Theoret. Chim. Acta (Berl.) 35, 369—378 (1974)

Relationes

The Interaction of Cations with Amides

Nonempirical Calculations on Energy Surface and Reaction Pathway for the Formation of the Li$(HCONH_2)^+$ Complex

Bernd M. Rode* and Heinzwerner Preuss

Institut für Theoretische Chemie der Universität Stuttgart, Germany

Received May 17, 1974

The interaction of Li^+ with a formamide molecule has been studied systematically. The energy surface for the formation of the $Li(HCONH_2)$ complex is discussed, in connection with a SCF-MO-LCGO treatment of the corresponding adiabatic reaction pathway. The energetic situation for a bonding of the cation to nitrogen and the nonplanar conformation formed thereby has been calculated and compared to the more stable planar arrangement. The description of the ion-amide-interaction is completed by density maps and localized molecular orbitals.

Key words: Ion-solvent interaction – Reaction pathway of $Li(HCONH_2)^+$ formation – Energy surface of $Li(HCONH_2)^+$

1. Introduction

The investigation of ion-neutral molecule interaction has been subject of numerous theoretical and experimental studies during the last years [1–18]. This interest can be explained by several motivations ranging from questions concerning the solvation of inorganic compounds in various solvents [2–8, 17] to biological and pharmalogical problems [1, 15, 16].

In the case of formamide, almost all of these motivations play a role, as it represents an important, water-like solvent in inorganic and organic reactions, and, on the other hand, the simplest model compound containing the $-HN-C=O$-group, which is of great interest in connection with ion binding and transport in biological systems. The intention of the study presented here was to investigate systematically the energy surface for a cation in the field of a formamide molecule, to describe the reaction pathway of complex formation and to obtain thus a satisfactory theoretical background for experimental work, which is being carried out presently.

2. Method

The *ab initio* LCGO-SCF calculations have been performed using an uncontracted Gaussian lobe basis set, which has proven to give good results for formamide and its dimer [19, 20]. Four ion optimized [21] *s* functions have been assigned to lithium, completed by a group of *p* polarization

---

* Permanent address: Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Austria.

Table 1. Total energies obtained in the 4*s*/2*p* basis set used

System	Total energy (hartrees)
Li^+	− 7.221377
$HCONH_2$	−164.740443
$Li(HCONH_2)^+$	−171.050886[a]

[a] Minimum position.

functions with standard choice exponent of 0.1. The energy values obtained in this basis for Li^+, $HCONH_2$, and the complex in its equilibrium position are listed in Table 1.

For the construction of the energy surface for a planar complex conformation, 95 different ion positions in the molecular plane have been calculated. In these calculations, the geometry of formamide was kept constant using the experimentally determined values [22].

In addition, we have investigated the energetic situation for a tetrahedral arrangement at nitrogen, which could result from exclusive bonding of the ion to this atom.

All calculations have been performed at the CDC 6600 computer of the "Rechenzentrum der Universität Stuttgart", using the program MOLPRO III of W. Meyer and P. Pulay.

3. Results and Discussion

3.1. The Planar Arrangement

The energy surface for the planar conformation of the system $Li(HCONH_2)^+$ (Fig. 1) shows the stablest position for Li^+ to be in the direction of the CO axis, at a distance of 1.715 Å from the oxygen atom. The stabilization energy for this case amounts to 55.9 kcal/mole. On the other hand, the energy surface indicates, that stabilization decreases only slightly within a wide range

