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Theoretical Study of the Inclusion Properties of 1,2,4,5-Tetra(morpholinocarbonyl)benzene

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Abstract. Molecular inclusion by the new amide host molecule (TMB) has been reconsidered by calculating the crystal stabilization energies for the guest molecules in the TMB + guest system from the simple intermolecular potential functions of Caillet and Claverie. Water, ethylene glycol, methanol, and ethanol have been employed as guest molecules and their relative stabilities have been considered. Water has been found to be the most suitable guest molecule in the TMB + guest system. It also has been found that the guest–host interaction is the most important contributor in determining the relative stabilities of the guest molecules in the TMB + guest system, but the guest–guest interaction is very important, too. Moreover, the electrostatic interaction has been found to be the most important contributor to the total interaction energy in the TMB + guest system.

Key words. 1,2,4,5-Tetra(morpholinocarbonyl)benzene, water, ethylene glycol, methanol, ethanol, guest–guest interaction, guest–host interaction, crystal stabilization, relative stability.

1. Introduction

Various host molecules have been found to separate selected species from mixtures and/or solutions [1–8]. Especially, 1,2,4,5-tetra(morpholinocarbonyl)benzene (TMB) is very useful in the extraction of water from aqueous solutions of various alcohols [1]. On the other hand, in the previous work [2], hydroxy host molecules (9-hydroxy-9-(1-propynyl)fluorene and 1,1-bis(2,4-dimethylphenyl)-2-butyn-1-ol) were theoretically investigated, in which alcohol is more suitable than water as a guest molecule. Recently, the amide host molecule (TMB) has been found to form inclusion complexes with water and a variety of alcohols [1]. TMB forms a 1 : 4 complex with water, a 1 : 2 complex with ethylene glycol, and a 1 : 2 complex with methanol. However, TMB by itself is almost insoluble in ethylene glycol or methanol, and furthermore does not form an inclusion complex with ethanol.

In order to investigate why water is most suitable in the TMB + guest system, the interaction energies for the guest molecules were calculated using an empirical potential function. Although empirical potential functions cannot give an accurate interaction energy in comparison with *ab initio* methods, they are important because

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inclusion phenomena may not be explained by considering only a single pair interaction between one host and one guest molecule [2].

In this study, we report the results of the investigation of the inclusion phenomena in the TMB + guest system. Furthermore, the relative stabilities of the guest molecules in the TMB + guest system are compared with the experimental results [1].

2. Model Compound

Computations have been carried out on the TMB + guest system. TMB has relatively high molecular symmetry compared with other inclusion compounds [2–8]. The molecular shapes of TMB and TMB·$4H_2O$ are shown in Figure 1. In addition, the crystal structure of TMB·$4H_2O$ is well known [1].

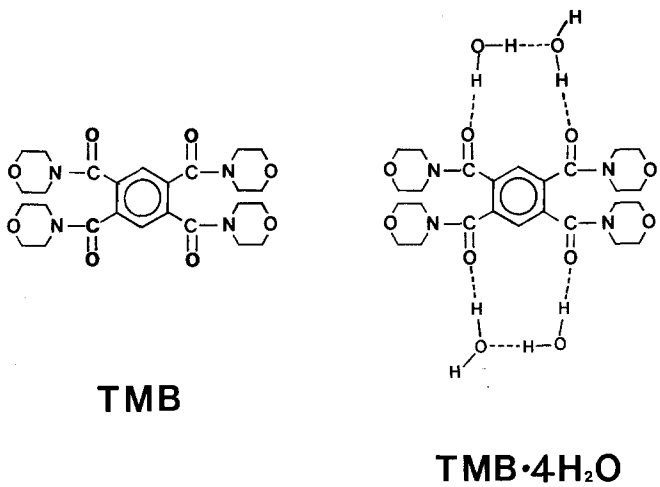

Fig. 1. Molecular shapes of 1,2,4,5-tetra(morpholinocarbonyl)benzene (TMB) and TMB·$4H_2O$.

