The Interaction of Magnesium Cyclen Complex with Water

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An intermolecular potential function for the magnesium complex of 1,4,7,10-tetraazacyclododecane (cyclen) and water has been derived from ab initio molecular orbital calculations. The form of this interaction function is obtained by fitting 250 points of the calculated energy surface.

Introduction

Computer simulations by Monte Carlo (MC) [1] and Molecular Dynamics (MD) [2] techniques need analytical pair potential functions for evaluating the interaction energy between all particles. The reliability of the results of such simulations therefore depends strongly on the quality of these pair potential functions.

Experimental studies [3] of macrocyclic compounds such as cyclen and its complexes can be complemented by theoretical studies on similar systems. We studied the magnesium cyclen complex/water system, in order to understand better the principle interactions in such systems.

Method

The optimized geometries for water and the 1,4,7,10-tetraazacyclododecane ligand, which has S_4 symmetry, are taken from [4–7]. The stabilisation energies between the magnesium cyclen complex and water molecule were obtained from ab initio MO SCF calculations performed with a well-tested minimal Gaussian Lobe Orbital basis set [5]. The charges of atoms were derived according to Mulliken population analysis [8] and kept constant in the optimization procedure of the pair potential function. The final form of the analytical potential function has been accomplished by fitting 250 energy surface points of complex-water interaction, situated within one-eight of the whole space around the complex (according to the S_4 symmetry of the complex).

Results and Discussion

The shape of the pair potential (in kcal/mole) is given by

$$E(C, W) = \sum_{i=1}^{3} \sum_{j=1}^{33} [B_{ij}^{ab}/r_{ij}^{12} - A_{ij}^{ab}/r_{ij}^{6} + (q_i q_j/r_{ij})(1 + C_{ij}^{ab}/r_{ij} + D_{ij}^{ab}/r_{ij}^{2})], \quad (1)$$

where A_{ij}, B_{ij}, C_{ij} and D_{ij} are the fitted parameters (Table 1), r_{ij} is the distance between an atom i of water (W) and an atom j of the complex (C) (in atomic units), q_i and q_j are the net charges of atoms i and j (in atomic units) of the isolated molecules, obtained from the Mulliken population analysis [8]. The superscripts a and b specify types of atoms of water and complex, as both molecules contain some equivalent atoms. Six different classes of atoms are contained in the complex (H_C = equatorial, $H_{C'}$ = axial, H_N, C, N and Mg^{2+}) and two classes in water (O and H). Due to the polynomial character of the potential, the parameters could be derived with non-iterative fitting techniques.

Due to all possible combinations of classes of atoms from both molecules and the number of constants for each atom-atom interaction, the total number of parameters is 48.

The term of (1) can be said to be composed of two parts, the Lennard-Jones-type term, $B_j^{ab}/r_{ij}^{12} - A_{ij}^{ab}/r_{ij}^{6}$, and a coulombic term, $(q_i q_j/r_{ij})(1 + C_{ij}^{ab}/r_{ij} + D_{ij}^{ab}/r_{ij}^{2})$ in which the factor $(1 + C_{ij}^{ab}/r_{ij} + D_{ij}^{ab}/r_{ij}^{2})$ takes into account the distance-dependencies of q_i and q_j [9].

The reliability of any pair potential function depends on the number of fitting points and the distribution of these points on the total energy surface. The 250 points on the energy surface calculated and used in our fitting procedure can be re-

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Table 1. Fitting parameters for H_C, $H_{C'}$, H_N, C, N and Mg^{2+} atoms of magnesium cyclen complex interaction with oxygen (a) and hydrogen (b) atoms of water molecule ($q_O = -0.380$, $q_H = +0.190$).