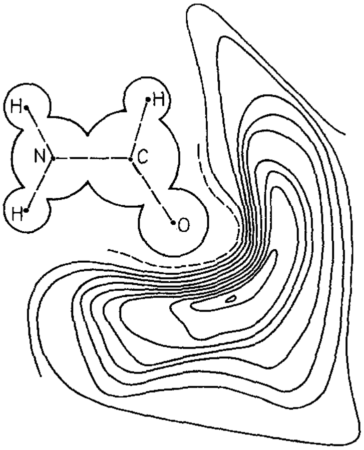

Fig. 1. Energy surface for the formation of the $Li(HCONH_2)^+$ complex in planar arrangement Isoenergetic lines are separated by 0.01 hartrees each

of geometrical arrangements. This result agrees well with investigations of the angular dependence of the stabilization energy for K^+ and Na^+ interacting with N-methylacetamide [16]. For the chemistry of the system studied in our work, one therefore has to take into consideration, that several of these positions may be realized in chemical reactions, due to molecular vibrations and the rapid exchange of ions. This will be of considerable importance for the interpretation of any experimental, especially spectroscopic results, as the various geometrical conformations will lead to different influences on charge distributions, bond character and other molecular properties reflected by methods like NMR, IR or Raman spectroscopy. The electron density maps discussed below give a first impression of these influences.

3.2. The Tetrahedral Arrangement

Although an exclusive bonding of the cation to nitrogen does not seem very probable in the case of formamide, it was of some interest to see how large the energy differences would be in comparison to the most stable complex conformation and in addition, to find out, whether any stabilization occurs at all in this case. It is to be expected, that owing to ion bonding to nitrogen, an approximately tetrahedral arrangement will be formed at this atom. We therefore chose the tetrahedral angles and varied only the Li...N distance, with the lithium ion positioned throughout in the NCO plane. The resulting energy curve (Fig. 2) shows a minimum at a Li...N distance of 2.037 Å, connected with a stabilization energy for the complex of 13.9 kcal/mole.

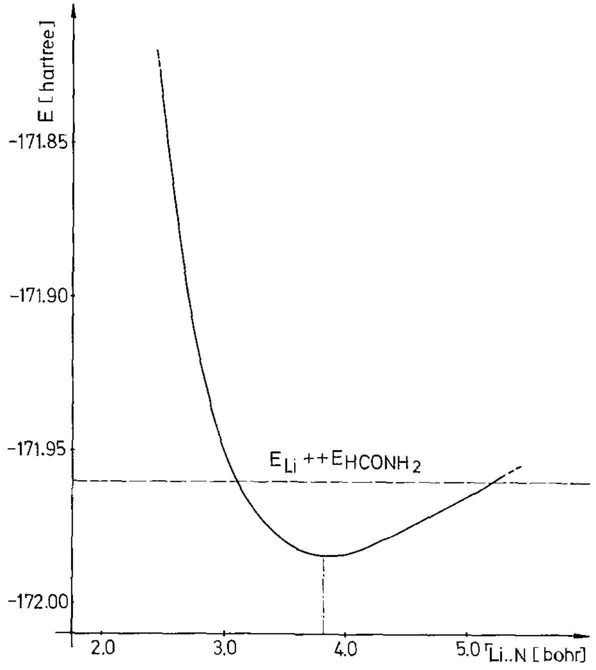

Fig. 2. Energy curve for the formation of a tetrahedral arrangement of the $Li(HCONH_2)^+$ complex, in dependance of the Li...N distance

This is, as expected, much less than for the planar arrangement, and such a conformation should thus not have a remarkable influence in any ion bonding process.

3.3. *The Formation of the* $Li(HCONH_2)^+$ *Complex*

Density maps are frequently used for the discussion of the electronic structure of molecular systems. As can be seen from the density maps presented in this study (Figs. 3–7), they can give also an illustrative representation of a whole chemical reaction.

For the description of the reaction pathway of Li^+ formamide, the energetic minimum pathway has been chosen, corresponding to an approach of the ion in the direction of the CO axis. The density maps for the formamide molecule and some characteristic steps of the reaction, allow to point out some features of the successive interaction occuring between the two chemical systems. The impressions obtained thereby are supplemented by the corresponding energy curve (Fig. 8).