Water, ethylene glycol, methanol, and ethanol were investigated as the guest molecules in the TMB + guest system. These guest molecules were inserted between TMB host molecules. At this time, in order to make a reliable calculation, the coordinates of TMB were fixed in accordance with those from the X-ray data of the TMB·$4H_2O$ crystal. The geometries of the rigid guest molecules, which have fixed bond lengths and bond angles, were based on experimental data in the literature [9–12].

3. Methods of Calculation

3.1. POTENTIAL FUNCTIONS

The basic formulae and parameters used for the potential energy functions follow the general scheme presented by Caillet and Claverie [13, 14]. The interaction energy is composed of three long-range contributions (electrostatic, polarization, and dispersion) and a short-range repulsive contribution. To describe the hydrogen bonding, incidental parameters [13, 14] for the repulsive term at short distances are

used. The atomic partial charges were readily obtained using the semiempirical Del Re method [15, 16] for σ-charges and the Hückel method [17, 18] for π-charges.

3.2. CALCULATIONAL PROCEDURE

In order to ensure the convergence of the interaction energies of the guest molecules, the calculation was carried out on 90 TMB + guest units. To make a reliable explanation about the inclusion phenomena of TMB, all intermolecular interactions should be considered, but it may cost a lot of computing time to calculate the energies for all intermolecular interactions. Moreover, since this study is focused on the relative stabilities of the guest molecules in the TMB + guest system, it may be sufficient to consider the interaction only between the guest molecule of interest and its environment. For example, in the 90 TMB + water crystal, there are 4×90 water molecules, but the water molecules of interest are only those four that are located near the center of the crystal. The interaction energies of these four waters with their environments may be a reasonable representation of the relative stability of water molecules in the TMB + guest inclusion complexes. Other guest molecules can also be considered in the same way as the water molecule.

Each set of guest molecules was successively inserted at their corresponding X-ray sites in the fixed TMB host molecule network [1]. Since the coordinates of the host molecules were fixed at those of the X-ray data, the degrees of freedom for the optimization are restricted to each type of guest molecule, and these variables were optimized by the use of the quasi-Newton–Raphson procedure [19].

As mentioned earlier, since only the interaction between the guest molecule of interest and its environment was considered, the meaning of the total interaction energy used here is somewhat different from the real total interaction energy of the TMB + guest system.

4. Results and Discussion

The interaction energies for water in the TMB + guest system were calculated in accordance with the number of the TMB + guest units. From Table I, it can be seen that the magnitudes of the total interaction energies may be indicative of convergence in the 90 TMB + guest units. To see whether optimization was satisfactorily

Table I. Interaction energies per one water molecule (kcal/mole).

	3[a]	5	7	9	11	90
E_{el}^{b}	−18.29	−18.39	−20.80	−20.52	−20.64	−21.67
E_{KIT}^{c}	2.60	2.58	1.42	−0.12	−0.04	−0.02
E_{pol}^{d}	−4.83	−4.85	−5.72	−5.41	−5.48	−5.77
E_{total}^{e}	−20.52	−20.66	−25.10	−26.05	−26.16	−27.46

[a] Number of TMB·4H_2O units
[b] Electrostatic energy
[c] Dispersion and repulsion energy
[d] Polarization energy
[e] Total interaction energy.

Table II. Interaction energies per one water molecule (kcal/mole)

	Optimization	X-ray data
E_{el}	−21.67	−18.16
E_{KIT}	−0.02	−1.86
E_{pol}	−5.77	−4.22
E_{total}	−27.46	−24.24

accomplished, the interaction energies obtained by the optimization were compared with those obtained from X-ray data. As shown in Table II, the interaction energies are similar to each other. Some differences seem to come from the assumption that the water molecule was rigid in the optimizing process.

Although TMB does not form an inclusion complex with ethanol, in order to investigate the relative stabilities, the interaction energies for the TMB + ethanol system were calculated and are summarized in Table III. Since a 1 : 1 complex with ethanol is more favorable than a 1 : 2 complex, comparison was carried out by assuming that TMB forms a 1 : 1 complex with ethanol.

