Inorganica Chimica Acta, 138 (1987) 131–133

Cation Binding Effect on Hydrogen Bonded Dimer of Imidazole and Water

JUMRAS P. LIMTRAKUL
Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
SUPOT V. HANNONGBUA, SIRIRAT U. KOKPOL and BERND M. RODE†
Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10500, Thailand

(Received March 31, 1987)

Abstract

The influence of small monovalent cations on neighbouring hydrogen bonds is studied for imidazole–water adducts by means of *ab initio* calculations using minimal Gaussian basis sets. Metal binding is found to have a significant effect on both hydrogen bond energy and the equilibrium intermolecular distance. A redistribution of electron density in the complex is also indicated by Mulliken population analysis. The net stabilization of the H-bond due to Li(I) ion is −8.9 kcal mol^{-1}, the N–H······O distance is contracted by 0.12 Å.

Introduction

The influence of cation binding to biological macromolecules is of importance for understanding chemical and particularly biological processes which take place in solution, and has been the subject, therefore, of a number of theoretical and experimental model investigations [1–11].

Hydrogen bonding involving biomolecules has been widely studied [12–14], since this type of bond is especially important for the fundamental linking of DNA and RNA. Hydrogen bonds also stabilize the structure of other biological macromolecules, e.g. proteins [15].

Imidazole (ImH) can be considered as an interesting model system because certain imidazole compounds are essential in biochemistry, e.g. the amino acid histidine and related compounds, vitamin B12, biotin, and other imidazole-containing biomolecules. Thus, studies concerning the influence of metal ions on hydrogen bonds of imidazole with water should also give an insight into principal interactions through hydrogen bonding for more complex biological systems.

In previous studies, we have investigated the influence of Li(I) on water/amide adducts [18]. In this study, we continue to examine the Li(I) binding effect to hydrogen-bonded dimers of imidazole and water. In order to be able to discuss the results in comparison with the previous work, the same basis sets have been used.

Details of Calculation

The geometries of water and imidazole molecules were taken from experimental data [19] and kept constant throughout the calculation, as it is known that the minimal basis set is suitable for the optimization of the intermolecular parameters but less so for that of the intramolecular geometrical parameters [10].

The intermolecular geometrical parameters reported here are the result of an optimization by means of an *ab initio* LCAO-MO-SCF method [15–18, 20–27]. All calculations were performed on the IBM 3031/08 computer of Chulalongkorn University and the IBM 4361 computer of Kasetsart University. The program used has been discussed in detail in ref. 28.

Results and Discussion

Table I summarizes the stabilization energies of all systems, and the optimized intermolecular geometrical parameters are listed in Table II. The data of the Mulliken population analysis for all species are reported in Table III. The changes in atomic charge distribution resulting from complex formation are illustrated in Fig. 1.

The Imidazole–Lithium Complex

The binding site for Li(I) is N_3. The optimized Li(I)·····N_3 distance is found to be 1.86 Å, the Li(I)–N_3–C_2 angle is 95.8°, and the corresponding energy is −55.6 kcal mol^{-1}. The equilibrium distance

---

†Permanent address: Department of Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria.

0020-1693/87/$3.50

TABLE I. Energy Data

System	Total energy (Hartree)	Ion binding energy (kcal mol^{-1})	H-Bond energy (kcal mol^{-1})
Li(I)	−6.4100		
H_2O	−64.5164		
ImH	−190.6812		
Li(I)–ImH	−197.1788	−55.6	
ImH–H_2O	−255.2279		−19.0
Li(I)–ImH–H_2O	−261.7320	−83.6	−27.9

TABLE II. Optimized Geometrical Parameters

System	$N_1\cdots\cdots O_1$ (Å)	Li(I)$\cdots\cdots N_3$ (Å)
Li(I)–ImH		1.86
ImH–H_2O	2.66	
Li(I)–ImH–H_2O	2.54	1.86

TABLE III. Atomic Populations

Atom	System				
	H_2O	ImH	ImH/Li(I)	ImH/H_2O	ImH/Li(I)/H_2O
O_1	8.383			8.404	8.431
N_1		7.879	7.864	7.936	7.928
N_3		7.356	7.683	7.371	7.707
C_2		5.745	5.626	5.747	5.636
C_4		6.260	6.298	6.271	6.288
C_5		6.151	6.083	6.150	6.088
H_1		0.516	0.468	0.484	0.447
H_2		0.722	0.690	0.734	0.709
H_4		0.674	0.631	0.682	0.642
H_5		0.698	0.653	0.711	0.668
H_6	0.801			0.756	0.727
H_7	0.809			0.753	
Li(I)			0.005		0.006

is about 0.1 Å shorter than Li(I)$\cdots\cdots$N in Li(I)–NH_3 [17], in accordance with the higher binding energy ($\Delta E_{NH_3} = -44.0$ kcal mol^{-1}, $\Delta E_{ImH} = -55.6$ kcal mol^{-1}). These data indicate that the more delocalized electron system of the ring apparently favours the ion binding. The value of 1.86 Å also agrees very well with Li(I)–N distances found in some biological systems [29].