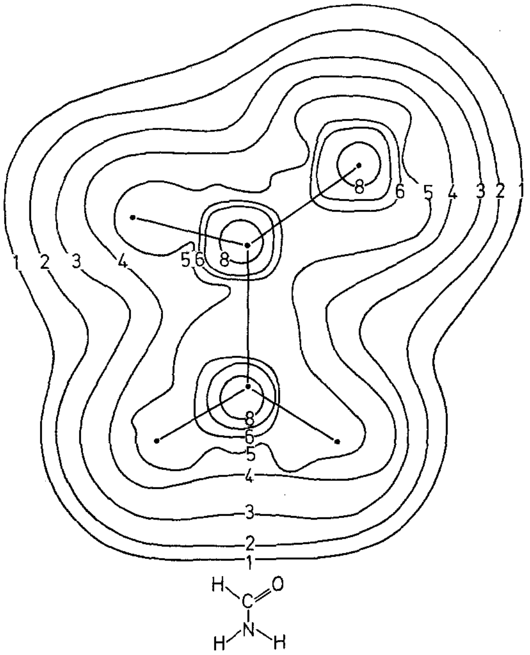

Fig. 3

Figs. 3–7. Density maps of formamide and of the system $Li(HCONH_2)^+$ at Li...O distances of 8, 6, and 4 bohrs and in equilibrium position

The numbers in the maps represent the following values:

1 — 0.001
2 — 0.003
3 — 0.010
4 — 0.032
5 — 0.100
6 — 0.316
7 — 1.000
8 — 3.160
9 — 10.000

