Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2011, **21**, 291–292

Mendeleev Communications

Molecular recognition of chloroform by divergent polymorphic transitions in *tert*-butylthiacalix[4]arene tetrasubstituted with *N*-(2-hydroxyethyl)-carbamoylmethoxy groups in a lower rim

Goulnaz D. Safina, Olga M. Gavrilova, Marat A. Ziganshin,
Ivan I. Stoikov, Igor S. Antipin and Valery V. Gorbatchuk*

A. M. Butlerov Institute of Chemistry, Kazan (Volga Region) Federal University, 420008 Kazan, Russian Federation.
Fax: +7 843 233 7416; e-mail: Valery.Gorbatchuk@ksu.ru

DOI: 10.1016/j.mencom.2011.09.022

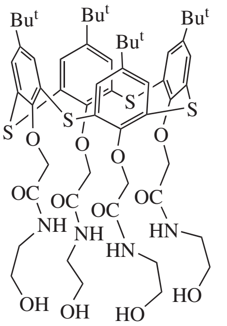
The genuine molecular recognition of chloroform by a *tert*-butylthiacalix[4]arene derivative was observed, where the host remembers the guest above its elimination point showing two polymorphic transitions with opposite heat effects.

The polymorphism of solid receptors, giving the formation and collapse of metastable porous structures, can affect significantly their binding ability for vapours and gases.[1–4] In addition, it can be used for molecular recognition because the temperature and heat of polymorphic transition may depend on the receptor history, in particular, on the structure of the previously bound guest.[2]

Typically, a curve of differential scanning calorimetry (DSC) for clathrates of macrocyclic receptors has only *endo*-effects[1,5,6] or only *exo*-effects[2,3] corresponding to polymorphic transitions along with pseudopolymorphic transitions of guest release. Two different polymorphic transitions of a macrocyclic host with divergent heat effects in one run of thermoanalysis are very unusual, which had not been observed earlier. In this study, this phenomenon was observed for the clathrate of chloroform with *tert*-butylthiacalix[4]arene tetrasubstituted with *N*-(2-hydroxyethyl)carbamoylmethoxy groups in a lower rim, in the stable cone configuration (**1**),[7] above the point of the guest removal.

The combined method of thermogravimetry and DSC with the mass-spectrometric analysis of evolved gases (TG/DSC/MS experiment)[3] was used to analyze products of host **1** saturation by the vapours of methanol, ethanol, *n*-propanol and isopropanol, acetonitrile, propionitrile, benzene, toluene, pyridine, *n*-hexane, cyclohexane, dichloromethane, chloroform, tetrachloromethane, trichloroethylene and pentachloroethane with the relative vapour pressure $P/P_0 = 1$ at $T = 291$ K during 24 h[†] prepared as described elsewhere.[3] The TG/DSC/MS data are given in Figure 1.

In this experiment, thiacalixarene **1** was found to form relatively stable clathrates only with chloroform ($\mathbf{1}\cdot 0.96\,CHCl_3$) [Figure 1(*a*)], methanol ($\mathbf{1}\cdot 0.98\,MeOH$), ethanol ($\mathbf{1}\cdot 0.70\,EtOH$), *n*-propanol ($\mathbf{1}\cdot 0.36\,PrOH$), isopropanol ($\mathbf{1}\cdot 0.25\,Pr^iOH$), acetonitrile ($\mathbf{1}\cdot 1.01\,MeCN$) [Figure 1(*d*)], propionitrile ($\mathbf{1}\cdot 0.43\,EtCN$), dichloromethane ($\mathbf{1}\cdot 0.58\,CH_2Cl_2$) [Figure 1(*e*)], and pyridine ($\mathbf{1}\cdot 0.41\,C_5H_5N$) [Figure 1(*f*)]. Guest release from studied clathrates started at 30–40 °C, except for a clathrate of **1** with pyridine, which is stable to 90 °C. Ion thermograms (MS curve) show that only bound guests are evolved in this experiment. The other studied guests do not form stable clathrates under sample pre-equilibration conditions of thermal analysis: argon flow at room temperature for 20 min before heating.



1

The decomposition of the most of **1** clathrates with test guests shows only *endo*-effects of guest release in DSC curves [Figure 1(*d*)–(*f*)]. The exception is the DSC curve of $\mathbf{1}\cdot 0.96\,CHCl_3$ clathrate having an endothermic peak of chloroform removal at 50 °C, an exothermic peak at 116 °C with a heat value of $\Delta H = -20.5$ kJ mol^{-1} and endothermic peak at 160 °C with $\Delta H = 2.8$ kJ mol^{-1}. The mass loss of the sample in the temperature range of 105–125 °C is only 0.09% or 0.008 mol of CHCl$_3$ per mole of **1**. An *exo*-peak in the DSC curve indicates a collapse of the loose β_0-phase formed during the decomposition of $\mathbf{1}\cdot 0.96\,CHCl_3$ clathrate (β-phase) and the formation of a dense form of the host (α-phase).[2,3] Probably, a small residual amount of the guest in a β_0-phase stabilizes this metastable form of the host.[4] An *endo*-peak in the DSC curve without mass loss corresponds to a polymorphic transition from the dense α-phase to a low-dense packing (α'-phase).[5,6]

The loose β_0-phase of guest-free thiacalixarene **1** was prepared by the heating of $\mathbf{1}\cdot 0.96\,CHCl_3$ to 90 °C with a rate of 4 K min^{-1} and fast cooling to 28 °C. Thermal analysis data for a β_0-phase sample are shown in Figure 1(*b*). According to the ion thermogram, this form of **1** does not contain chloroform. The enthalpies (–20.6 and 3.0 kJ mol^{-1}) and temperatures of polymorphic transitions for this sample coincide with the data observed for $\mathbf{1}\cdot 0.96\,CHCl_3$.[‡]

The exothermic effect for host **1** is comparable with the collapse enthalpies of β_0-phase prepared from *tert*-butylcalix[6]arene[2] and adamantylcalix[4]arene.[3] Using a published procedure,[2] the free

---

[†] Thermoanalysis was performed in an argon atmosphere with a flow rate of 75 ml min^{-1} at 4 K min^{-1} for **1** clathrates and β_0-phase, and at 10 K min^{-1} for α'-phase of guest-free **1**. Clathrates were prepared by the saturation of host α'-phase with guest vapours.

[‡] The saturation of all polymorphs of thiacalixarene **1** (α-phase, α'-phase and β_0-phase) by chloroform vapour with $P/P_0 = 1$ at 298 K results in the formation of clathrate $\mathbf{1}\cdot 0.96\,CHCl_3$ with the same TG/DSC/MS curves as in Figure 1(*a*).