Li(I) ion binding to the N_3 atom of imidazole leads to the redistribution of electron density indicated in Fig. 1. One point of interest is that the complex formation leads to an increased positive charge for the H_1 hydrogen by about 0.048. This

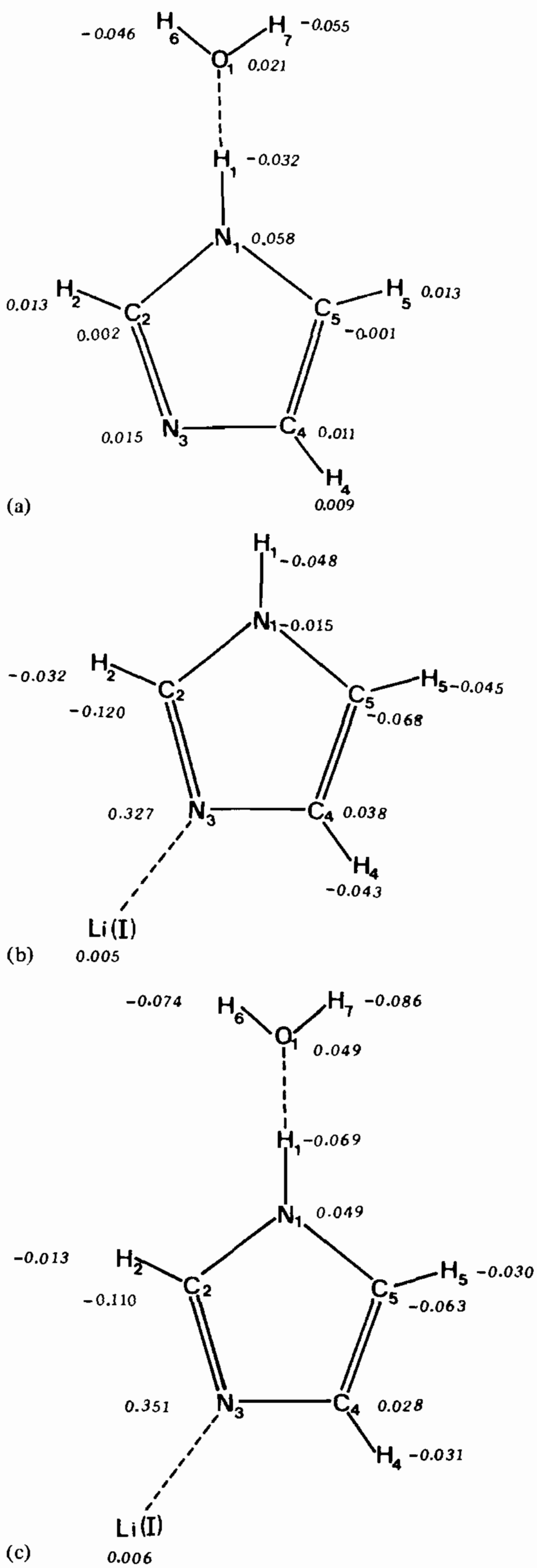

Fig. 1. Changes in charge distribution due to complex formation: a) imidazole/water; b) imidazole/Li(I); c) imidazole/Li(I)/water.

suggests that the ability of the imidazole molecule to form a hydrogen bond as a proton-donor molecule is enhanced when Li(I) is attached to the N_3 atom.

The Imidazole–Water Complex

The geometry resulting from our basis set is exactly the same as that of ref. 30 (using STO-3G basis), the optimized $N_1\cdots\cdots O_1$ distance being 2.66 Å. The rotation energy barrier (0.4 kcal mol^{-1}) is lower than kT, indicating free rotation of this complex at room temperature.

The hydrogen bond energy of the imidazole–water adduct is evaluated as 19.0 kcal mol^{-1}. This value is comparable to the calculated $N{-}H\cdots\cdots O$ hydrogen bond energy of the formamide–water complex (14.4 kcal mol^{-1}, ref. 16), and probably too high due to basis set superposition effects.

The net charge of the H_1 proton is about 0.032 higher than in imidazole. This decreased electron density on the H_1 proton leads to electrostatic stabilization of the hydrogen bond between imidazole and water.

The Imidazole–Lithium–Water Complex

The optimized Li(I)–N_3 distance remains as in the imidazole–lithium complex. The rotational energy barrier around the $N_1{-}H\cdots\cdots O$ bond of the complex is 0.8 kcal mol^{-1}. Thus the cation seems to hinder the free rotation of the water molecule, in contrast to the system water/formamide [16].

A further interesting result is the shortening of the $N_1{-}H_1\cdots\cdots O_1$ hydrogen distance by about 0.12 Å. This reduced $N_1{-}H_1\cdots\cdots O_1$ distance reflects an increase of hydrogen bond energy due to the cation. This can also be simply rationalized on the basis of the hydrogen atom population.