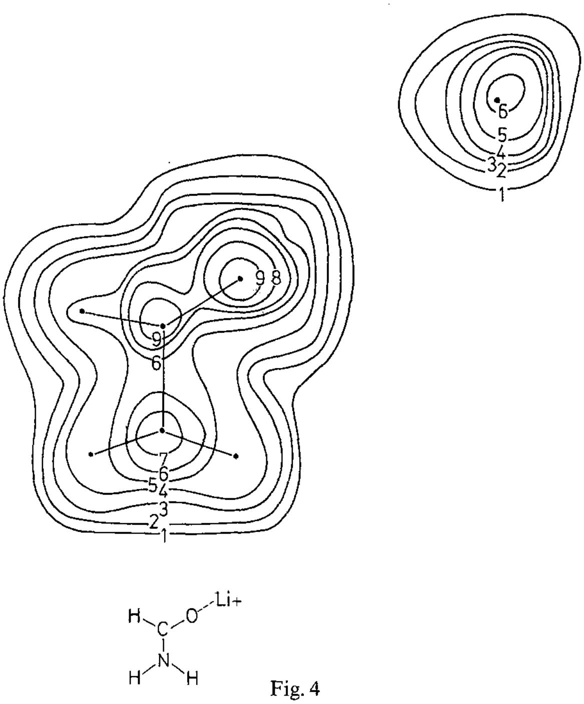

Fig. 4

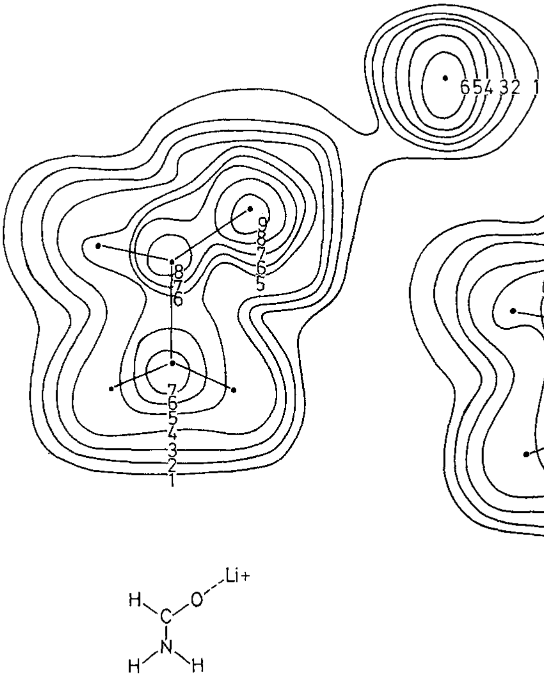

Fig. 5

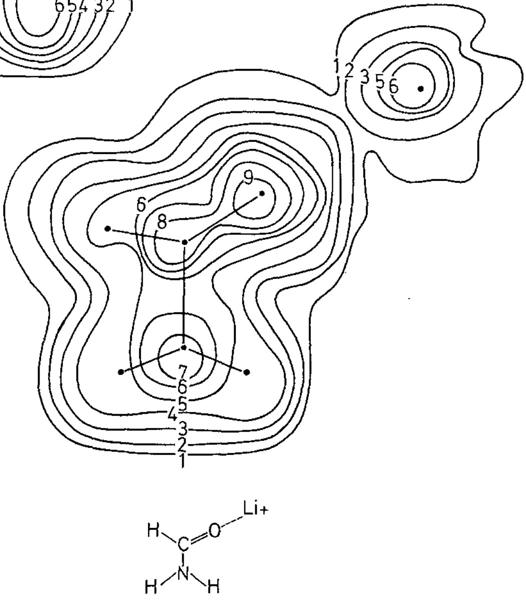

Fig. 6

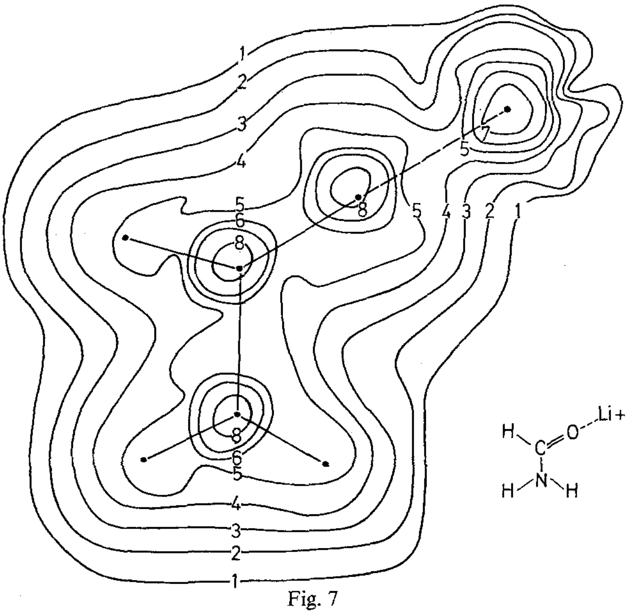

Fig. 7

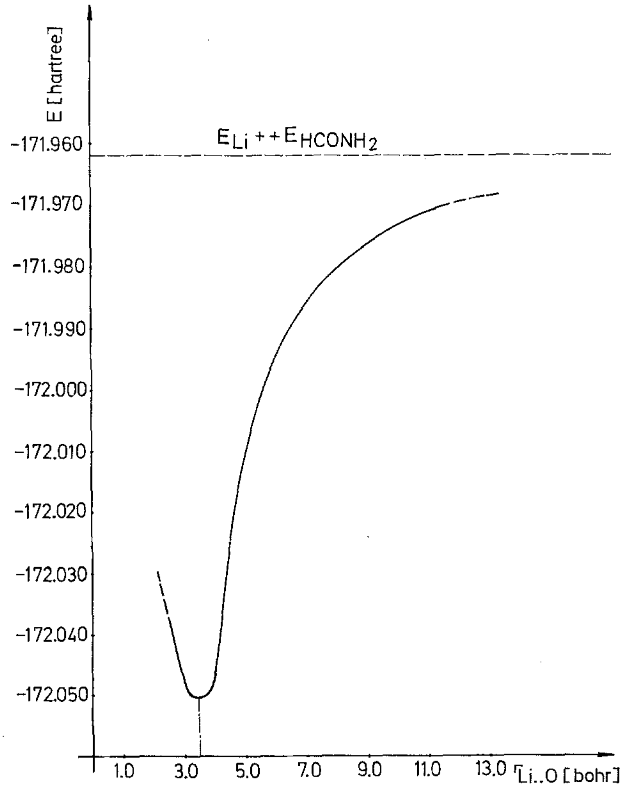

Fig. 8. Energy curve for the energetic minimum reaction pathway

a) Li...O distance 8 bohr:

In the very beginning of the reaction, a remarkable polarization of the neutral molecule and light polarization effects on the inner shell electrons of the cation occur. The electron density in the region of the CO bond is increased. Typical bonding is not yet observed ("Polarization phase").

b) Li...O distance 6 bohr:

Non-zero electron density is observed for the first time between the cation and formamide, representing the beginning of a "bonding phase". Polarization effects in the formamide molecule are increased. The energy gain is still very small.

c) Li...O distance 4 bohr:

The electron density in the CO bond reaches its maximum, Li^+ and formamide are still separated by a zone of rather low electron density. Stabilization energy has increased strongly.

d) Equilibrium distance (3.24 bohr): During the final approach to the equilibrium position, striking changes occur: Electron density is rapidly

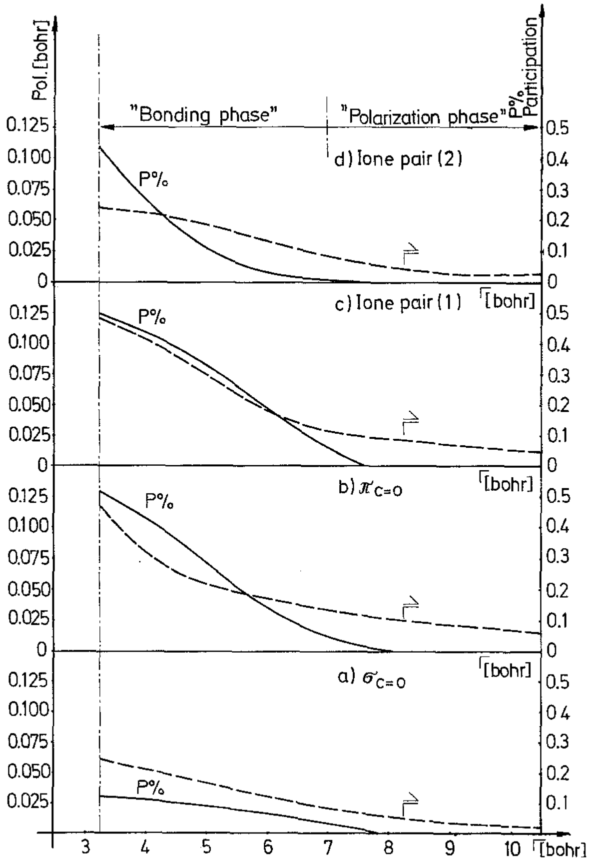

Fig. 9. Polarization of localized molecular orbitals and percentual participation of lithium functions in these orbitals in the course of complex formation. $a: \sigma_{C-O}$; $b: \pi_{C-O}$; c and d: oxygen – lone pairs

increased in the Li...O region, whereas the electronic situation of the CO bond is again more similar to that of the isolated formamide molecule. Polarization effects at the ion become more significant.

Although the separation of the reaction into a "polarization" and a "bonding" phase is rather arbitrary, since polarization effects contribute as well to bonding, this separation seems to be illustrative and helpful, especially for a quantum chemical discussion of "hard" and "soft" acids or bases. A similar separation of these two reaction phases can be performed also for other reactions [23, 24] and the distance up to which mere polarization effects are observed, depends strongly on the character of the interacting systems.

In order to enable a more detailed discussion of the reaction pathway, we have localized the eigenfunctions of the reacting systems at several stages of their interaction, according to the criterium of Boys [25]. In this form, molecular orbitals can be assigned to "classical" chemical bonds and allow a discussion of the participation of the ion's functions in these bonds. A measure

