Chem. Pharm. Bull.
27(12)3180—3182(1979)

UDC 547.898.02 : 546.13–128.03

Molecular Orbital Study on a Chlorine Anion Cryptate

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(Received June 5, 1979)

Closed shell LCAO-SCF-MO calculations were carried out for the chloride anion cryptate, which is of interest in connection with organic anion receptors and carriers.

In the Cl^- cryptate of $[(C_9H_{18})_3(NH)_2Cl]^+Cl^-$, Cl^- is encapsulated in the host molecule. Since the positions of the two protons bonded to the two nitrogens of the host molecule were not determined in the reported X-ray diffraction analyses, the positions of the two protons in the inclusion complex were decided by calculation using the *ab initio* molecular orbital method. A structure $N^+–H\cdots Cl^-\cdots H–N^+$ in which Cl^- is in between the two nitrogens was most stable at values of r(NN) less than 7.0 Å. The structure $N^+–H\cdots Cl^-\cdots H–N^+$ was most stable at $r(NN)=6.023$ Å. In the most stable structure, the two protons are covalently bonded to the two nitrogens. The structure obtained by geometry optimization for the two ammonium ions and Cl^- was similar to that determined by X-ray diffraction analysis.

Keywords——molecular orbital study; structure; cryptate; complex; inclusion complex; anion carrier; interaction

In studies to develop strategies for the rational design of organic anion receptors and carriers, Cl^- cryptates have been reported.[2,3] These compounds may also be of interest in biology in view of the current interest in anion binding and transport in biological membranes. Bell *et al.* determined the structure of $[(C_9H_{18})_3(NH)_2Cl]^+Cl^-$ by X-ray diffraction analysis.[2] The structure is shown in Fig. 1. The cage compound consists of a chloride ion encapsulated within a triply bridged diammonium species, with hydrogen bond distances N(H)···Cl of 3.10±0.01 angstroms. It has the crystallographic symmetry mm $2(C_{2v})$, one of the mirror planes passing through one of the clamps and the other lying perpendicular to them. In this structure, two-dimensional binding with inclusion may produce a stable and selective anion cryptate. Cl^- is held in the cavity of biprotonated macrobicyclic diamines $^+HN[(CH_2)_9]_3NH^+$ by two hydrogen bonds, $^+N–H\cdots X^-\cdots H–N^+$. In this paper, the system of the two hydrogen bonds is studied from a quantum chemical point of view.

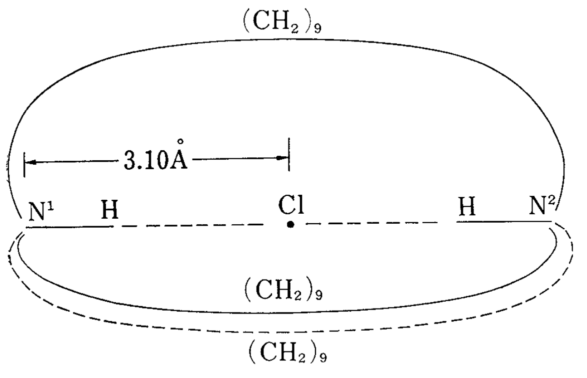

Fig. 1. Structure of $[(C_9H_{18})_3(NH)_2Cl]^+Cl^-$ reported by Bell *et al.*

Method

All the calculations were carried out within the closed shell LCAO-SCF-MO approximation. The Gaussian 70 program was used.[4] The 4-31G split-valence shell basis set with the recommended exponents, contraction coefficients, and scale factors was used.[5]

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1) Location: *9-1, Shirokane 5-chome, Minato-ku, Tokyo 108, Japan.*

2) R.A. Bell, G.G. Christoph, F.R. Fronczek, and R.E. Marsh, *Science*, **190**, 151 (1975).

3) E. Graf and J.M. Lehn, *J. Am. Chem. Soc.*, **98**, 6403 (1976).

4) W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton, and J.A. Pople, Gaussian 70, Quantum Chemistry Program Exchange, Indiana University, 1974.

5) R. Ditchfield, W.J. Hehre, and J.A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

In a molecular orbital study of tetranactin-NH_4^+, the interaction between NH_4^+ and the ether and carbonyl oxygens which are oriented towards NH_4^+ was significant.[6] In this paper, therefore, a model of two ammonium ions in place of the biprotonated macrobicyclic diamine $^+HN[(CH_2)_9]_3NH^+$ was used. NH_4^+ was assumed to be tetrahedral.

Calculations were carried out using a HITAC M-180 computer at the Institute for Molecular Science.

