Metastable *tert*-butylcalix[6]arene with unusually large tunable free volume for non-threshold enclathration of volatiles†

Alexey V. Yakimov,[a] Marat A. Ziganshin,[a] Aidar T. Gubaidullin[b] and Valery V. Gorbatchuk*[a]

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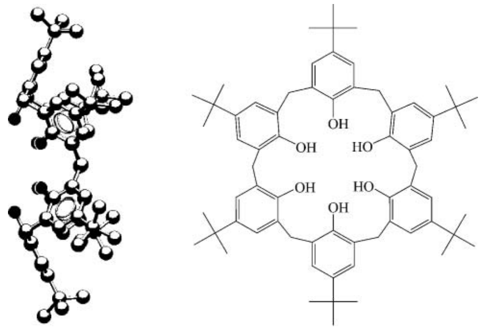
A metastable material with tunable free volume of molecular size, vapor sorption properties of a porous sorbent and variable thermal stability was prepared from *tert*-butylcalix[6]arene.

The preparation of molecular containers for volatile substances and gases is vital both for gas storage and vapor sensing. Solid calixarenes are prospective materials for these applications having relatively high kinetic stability of binding products.[1] This stability is a result of clathrate cooperativity and the specific shape of calixarene molecules. The release of guest from the capsules formed by calixarene bowls in the clathrate may have a much higher barrier than release from channels of rigid pores in covalent, ionic or coordinated lattices.[2] Still, the clathrate-forming hosts have a disadvantage related to the existence of a threshold preventing guest inclusion at low relative vapor pressures.[3] This threshold can be decreased practically to zero by small additives of another guest,[4]or by preparation of a metastable porous host structure.[1] A search of such structures is not simple, because, in many cases, clathrates collapse upon guest removal.[1,2,5]

In this work, a metastable calixarene material was prepared, which has an unusually large free space in its molecular packing. For this, the decomposition of *tert*-butylcalix[6]arene (**1**) clathrates with various guests was used. These clathrates were prepared using saturation of thermally equilibrated **1** (α-phase)‡ with guest vapors at 298 K.[3b] The formation of a loose guest-free phase (β_0) upon elimination of some guests from their clathrates with **1** was proved using simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC). TG–DSC curves for clathrates of **1** were obtained as described elsewhere.[3b]

The formation of the β_0-phase can be seen on TG-DSC curves by the presence of a large exothermic DSC peak without mass loss§ above the temperature range of clathrate decomposition. This was observed for clathrates of host **1** with benzene (Fig. 1), toluene, acetone, acetonitrile, tetrachloromethane and dichloromethane, see also Electronic Supplementary Information (ESI). Such behavior is distinct from that of studied *tert*-butylcalix[4]arene and *tert*-butylcalix[5]arene clathrates having no *exo*-peaks on the DSC curves.[3b,6] The host **1** phase formed by decomposition of its clathrates with benzene and tetrachloromethane even has 2 *exo*-peaks. The second collapse peak, in each case, is rather small, Fig. 1b, ESI.



tert-butylcalix[6]arene (**1**)

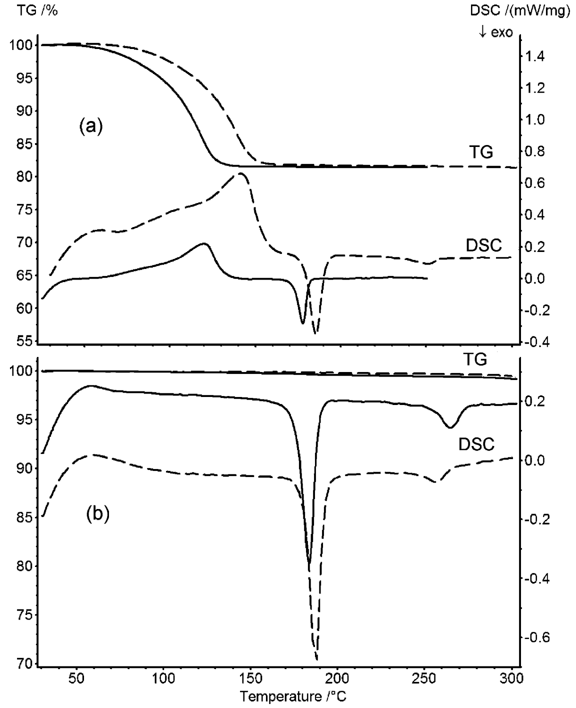


Fig. 1 The data from a simultaneous TG–DSC experiment for (a) saturated clathrate of **1** with benzene, heating rate 4 K min^{-1} (solid line) and 10 K min^{-1} (dotted line) and (b) β_0-phase of **1** formed after heating of the same clathrate up to 150 °C in air (dotted line) and after drying under a vacuum 0.3 kPa during 6 h at 25 °C (solid line), heating rate 10 K min^{-1}.

