# The Characterization of Toluene-*p*-*t*-butylcalix[4]arene Complexes Using Thermal Analyses

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Calixarenes[1] are a class of [1$_n$]metacyclophanes possessing a cavity capable of accepting a guest molecule. Particularly calix[4]arenes exist as a cup-like structure. In the cone conformation of calix[4]arenes[2] a cavity is present which can eventually provide a binding site for a neutral molecule of complementary size. It was found that *p*-*t*-butylcalix[4]arene formed complexes with chloroform,[3] benzene,[4] toluene,[5] xylene,[6] and anisole[3]. The *p*-*t*-butylcalix[8]arene loses its guest chloroform upon standing a few minutes at room temperature and atmospheric pressure. On the other hand, the *p*-*t*-butylcalix[4]arene hold a guest molecule very tightly, retaining recrystallization solvent even after long heating at high temperature under vacuum. In order to investigate inclusion behaviors of toluene into *p*-*t*-butylcalix[4]arene in detail, we carried out molecular simulation as well as DSC and TGA experiments.

Figure 1 gives DSC thermograms of the free *p*-*t*-butylcalix[4]arene and the toluene-trapped *p*-*t*-butylcalix[4]arene. The DSC thermogram of the free *p*-*t*-butylcalix[4]arene (Figure 1(a)) shows the endothermic reaction at 333-355 °C. This may be the melting point of the free *p*-*t*-butylcalix [4]arene. The DSC thermogram of the toluene-trapped *p*-*t*-butylcalix[4]arene (Figure 1(b)) also shows the endothermic reaction at 347-363 °C corresponding to the melting point. The melting points of the free *p*-*t*-butylcalix[4]arene and the toluene-trapped *p*-*t*-butylcalix[4]arene are different each other. The melting point of the free *p*-*t*-butylcalix [4]arene (350.96 °C, peak point) is lower than that of the toluene-trapped *p*-*t*-butylcalix[4]arene (355.42 °C, peak point) by about 5 °C. This may be due to the initial crystalline structure of the toluene-trapped *p*-*t*-butylcalix[4]arene.[5] Since the toluene-trapped *p*-*t*-butylcalix[4]arene has a crystalline structure, it need an extra energy to break the crystalline structure and melt.

The DSC thermogram of the toluene-trapped *p*-*t*-butylcalix[4]arene (Figure 1(b)) shows another important peak at 295-311 °C. This peak is not observed in the DSC thermogram of the free *p*-*t*-butylcalix[4]arene. This peak may result from excluding of the toluene from the *p*-*t*-butylcalix [4]arene in the inclusion system. The enthalpy change of the exclusion is 16.27 J/g. The enthalpy change of the exclusion of toluene from the *p*-*t*-butylcalix[4]arene is about 12 kJ/mol since the molecular weight of the toluene-trapped *p*-*t*-butylcalix[4]arene is 732.

Figure 2 gives TG thermograms of the free *p*-*t*-butylcalix[4]arene and the toluene-trapped *p*-*t*-butylcalix[4]arene. The TG thermogram of the free *p*-*t*-butylcalix[4]arene (Figure 2(a)) shows the weight loss at 170-230 °C by about 10%. This may corresponds to the evaporation of free organic materials such as solvent. For the TG thermogram of the toluene-trapped *p*-*t*-butylcalix[4]arene (Figure 2(b)), the initial weight loss can be seen at 140-160 °C by about 4%. This may corresponds to the evaporation of the free toluene.

There is one very important weight loss at 300-330 °C in the TG thermogram of the toluene-trapped *p*-*t*-butylcalix [4]arene. This may be due to the exclusion and evaporation of the trapped toluene from the inclusion system. The exclusion temperatures of the toluene included by the *p*-*t*-butyl-

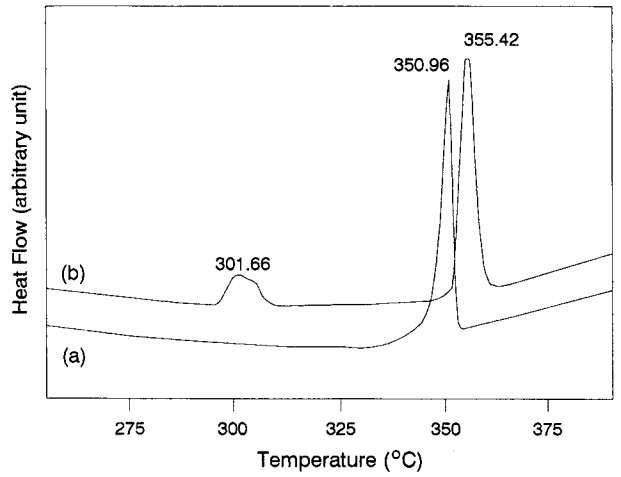


**Figure 1.** DSC thermograms of the free *p*-*t*-butylcalix[4]arene (a) and the toluene-included *p*-*t*-butylcalix[4]arene (b).

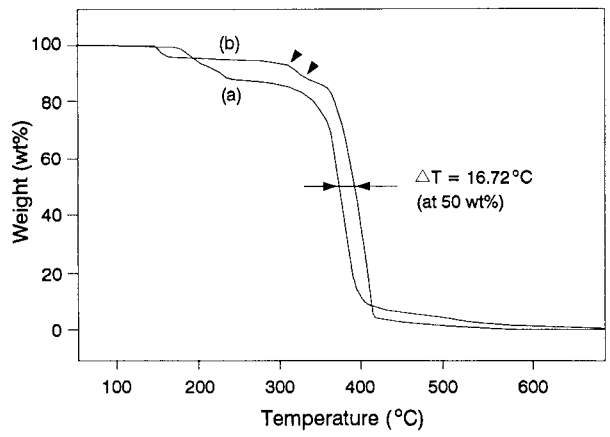


**Figure 2.** TG thermograms of the free *p*-*t*-butylcalix[4]arene (a) and the toluene-included *p*-*t*-butylcalix[4]arene (b).