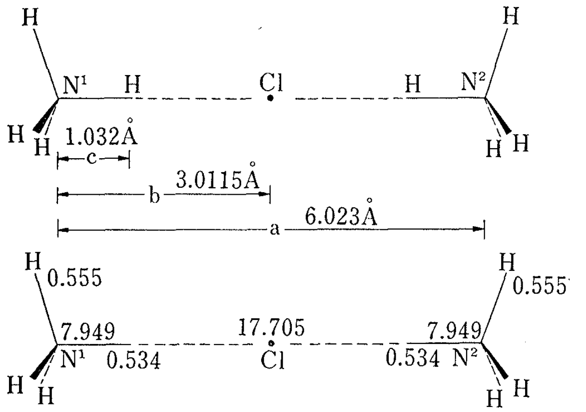

Fig. 2. The Optimized Structure obtained from MO Calculations and the Total Electron Densities

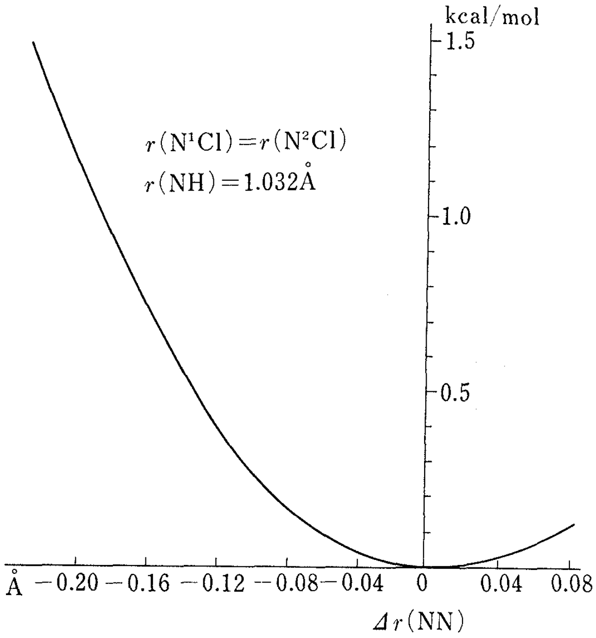

Fig. 3. Total Energy Change from the Most Stable Structure against r(NN)

Results and Discussion

Figure 2 shows the interacting structure for two ammonium ions and Cl^-. Geometry optimization calculations were carried out for three length parameters r(NN), r(NCl) and r(NH), as shown by a, b and c, respectively. The most stable structure is shown in Fig. 2. Figure 3 shows the total energy change from the most stable structure against r(NN) in the structure with $r(N^1Cl)=r(N^2Cl)$ and $r(NH)=1.032$ Å. Figure 4 shows the total energy change from the most stable structure against $r(N^1Cl)$ in the structure with $r(NN)=6.023$ Å and $r(NH)=1.032$ Å. Figure 5 shows the total energy change from the most stable structure against r(NH) in the structure with $r(NN)=6.023$ Å and $r(NCl)=3.0115$ Å.

$r(NN)=6.023$ Å was shorter than the experimental value of $^+HN[CH_2)_9]_3NH^+$ including Cl^- by 0.18 Å. Cl^- was in between the two nitrogen atoms; this result is in agreement with the results of X-ray diffraction analysis. The total energy changes were calculated against r(NCl) in the structure with $r(NH)=1.032$ Å at various distances of r(NN). The results are shown in Fig. 6. At the distances of $r(NN)=6.2$, 6.4, 6.6 and 7.0 Å, Cl^- was in between the two nitrogens. At the distances of $r(NN)=8.0$ and 9.0 Å, however, double well potential curves for Cl^- transfer were obtained. Figure 7 shows the proton transfer potential from the nitrogen of NH_4^+ to Cl^- in the structure with $r(NN)=8.0$ Å and $r(N^1Cl)=3.023$ Å. The proton transfer potential increased, monotonically. The structure in which Cl^- forms an asymmetric hydrogen bond with one nitrogen was stable for proton transfer in the structure with $r(NN)=8.0$ Å. Therefore, when the distance r(NN) in the structure of $^+HN[(CH_2)_n]_3NH^+$ is more than 8.0 Å, Cl^- will be bonded to the hydrogen of an NH^+ group.

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6) H. Umeyama and T. Nomoto, *Chem. Pharm. Bull.* (Tokyo), **27**, 2504 (1979).