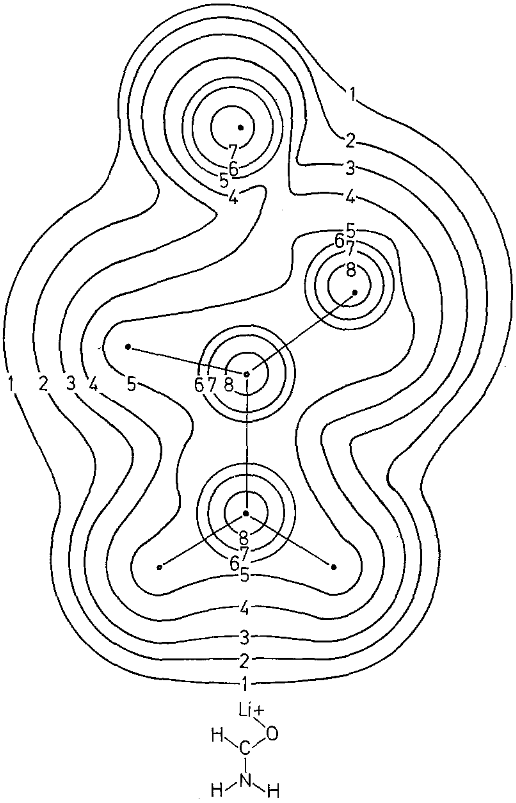

Fig. 10

Figs. 10 and 11. Density maps of the $Li(HCONH_2)^+$ complex in selected geometrical conformations in the HCO and NCO region, respectively

The numbers in the maps represent the following values:

1 — 0.001
2 — 0.003
3 — 0.010
4 — 0.032
5 — 0.100
6 — 0.316
7 — 1.000
8 — 3.160
9 — 10.000

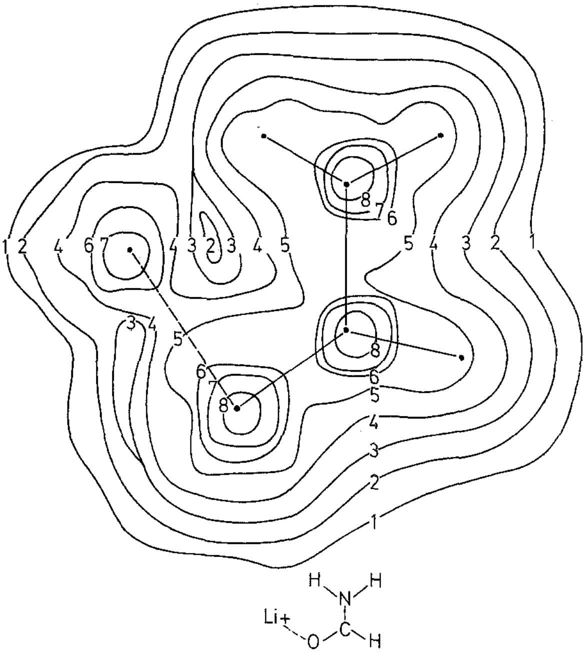

Fig. 11

for the polarization effects can be derived from the respective positions of the charge-centres of these bonds in the course of the reaction. Figure 9 shows the absolute shift of the charge-centres of the most interesting localized molecular orbitals and the percentual participation of the atomic functions of lithium in these orbitals, calculated for increasing Li...O distance.

The results obtained thereby agree fully with the picture given by the density maps: Polarization effects are observed already at large distances, whereas a participation of lithium functions in molecular orbitals, representative for a "bonding phase", cannot be found until the cation has reached a distance of 7–8 bohrs from the oxygen atom. A comparison with the corresponding energy curve (Fig. 8) indicates, that the long range polarization effects are accompanied by minor changes in total energy. This is to be seen also by the increasing separation of isoenergetic lines of the energy surface (Fig. 1) in the CO direction.

3.4. Electronic Structure of other Conformations

As pointed out before, many positions in the molecular plane will be occupied by the cation in the course of molecular vibrations. We were interested therefore in the changes of electronic structure of the complex, which might occur within reasonable changes of geometry. Density maps proved again to be the most illustrative way of describing such effects. Two positions of the cation, in the NCO and HCO region, have been arbitrarily chosen, connected with stabilization energies of 13.0 and 34.7 kcal/mole respectively. The density maps corresponding to these geometrical arrangements are given in Figs. 10 and 11.