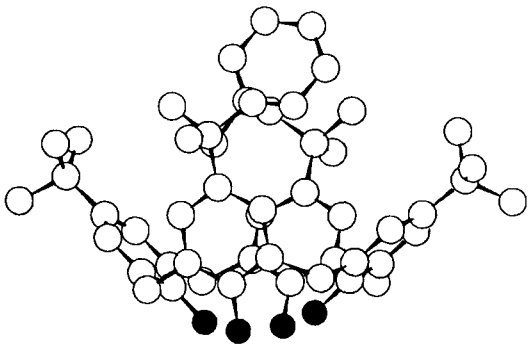

**Figure 3.** Energy-minimized structure of the toluene-included *p-t*-butylcalix[4]arene obtained by the conformational search. The solid and open circles indicate oxygen and carbon atoms, respectively. The interaction energy between toluene and *p-t*-butylcalix[4]arene is -66.94 kJ/mol.

calix[4]arene are constitent relatively each other from the DSC and TG analyses. The evaporation of the calixarene in the toluene-trapped *p-t*-butylcalix[4]arene occurs at higher temperature than that in the free *p-t*-butylcalix[4]arene. The temperature difference at 50 wt% loss between the toluene-trapped *p-t*-butylcalix[4]arene and the free *p-t*-butylcalix [4]arene is about 17 °C. This can be explained by the initial crystalline structure of the toluene-trapped *p-t*-butylcalix[4] arene as discussed above.

Structures of neutral molecule-included *p-t*-butylcalix[4] arene have been studied using X-ray crystallography.[3-5] In this study, we calculated the structure of the toluene-trapped *p-t*-butylcalix[4]arene and the intermolecular interaction energy between the toluene and *p-t*-butylcalix[4]arene in the inclusion system using molecular simulation technique. Figure 3 gives the structure of the toluene-trapped *p-t*-butylcalix[4]arene obtained by the conformational search. The *p-t*-butylcalix[4]arene has a structural characteristics that hydroxyl groups cluster in the center of one side of the molecule by sequent intramoleculr hydrogen bonds between adjacent hydroxyl groups. The methyl group of the toluene is docked to the *p-t*-butylcalix[4]arene. This structure is consistent with the result of X-ray crystallography.[5] In the energy-minimized structure of the toluene-trapped *p-t*-butylcalix[4]arene, distances between carbon atom of the methyl group of the toluene and *para*-carbon atoms of the *p-t*-butylphenolic units of the calixarene are 3.75-4.08-6.52-4.26 Å, while those between carbon atom of the methyl group of the toluene and 1-carbon atoms of the *p-t*-butylphenolic units of the calixarene are 4.21-5.14-5.59-4.84 Å. The interaction energy between toluene and *p-t*-butylcalix[4]arene in the energy-minimized structure is -66.94 kJ/mol.

## Experimental and Calculation

*p-t*-Butylcalix[4]-arene was prepared by following the previously reported method.[6] Toluene inclusion into *p-t*-butylcalix[4]arene was done by recrystallizing crude product in toluene.

Thermal analyses of the toluene-trapped *p-t*-butylcalix [4]arene and the free *p-t*-butylcalix[4]arene were performed using DSC (differential scanning calorimeter) and TG (thermogravimeter). The DSC and TG analyses were performed under $N_2$ condition. A DSC 7 differential scanning calorimeter of Perkin Elmer was used. The temperature program of DSC was as follows. The initial and final temperatures were 50 and 500 °C, respectively, and the rate was 20 °C/min. A TGA 7 thermogravimetric analyzer of Perkin Elmer was used. The temperature program of TG analysis was as follows. The initial and final temperatures were 50 and 700 °C, respectively, and the rate was 20 °C/min.

In order to calculate the interaction energy between toluene and *p-t*-butylcalix[4]arene in the toluene-included *p-t*-butylcalix[4]arene system, we generated the assembly of one toluene and one *p-t*-butylcalix[4]arene and used the restraint dynamics. The initial structures of those molecules were generated by the *Insight II* package and molecular dynamics and molecular mechanics were performed using the *Discover* of MSI. We used one of the parameter sets, CFF91 force field. Potential cutoff distance of 10.0 Å and dielectric constant of 1.0 were employed. The constraint condition was artificial bonding potential possessing 1,000 N/cm of force constant and 5 Å of equilibrium distance between 1-carbon atom of the toluene and *para*-carbon atoms of the *p-t*-butylphenolic units of the calixarene. Upon the constraint, the molecular dynamics was done on the assemblies at 900 K during 300 ps. The intermediate structure at every 1 ps was put in minimization to get the 300 conformers of the assemble system. The lowest energetic conformation among the 300 conformers was chosen to do further simulation. The molecular dynamics was done again with the lowest energetic conformation at 900 K after removing constraint condition during 1 ps. 10 conformers were sampled at every 100 fs and minimized to get the most energetically favorable structure. The non-bond interactions such as van der Waals and electrostatic interactions between toluene and *p-t*-butylcalix[4]arene in the most stable conformation were calculated.

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