	Atom		Parameter			
	Type	Charge	*A*	*B*	*C*	*D*
(a)	H_C	+ 0.283	− 0.1374409993 E + 06	− 0.1122494785 E + 08	− 0.7501503519 E + 02	0.2469770488 E + 03
	$H_{C'}$	+ 0.236	− 0.1340070407 E + 06	− 0.1309636516 E + 08	− 0.7957268054 E + 02	0.2672676856 E + 03
	H_N	+ 0.405	− 0.2972188680 E + 05	− 0.5444340021 E + 06	− 0.2907535324 E + 02	0.8232835867 E + 02
	C	− 0.247	0.4348846292 E + 06	0.5912829109 E + 09	− 0.1353356664 E + 03	0.5171515637 E + 03
	N	− 0.925	0.6769382907 E + 05	0.1104162946 E + 09	− 0.6503992705 E + 02	0.2043579072 E + 03
	Mg	+ 1.918	− 0.7400622029 E + 06	− 0.8864033310 E + 08	− 0.5985694488 E + 02	0.1971801680 E + 03
(b)	H_C	+ 0.283	− 0.2691711474 E + 03	− 0.4582628156 E + 03	− 0.9476857958 E + 01	0.1421481515 E + 02
	$H_{C'}$	+ 0.236	0.6208808988 E + 04	0.1741769088 E + 06	− 0.2499779867 E + 02	0.6247791397 E + 02
	H_N	+ 0.405	0.1344793134 E + 05	0.1332923830 E + 06	− 0.3568789140 E + 02	0.9230536430 E + 02
	C	− 0.247	0.1617699586 E + 06	0.7509612528 E + 08	0.9003871364 E + 02	− 0.3819965548 E + 03
	N	− 0.925	− 0.4742827451 E + 06	− 0.9436015378 E + 08	− 0.1123681503 E + 03	0.4020583091 E + 03
	Mg	+ 1.918	0.2898849490 E + 06	0.5371097919 E + 08	− 0.4728532674 E + 02	0.1525858393 E + 03

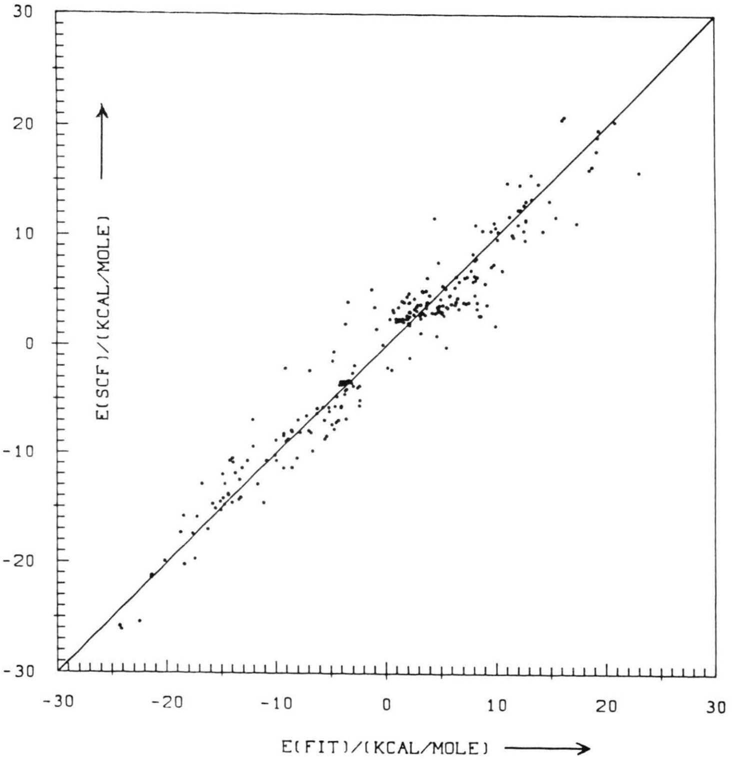

Fig. 1. Energy correlation between SCF MO calculated and fitted energies due to (1).

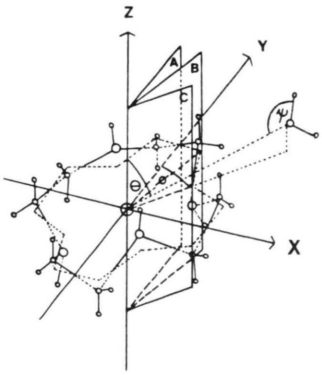

Fig. 2. The molecular planes of the magnesium cyclen complex (optimized structure) are defined as the plane A (*yz*-plane), plane B (the plane through two opposite carbon atoms), and plane C (the plane through two opposite nitrogen atoms). The angles θ, φ and ψ are also given. The planes A, B and C are the planes corresponding to angles $\varphi = 0°$, $16.1°$ and $45°$, respectively.

garded well sufficient for such a system [10], especially if one considers that this number of data points, due to the symmetry, actually represents 2000 points in the whole space around the complex.

The total standard deviation of the fitting, $\sigma_{\text{tot}} = 2.3$ kcal mole^{-1}, is satisfactory compared with the accuracy of the SCF-MO calculations and to general standard iterative fitting methods (11).