Parameters of clathrates and β_0-phases from TG–DSC experiments including clathrate stoichiometry (guest/host molar

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[a] *Institute of Chemistry, Kazan State University, Kremlevskaya 18, Kazan, 420008, Russia. E-mail: Valery.Gorbatchuk@ksu.ru; Fax: +7 843 2927418; Tel: +7 843 2315309*

[b] *A.E. Arbuzov Institute of Organic and Physical Chemistry, KSC RAS, ul. Akad. Arbuzova 8, 420088, Kazan, Russia*

† Electronic supplementary information (ESI) available: Additional XRPD and TG–DSC data for different forms of *tert*-butylcalix[6]arene and its clathrates, vapor sorption isotherms of dichloromethane on α and β_0 forms of this calixarene. See DOI: 10.1039/b800187a

Table 1 Parameters of *tert*-butylcalix[6]arene (**1**) clathrates and host phase formed upon their thermal decomposition from simultaneous TG–DSC data[a]

Guest	S	T_e (T_{col})/°C	ΔH_e/kJ mol^{-1}	$\Delta H^{(1)}_{col}$ ($\Delta H^{(2)}_{col}$)/kJ mol^{-1}
MeCN	1.27; 1.5[b,c]; 2[c]	91 (234)	27	−10
Me_2CO	1.04; 1[d]	139 (201)	50	−19
CH_2Cl_2	1.92; 2[e]	108 (205)	40	−14
C_6H_6	2.82; 3[f]	119 (178, 252[g])	47	−32 (−3.1[g])
CCl_4	3.5	123 (188, 242[g])	54	−33 (−3.9[g])
$C_6H_5CH_3$	1.05; 1[h]	147 (199)	70	−14
$CHCl_3$	1.11	217	66	
DMSO[i]	2.48; 2.5[j]	147	46	
C_5H_5N	1.16	194	58	
c-C_6H_{12}	2.14 (1.50[k]; 1.12[l])	75; 217	59[m]	
C_2Cl_4	1.07; 1[n]	207	41	

[a] Heating rate 4 K min^{-1}, error of ΔH_e and $\Delta H^{(1)}_{col}$ determination is 7% (10% for clathrates of Me_2CO, $C_6H_5CH_3$, $CHCl_3$), the error of $\Delta H^{(2)}_{col}$ is 20%, the error of S determination is 3–5% depending on the clathrate stability. [b] Ref.7*a*. [c] Ref.7*b*. [d] TG data from Ref. 8. [e] Ref.7*c*. [f] Ref.7*d*. [g] Data for second collapse peak from separate experiment with heating rate 10 K min^{-1}. [h] Ref.7*e*. [i] Heating rate 10 K min^{-1}. [j] Ref.7*f*. [k] Stoichiometry of clathrate stable at room temperature. [l] Stoichiometry of clathrate formed after the first decomposition step above room temperature. [m] Value for the second decomposition step. [n] Ref.7*g*.

ratio) S, temperatures of guest elimination T_e, corresponding to maximal rate of mass change, and host collapse T_{col}, and corresponding transition enthalpies, ΔH_e and ΔH_{col}, are given in Table 1.

For comparison, stoichiometry values are given in Table 1 from X-ray data for monocrystals prepared from host **1** solutions in liquid guests.[7] In most cases, except for the acetonitrile clathrate, there is an agreement within experimental error between the monocrystal data and the S values of vapor saturated host powders.

The exothermic phase collapse without mass loss is not intrinsic to an empty α-phase of **1** prepared by prolonged thermal equilibration (ESI). Besides, no *exo*-peaks were observed on TG–DSC curves for clathrates of **1** with cyclohexane, chloroform, dimethyl sulfoxide, pyridine and tetrachloroethylene, Table 1. The last step of the decomposition is rather narrow for these clathrates, Fig. 2a, ESI. They have also a high point of last guest elimination, $T_e >$ 190 °C, Table 1, except for the **1**·2.48DMSO clathrate with $T_e =$ 147 °C. The lower stability of this clathrate may be linked to a specific 1,2,3-alternate conformation of **1** in its crystal structure.[7f] In the other clathrates, for which monocrystal X-ray data are available, host **1** has a pinched-cone conformation.[7]

For **1**·$1.04Me_2CO$ and **1**·$1.05C_6H_5CH_3$ clathrates the guest elimination range overlaps the *exo*-peak of host collapse but does not mask it, Fig. 2b, ESI. Still, T_e values for these clathrates are relatively low, 139 and 147 °C, respectively.

