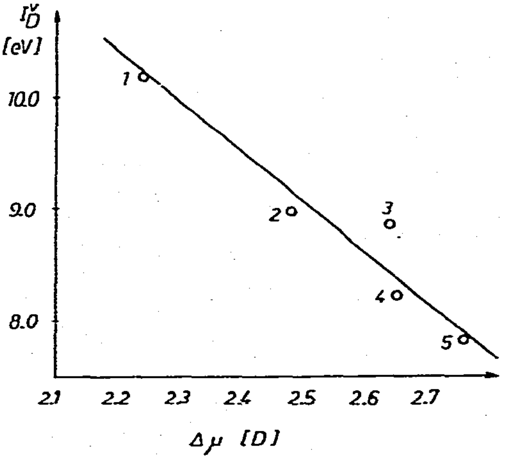

Fig. 2. Correlations between the ionization potential of the amine and the enhancement of dipole moment in dimethylberyllium—amine complexes. The numbering is: 1, NH_3; 2, CH_3NH_2; 3, $C_2H_5NH_2$; 4, $(CH_3)_2NH$; 5, $(CH_3)_3N$.

TABLE 2

AVERAGE MOLECULAR ORBITAL ENERGY SHIFTS (in a.u.) DUE TO THE COMPLEX FORMATION

Amine	$(\Delta E)_{av}$ Electron donor	$(\Delta E)_{av}$ Electron acceptor
NH_3	−0.1700	0.0615
CH_3NH_2	−0.0847	0.0416
$C_2H_5NH_2$	−0.0835	0.0636
$(CH_3)_2NH$	−0.0812	0.0655
$(CH_3)_3N$	−0.0740	0.0683

in all the molecular energies of the electron donor are apparent. Similar behaviour was noted for other organometallic—amine complexes [21, 22].

The change in charge distribution due to complex formation is of particular interest. Plots of the charge density as a function of the intermolecular distance (R) for dimethylberyllium—ammonia system are presented in Fig. 3. On formation of this complex there is a decrease of charge density at the nitrogen and hydrogen atoms, a slight decrease in that at the carbon and hydrogen atoms of

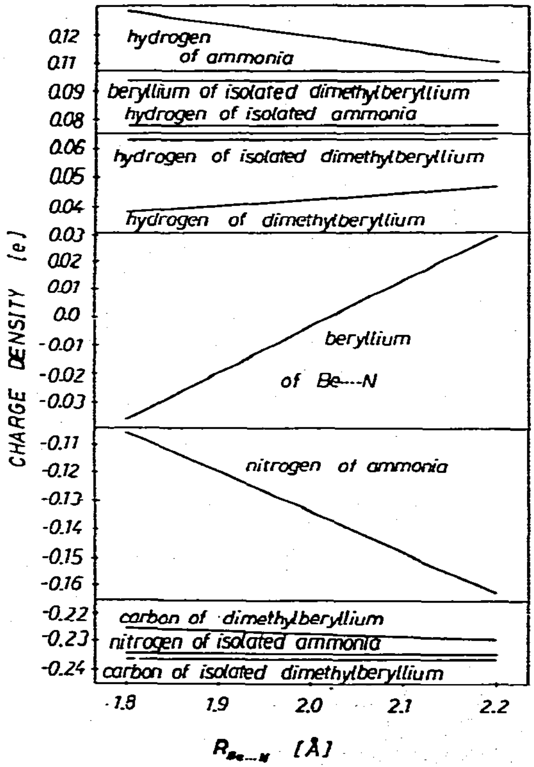

Fig. 3. Dependence of charge densities in $Be(CH_3)_2$—ammonia on the Be---N distance. The calculated equilibrium distance Be---N is 1.95 Å.

dimethylberyllium, and a marked increase in that at the beryllium atom. The change of the charge density on the metal is similar to that in other organometallic—amine complexes [21,22].

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