In the fitting, we have used a weighting technique for enhancing the accuracy of lower energies, according to their chemical significance. The accuracies of the lower and higher energies is reflected by

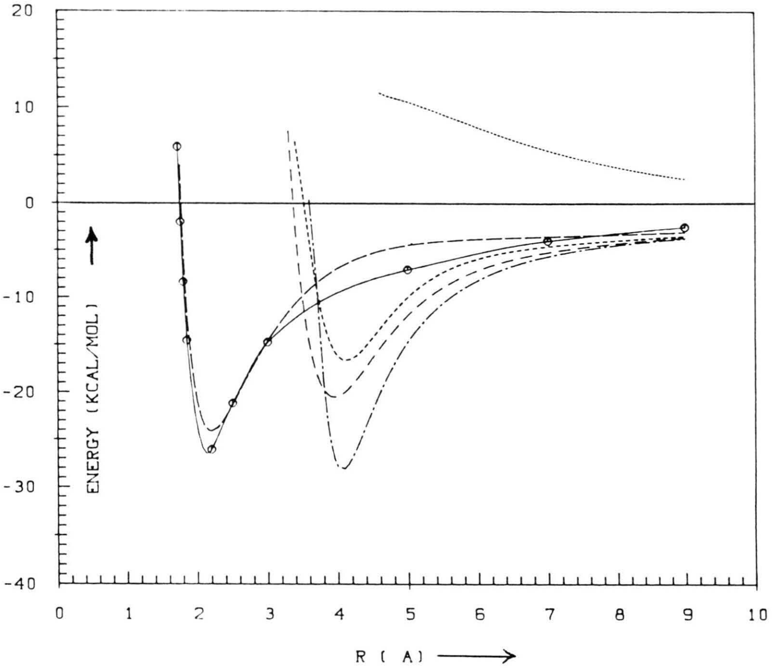

Fig. 3. Comparison between the lowest SCF energy surface data, -●-●-●-, and analytical potential curves, ----, of the same orientation $\theta, \varphi, \psi = 180°$, 45°, 127.8° ($z$-axis) and the potential curves in plane A, -----, ($\theta, \varphi, \psi = 40°$, 0°, 127.8°), plane B, ----, ($\theta, \varphi, \psi =$ 135°, 16.1°, 127.8°), and plane C, —·—·—·—, ($\theta, \varphi, \psi = 130°$, 45°, 127.8°) ($R$ is the distance between Mg^{2+} and water-oxygen atom). The planes A, B and C that include the water molecules go through the z-axis. (See also Figure 2).

the standard deviations of various energy intervals presented in Table 2. The energy correlation between SCF MOs and fitted energies is shown in Fig. 1, which demonstrates not only the small deviations of energy but also the fairly wide distribution of data points used. For checking the energies of some water orientations around the magnesium cyclen complex, three important planes A, B, and C, shown in Fig. 2, have been defined. The comparison of corresponding potential curves is shown in Figure 3.

The energy angular dependence curves of planes A, B, and C were also plotted in order to show the minimal energies of each orientation (Figure 4). The angles $\theta = 0°$ and 180° are also minima (and actually the lowest) in these plots if we consider the whole range of angles from 0° to 360°. We can conclude that water molecules prefer to be located at 2.2 Å above and below the main molecular plane in the z-axis, and 4.0 and 4.1 Å far from the Mg^{2+} ion with