The position of the exothermic peak of host collapse T_{col} depends on the guest eliminated. The higher the value of T_{col}, the lower the collapse enthalpy ΔH_{col}, Table 1. This relationship is analogous to the linear dependence of free volume in glassy polymers on their glass transition temperature, which has a negative coefficient of proportionality.[9] Thus, the $-\Delta H_{col}$ value may be a parameter of the collapsing free volume in the host.

The thermodynamic cycle of formation–decomposition for **1**·$2.82C_6H_6$ clathrate (β-phase) is shown in Fig. 3. All four forms of this cycle were characterized using the X-ray powder diffraction (XRPD) method, ESI. The three forms α, β, β_0 have essentially different crystal packing, which could be understood in the light of the high enthalpies of their mutual transitions. The α′-form with a rather small enthalpy of collapse to the α-phase, $\Delta H^{(2)}_{col} =$ −3.1 kJ mol^{-1}, has a packing close to that of the α-phase. XRPD data show that the powder of **1** saturated with benzene vapor (β-phase) has the same packing as the **1**·$3C_6H_6$ monocrystal prepared from the host solution in liquid benzene.[7d]

According to this scheme, one can estimate the enthalpy of guest elimination with complete collapse of host **1** as

$$\Delta H(\beta\rightarrow\alpha) = \Delta H_e + \Sigma\,\Delta H_{col}/S$$

where ΔH_e is the enthalpy of clathrate decomposition per 1 mol of guest, $\Sigma\,\Delta H_{col}$ is a sum of enthalpies for all exothermic transitions per 1 mol of host for a given clathrate with guest/host molar ratio

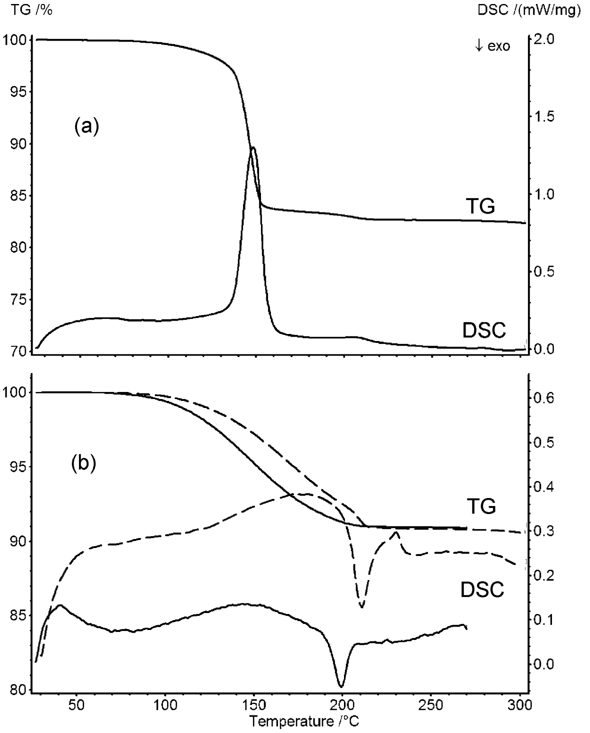

Fig. 2 The data from a simultaneous TG–DSC experiment for saturated clathrate of **1** (a) with dimethyl sulfoxide, heating rate 10 K min^{-1}, and (b) with toluene, 4 K min^{-1} (solid line) and 10 K min^{-1} (dotted line).