The Li(I) binding leads to a decrease of electron density at the H_1 hydrogen of 0.069 units, compared to 0.032 units in imidazole–water. The charge transfer to Li(I) is nearly the same for both complexes (0.006 and 0.005). The decrease of electron density at H_6 and H_7, as well as the pronounced donor ability of the nitrogen atom (N_1), indicate that the Li(I) effect is transferred through the ring according to Gutmann's bond variation rules.

The hydrogen bond energy in the ternary system is -27.9 kcal mol^{-1}. Subtracting the energy value of -19.0 kcal mol^{-1} computed for the imidazole–water dimer, we obtain the net stabilization energy (NSE) of the hydrogen bond between the dimer due to the presence of the cation as -8.9 kcal mol^{-1}. The NSE values resulting from the effect of Li(I) in this system and from previous work [16–18] using the same basis set can be ordered, therefore, as following: $NSE(NH_3/H_2O) > NSE(H_2O/H_2O) > NSE(ImH/H_2O) > NSE(Fa/H_2O)$.

Acknowledgements

The generous supply of computing time by the computer centres of Chulalongkorn University and Kasetsart University is gratefully acknowledged.

References

1 B. Pullman and N. Goldblum (eds.), 'The Jerusalem Symposia on Quantum Chemistry and Biochemistry', Parts I–II, Reidel, Dordrecht, 1975.

2 S. Forsen, *Inorg. Chim. Acta, 79,* 39 (1983).

3 M. Danne, 'Interaction of Metal Ions with Nucleic Acids, Metal Ions in Biological Systems', Vol. 3, Marcel Dekker, New York, 1974, p. 1.

4 G. L. Eichhorn (ed.), 'Inorganic Biochemistry', Elsevier, Amsterdam, 1973.

5 A. Pullman, T. Ebbesen and M. Rholam, *Theoret. Chim. Acta (Berlin), 51,* 245 (1979).

6 D. W. Urry, W. D. Cunningham and T. Onishi, *Biochim. Biophys. Acta, 292,* 853 (1973).

7 H. Einspahr and C. E. Buggs, *Calcium Binding to Proteins, Functions; Proc. 2nd Intern. Symposia,* Elsevier, New York, 1977, p. 13.

8 M. M. Probst and B. M. Rode, *Inorg. Chim. Acta, 78,* 135 (1983).

9 M. M. Probst and B. M. Rode, *Inorg. Chim. Acta, 92,* 75 (1984).

10 M. J. A. Rainer and B. M. Rode, *Monatsh. Chem., 113,* 399 (1982).

11 W. S. Kittl and B. M. Rode, *Inorg. Chim. Acta, 55,* 21 (1981).

12 G. C. Pimentel and A. L. McClean, 'The Hydrogen Bond', Reinhold, New York, 1960.

13 E. Clementi, J. W. Mehl and W. V. Niessen, *J. Chem. Phys., 54,* 508 (1971).

14 E. Clementi, G. Corongiu, J. Detrich, S. Chin and L. Domingo, *IBM Research Report Pok-39,* April 2, 1984.

15 K. P. Sagarik and B. M. Rode, *Inorg. Chim. Acta, 78,* 81 (1983).

16 B. M. Rode, *Theoret. Chim. Acta (Berlin), 56,* 245 (1980).

17 B. M. Rode and K. P. Sagarik, *Chem. Phys. Lett., 88,* 337 (1982).

18 K. P. Sagarik and B. M. Rode, *Z. Naturforsch. Teil A, 36,* 1357 (1981).

19 D. Christen, J. H. Griffiths and J. Sheridam, *Z. Naturforsch., Teil A, 37,* 1378 (1982).

20 M. M. Probst and B. M. Rode, *J. Mol. Structure (THEOCHEM), 88,* 97 (1982).

21 B. M. Rode and J. P. Limtrakul, *Z. Naturforsch., Teil A, 39,* 376 (1984).

22 B. M. Rode and G. J. Reibnegger, *J. Chem. Soc., Faraday Trans. II, 75,* 178 (1979).

23 B. M. Rode, G. J. Reibnegger and S. Fujiwara, *J. Chem. Soc., Faraday Trans. II, 76,* 1268 (1980).

24 B. M. Rode, *Monatsh. Chem., 106,* 339 (1975).

25 B. M. Rode and K. H. Gstrein, *J. Chem. Soc., Faraday Trans. II, 74,* 889 (1978).

26 S. V. Hannongbua and B. M. Rode, *Inorg. Chem., 24,* 2577 (1985).

27 J. P. Limtrakul, S. U. Kokpol and B. M. Rode, *J. Sci. Soc. Thailand, 11,* 129 (1985).

28 R. Ahlrichs, *Theoret. Chim. Acta (Berlin), 33,* 157 (1974).

29 K. P. Sagarik and B. M. Rode, *Inorg. Chim. Acta, 76,* L209 (1983).

30 J. E. Del Bene and I. Cohen, *J. Am. Chem. Soc., 100,* 5285 (1978).