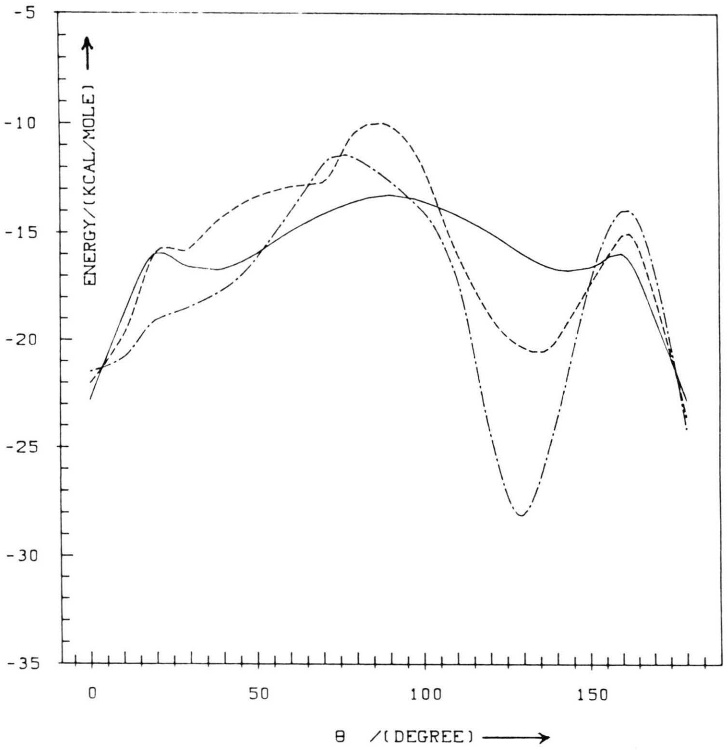

Fig. 4. Angular dependence of interaction potential between magnesium cyclen complex and water in plane A (———), plane B (----) and plane C (—·—·—·—), showing the minimum energies at $\theta = 40°$ (or 140°), 135° and 130° at 4.1, 4.0 and 4.1 Å, respectively.

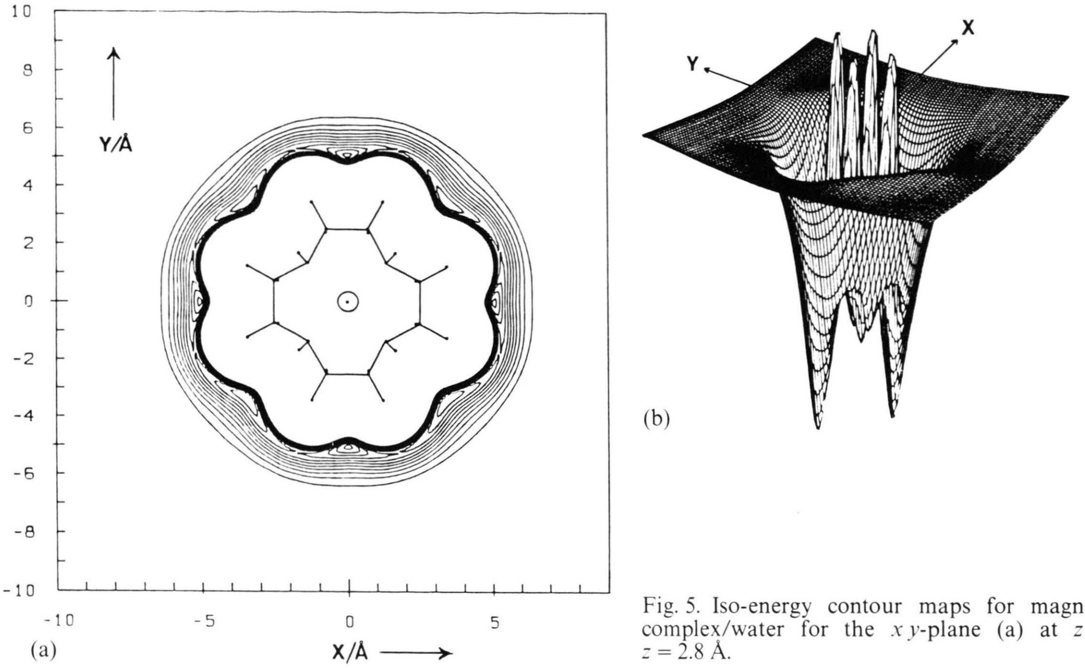

Fig. 5. Iso-energy contour maps for magnesium cyclen complex/water for the xy-plane (a) at $z = 0$ and (b) $z = 2.8$ Å.

Table 2. Standard deviation σ of fitted potential energies (kcal/mole).

$\sigma_{<-15}$	$\sigma_{<-10}$	$\sigma_{<-5}$	$\sigma_{<0}$	$\sigma_{<5}$	$\sigma_{<10}$	$\sigma_{<15}$	$\sigma_{<20}$
1.7	2.0	2.1	2.3	2.1	2.3	2.3	2.3

the orientations $\theta, \varphi, \psi = 135°,\ 16{,}1°,\ 127.8°$ and $\theta, \varphi, \psi = 130°, 45°, 127.8°$, respectively.

In Fig. 5, isoenergy contour maps for the system are shown in order to visualize the energy field for water molecules around the complex in planes $z = 0$ (a) and $z = 2.8$ Å (b). Figure 5(a) shows 8 distinct hydrophilic regions between the inner potential wall and the sharply increased outer potential curves. The 3-dimensional isoenergy contour map of Fig. 5(b) ($z = 2.8$ Å) visualizes the most favourable locations for first shell hydration waters above and below the molecular plane of the ligand.

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