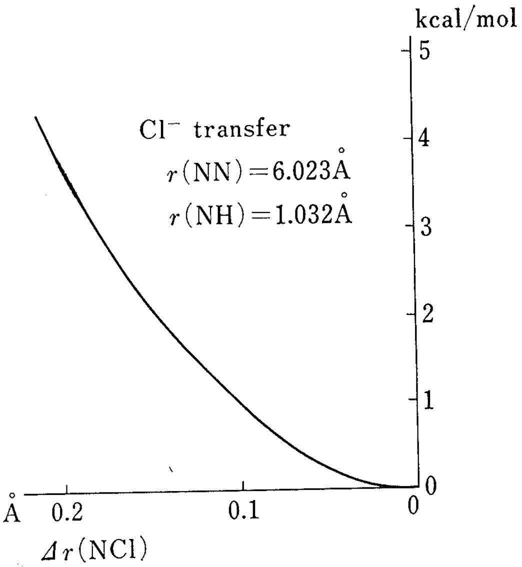

Fig. 4. Total Energy Change from the Most Stable Structure against $r(N^1Cl)$

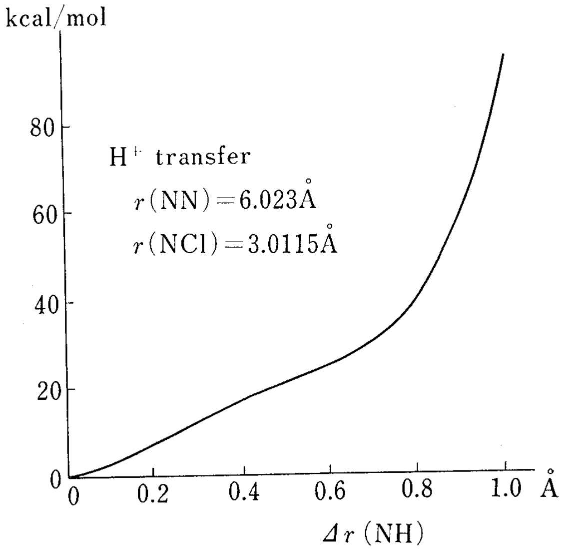

Fig. 5. Total Energy Change from the most Stable Structure against r(NH)

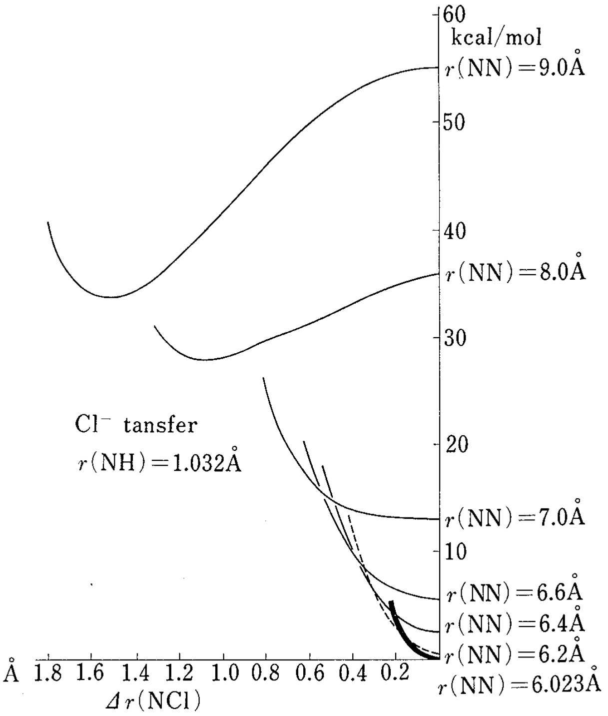

Fig. 6. Total Energy Change against r(NCl) in the Structure with r(NH)=1.032 Å at Various Values of r(NN)

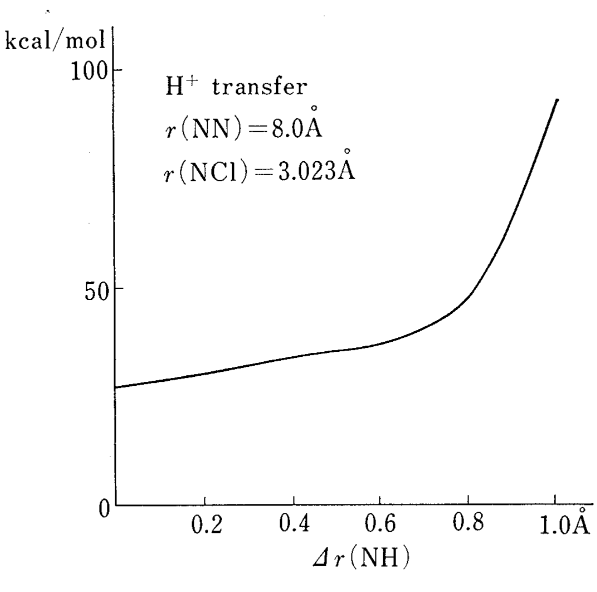

Fig. 7. Proton Transfer Potential from N of NH_4^+ to Cl^- in the Structure with r (NN)= 8.0 Å and $r(N^1Cl)$=3.023 Å

In conclusion, Cl^- was in between the two nitrogens at values of r(NN) less than 7.0 Å. The protons were covalently bonded to the nitrogens. The structure obtained by geometry optimization for the two ammonium ions and Cl^- was similar to the structure determined by X-ray analysis of the $^+HN[(CH_2)_9]_3NH^+$–Cl^- complex.