The interaction energies for the guest molecules in the TMB + guest system were calculated, and are summarized in Table IV. It can be seen that the electrostatic energy is the most important factor in the total interaction energy. Furthermore, the relative stabilities of the guest molecules in the TMB + guest system can be explained by considering the total interaction energies (E_{total} in Table IV). However, since E_{total} is the total interaction energy per one guest molecule, the relative stabilities of the guest molecules must be explained by considering the crystal stabilization energies (E_{st} in Table IV), which can be represented by multiplying E_{total} by the number of the guest molecules in the TMB + guest unit. As mentioned earlier in Section 2, in the calculation of E_{total}, only the interaction between the guest and its environment was considered. Therefore, in a precise calculation, the crystal stabilization energies for the guest molecules will be changed. Anyway, from this simple calculation, it is concluded that water is the most suitable guest molecule in the TMB + guest system, and that ethanol is the least suitable guest molecule, which is in good agreement with the experimental data.

To investigate the reason why water is the most suitable guest molecule, we divided the total interaction energies into the guest–host interaction energies and the guest–guest interaction energies. Since the polarization energy is a non-additive

Table III. Interaction energies per one ethanol molecule (kcal/mole)

	1 : 2 complex	1 : 1 complex
E_{el}	−17.09	−11.74
E_{KIT}	49.56	−0.03
E_{pol}	−14.57	−6.87
E_{total}	17.90	−18.64

Table IV. Interaction energies per one guest molecule (kcal/mole)

	Water	Ethylene glycol	Methanol	Ethanol
E_{el}	−21.67	−15.18	−10.83	−11.74
E_{KIT}	−0.02	−6.35	−5.13	−0.03
E_{pol}	−5.77	−7.26	−4.99	−6.87
E_{total}	−27.46	−28.79	−20.95	−18.64
E_{st}^{a}	−109.84	−57.58	−41.90	−18.64

[a] Crystal stabilization energy per host + guest complex unit

Table V. Guest–host interaction energies per one guest molecule (kcal/mole)

	Water	Ethylene glycol	Methanol	Ethanol
E_{el}	−11.83	−11.65	−9.42	−11.69
E_{KIT}	−0.02	−2.48	−3.61	−0.02
E_{pol}	−5.77	−7.26	−4.99	−6.87
E_{total}	−17.62	−21.39	−18.02	−18.58
E_{st}	−70.48	−42.78	−36.04	−18.58

Table VI. Guest–guest interaction energies per one guest molecule (kcal/mole)

	Water	Ethylene glycol	Methanol	Ethanol
E_{el}	−9.84	−3.53	−1.41	−0.05
E_{KIT}	0.00	−3.87	−1.52	−0.01
E_{pol}	–	–	–	–
E_{total}	−9.84	−7.40	−2.93	−0.06
E_{st}	−39.36	−14.80	−5.86	−0.06

property, it was included in the guest–host interaction energy for convenience. As shown in Tables V and VI, the energy gaps in the guest–guest interaction energies per one guest molecule are much larger than those in the guest–host interaction energies. This implies that the guest–guest interaction plays an important role in determining the relative stabilities of the guest molecules in the TMB + guest system. At this time, however, the number of guest molecules per TMB + guest complex unit must be considered, too. Although, in the TMB + guest system, the most important factor in determining the relative stability is the guest–host interaction like other host + guest system, the guest–guest interaction is very important. The absolute values of the guest–guest interaction energies for water or ethylene glycol are much larger than those for methanol or ethanol because water or ethylene glycol can be further interconnected by hydrogen bonds.

5. Conclusion

The following conclusions may be drawn from this study of the TMB + guest system:

(1) Water is the most suitable guest molecule in the TMB + guest system, and ethanol is the least suitable guest molecule, which is in good agreement with the experimental data.
(2) The electrostatic interaction is the most important contributor to the total interaction energy of the TMB + guest system.
(3) In the TMB + guest system, the guest–host interaction is the most important contributor in determining the relative stability, but the guest–guest interaction is very important too.

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