2 Computational Methods

The programs used were DGauss for the systems of the free base-ion and Gaussian92 for the systems of the d(TA)-ion having a hydration shell. In DGauss the VWM potential was used with nonlocal BP energies selfconsistently and in Gaussian92 the HF method was used at HF/STO-3G level.

3 Summary and Conclusions

The calculated equilibrium distances and dissociation energies for Mg and Ca complexes are presented in Table 1. Possible ion binding sites except those forming hydrogen bonds are $A(N_7)$ and $G(N_7)$ in the major groove of B-DNA and are $A(N_3)$, $G(N_3)$, and $T(O_2)$ in the minor groove. The total dissociation energies in the minor and major grooves of AT are -266, -162 kcal/mol (Mg system) and -203, -118 kcal/mol (Ca system), respectively and the enegies in the minor groove of both systems are lower than those in major groove, while in the case of GC pair the major groove coordinations in both systems are more stable. For d(TA)-Mg^{2+} and Ca^{2+} through the hydration shell the dissociation energies are 79 and 6 kcal/mol.

In conclusion, the O_2 atom of T and the N_7 atom of G played important roles for the recognition of AT and GC base pairs, respectively.

Table 1: Equilibrium distances r (pm) and dissociation energies Ed (kcal/mol) for Mg and Ca complexes

Mg systems	r	Ed	attribute	Ca system	r	Ed	attribute
$[Mg-A(N_1)]^{2+}$	203.8	-160	H bond	$[Ca-A(N_1)]^{2+}$	219.9	-98	H bond
$[Mg-A(N_3)]^{2+}$	203.1	**-136**	minor	$[Ca-A(N_3)]^{2+}$	218.1	**-98**	minor
$[Mg-A(N_7)]^{2+}$	202.4	-162	major	$[Ca-A(N_7)]^{2+}$	229.0	-118	major
$[Mg-T(O_2)]^{2+}$	184.8	**-130**	minor	$[Ca-T(O_2)]^{2+}$	202.7	**-105**	minor
$[Mg-T(O_4)]^{2+}$	182.6	-135	H bond	$[Ca-T(O_4)]^{2+}$	201.0	-112	H bond
$[Mg-G(N_7)]^{2+}$	207.4	-199	major	$[Ca-G(N_7)]^{2+}$	238.4	-156	major
$[Mg-G(O_6)]^{2+}$	197.8	-199	H bond	$[Ca-G(O_6)]^{2+}$	220.1	-156	H bond
$[Mg-G(N_3)]^{2+}$	204.3	**-140**	minor	$[Ca-G(N_3)]^{2+}$	223.3	**-72**	minor
$[Mg-C(N_3)]^{2+}$	213.5	-182	H bond	$[Ca-C(N_3)]^{2+}$	240.3	-145	H bond
$[Mg-C(O_2)]^{2+}$	195.5	-182	H bond	$[Ca-C(O_2)]^{2+}$	213.5	-145	H bond

Acknowledgement

This work was supported in part by a Grant-in-Aid for scientific research on the priority areas 'Genome Informatics' from the Ministry of Education, Science, Sports and Culture of Japan. Highly network supercomputing environments were provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University and the Human Genome Center, Institute of Medical Science, University of Tokyo.

A Study of Molecular Recognition between DNA and Metal Ions

N. Fukushima [1] M. Kanehisa [2]
ayui@cray.com kanehisa@kuicr.kyoto-u.ac.jp

[1] Computational Chemistry Group,
Cray Research Japan Ltd.
5-5 Shin-Yokohama 2-chome, Kohoku-ku,
Yokohama-shi, Kanagawa 222, Japan

[2] Institute for Chemical Research, Kyoto University
Gokasho, Uji, Kyoto 611, Japan

Abstract

The dissociation energies have been calculated between A, C, G, or T of DNA and divalent metal ions (Mg^{2+} and Ca^{2+}) and between a double-stranded DNA dimer d(AT) and a hydration shell including either Mg^{2+} or Ca^{2+} in order to investigate the ability of the sequence recognition of the ions. All calculations were carried out using the Hartree-Fock and the density functional methods on CRAY supercomputers. From the results of calculations it was shown that the O_2 atom of T ($T(O_2)$) and the N_7 atom of G ($G(N_7)$) played important roles for the recognition of AT and GC base pairs, respectively and that Mg^{2+} interacted more strongly than Ca^{2+} to the AT stack-site of the minor groove in B-DNA through the hydration shell.

1 Introduction

The metal ions binding to biomolecules contribute to the molecular recognition, stabilization of structure, association process, and catalytic reaction and have various important roles for their biochemical phenomena depending on the kinds of metal ions. Recently it was reported that Mg^{2+} recognized the sequence of DNA through its hydration shell (V. A. Buckin et. al., *J. Am. Chem. Soc*, **116**, 9423 (1994)). In order to theoretically clarify the interaction we performed *ab initio* calculations for complexes of DNA-ion (having a hydration shell) and ion-A, C, G, or T as a model for the first step of the molecular recognition.

[1]福島信弘：日本クレイ株式会社総合技術センター，〒 222 横浜市港北区新横浜 2 丁目 5 番 5 号
[1]現住所：京都大学化学研究所，〒 611 京都府宇治市五ヶ庄
[2]金久 實：京都大学化学研究所，〒 611 京都府宇治市五ヶ庄