In both conformations, it can be seen clearly, that almost all bonding of the cation to formamide is still directed towards the oxygen atom. This situation can strikingly change upon bonding of a second ligand to the metal ion, as could be shown in the case of $[Li(HCONH_2)_2]^+$ [26].

4. Conclusion

The results obtained in this work are believed to give a good theoretical basis for the interpretation of experiments concerning the interactions between cations and formamide. They may allow also, to a certain extent, a more general discussion of the interaction of small cations with other amides. The investigation of reaction pathways by the use of density maps and localized molecular orbitals seems to be a powerful tool for the theoretical treatment of chemical reactions and at the same time, provides a consistent quantum chemical treatment and a graphic description in terms of "classical" chemistry.

Acknowledgement. B. M. R. wants to thank Prof. Dr. H. Preuss and his staff for the kind and generous hospitality during the performance of this work. The authors are indebted to the "Rechenzentrum der Universität Stuttgart", namely to Mrs. E. Fischer, for providing kindly the necessary computing time.

References

1. Roach, E.T., Handy, P.R., Popov, A.I.: Inorg. Nucl. Chem. Letters **9** (1973)
2. Herlem, M., Popov, A.I.: J. Am. Chem. Soc. **94**, 1431 (1972)
3. Erlich, R.H., Popov, A.I.: J. Am. Chem. Soc. **93**, 5620 (1974)
4. Shimokawa, S., Fukui, H., Sohma, J., Hotta, K.: J. Am. Chem. Soc. **95**, 1777 (1973)
5. Yamdagni, R., Kebarle, D.: J. Am. Chem. Soc. **94**, 294 (1972)
6. Benoit, R.L., Buisson, C.: Inorg. Chim. Acta **7**, 256 (1973)
7. Gamble, D.S.: Can. J. Chem. **51**, 3217 (1973)
8. Rode, B.M.: Z. Anorg. Allg. Chem. **399**, 239 (1973)
9. Clementi, E., Popkie, H.: J. Chem. Phys. **57**, 1077 (1972)
10. Schuster, P., Preuss, H.: Chem. Phys. Letters **11**, 35 (1971)
11. Russegger, P., Schuster, P.: Chem. Phys. Letters **19**, 254 (1973)
12. Lischka, H., Plesser, Th., Schuster, P.: Chem. Phys. Letters **6**, 263 (1970)
13. Breitschwerdt, K., Kistenmacher, H.: Chem. Phys. Letters **14**, 288 (1972)
14. Russegger, P., Lischka, H., Schuster, P.: Theoret. Chim. Acta (Berl.) **24**, 191 (1972)
15. Kostetsky, P.V., Ivanov, V.T., Ovchinnikov, Yu.A., Shchembelov, G.: FEBS Letters **30**, 205 (1973
16. Perricaudet, M., Pullman, A.: In press
17. Rode, B.M.: Chem. Phys. Letters **20**, 366 (1973)
18. Rode, B.M.: J. Chem. Soc. Faraday II, 1439 (1973)
19. Mely, B., Pullman, A.: Theoret. Chim. Acta (Berl.) **13**, 278 (1969)
20. Dreyfus, M., Maigret, B., Pullman, A.: Theoret. Chim. Acta (Berl.) **17**, 109 (1970)
21. Janoschek, R.: J. Mol. Struct. **6**, 283 (1970)
22. Ladell, J., Pust, B.: Acta Cryst. **7**, 559 (1954)
23. Rode, B.M.: Chem. Phys. Letters **25**, 369 (1974)
24. Rode, B.M.: To be published
25. Boys, S.F.: Revs. Mod. Phys. **32**, 296 (1960)
26. Rode, B.M.: Chem. Phys. Letters **26**, 350 (1974)

Dr. B. M. Rode
Institut für Anorganische
und Analytische Chemie
Universität Innsbruck
A-6020 Innsbruck
Innrain 52a, Austria