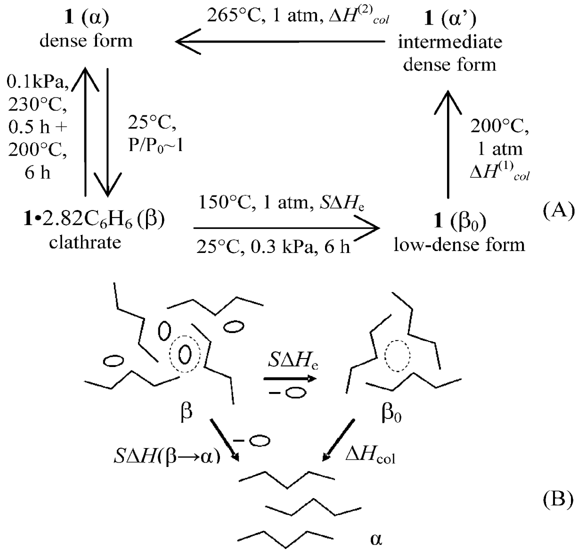

Fig. 3 Thermodynamic scheme of $\mathbf{1}\cdot 2.82C_6H_6$ clathrate formation and decomposition cycle (A), and generalized structural scheme of clathrate (β) decomposition to the loose β_0-phase and then to the dense α-phase of host **1** (B). The clathrate packing in scheme B corresponds to that of **1**·toluene clathrate.[7e] Dotted lines indicate the surface of molecular contacts lost by the guest upon leaving the clathrate and the possible free surface collapsing in the host exothermic transition.

S. For two guests, benzene and tetrachloromethane this value, $\Delta H(\beta\rightarrow\alpha)$ is equal to 35 and 43 kJ mol^{-1}, respectively, which are quite comparable by absolute value with the collapse enthalpies $\Sigma\Delta H_{\mathrm{col}}$ of the host produced from their clathrates, Table 1. In these cases, the loose β_0-phase has the same excess energy as required for one guest molecule to leave the clathrate with formation of the stable α-phase, $\Delta H(\beta\rightarrow\alpha) \approx -\Sigma\Delta H_{\mathrm{col}}$.

This equation helps to estimate the collapsing free volume in the loose β_0-phase, if the energy of molecular contacts lost by guest leaving the clathrate in $\beta\rightarrow\alpha$ transition is equal to the energy of molecular contacts restored in the exothermic collapse $\beta_0\rightarrow\alpha$ of host, Fig. 3b. In this case, the ratio of $\Delta H(\beta\rightarrow\alpha)$ and $-\Sigma\Delta H_{\mathrm{col}}$ is equal to the ratio of guest volume and the collapsing free volume in the host β_0-phase. So, in the β_0-phase formed after decomposition of saturated benzene clathrate, this volume per 1 mol of host **1** should be close to the molar volume of benzene, because this guest has nearly the same group composition as the neighboring host groups in clathrate.

The value of host **1** collapse enthalpy after benzene elimination $\Sigma\Delta H_{\mathrm{col}} = -35$ kJ mol^{-1} is 3.5 times higher by absolute value than the enthalpy of endothermic transition of *tert*-butylcalix[4]arene from the tightly packed α-phase to the loose β_0-phase at 230 °C.[3b,6] For comparison, the loose β_0-phase of *tert*-butylcalix[4]arene binds 0.5 mol of CO_2,[10] or 1 mol of CH_4[11] per 1 mol of host, which corresponds to 25% of the benzene molar volume.

The loose β_0-forms of **1** are stable at room temperature. The β_0-form of **1** prepared by heating of $\mathbf{1}\cdot 2.82C_6H_6$ clathrate to 150 °C at an average rate of 13 K min^{-1} in an oven in air and further immediate cooling to room temperature has the same collapse profile ($\Delta H^{(1)}_{\mathrm{col}} = -31$ kJ mol^{-1} at 188 °C; $\Delta H^{(2)}_{\mathrm{col}} = -4.0$ kJ mol^{-1} at 258 °C) as the initial clathrate, Fig. 1b, Table 1. The same TG–DSC curve was observed for the β_0-form of **1** prepared by drying of this clathrate during 6 h under a vacuum of 300 Pa at room temperature, 25 °C, Fig. 1b. Vacuum drying of $\mathbf{1}\cdot 1.92CH_2Cl_2$ clathrate under the same conditions also gives the β_0-phase of **1** having an exothermic peak at 211 °C with $\Delta H^{(1)}_{\mathrm{col}} = -12$ kJ mol^{-1}. These parameters are also very close to those of the initial clathrate, Table 1.

The ability of host **1** clathrates to decompose with formation of the β_0-phase at room temperature does not depend directly on the guest volatility. Attempts to decompose $\mathbf{1}\cdot 1.04(CH_3)_2CO$ clathrate by vacuum drying at room temperature failed.

The empty β_0-phase prepared by heating $\mathbf{1}\cdot 3.5CCl_4$ clathrate at 150 °C under vacuum (0.1 kPa) behaves as the porous sorbent for vapors of cyclohexane and dichloromethane. Their sorption isotherms do not have a threshold by guest relative vapor pressure P/P_0, Fig. 4, ESI. Such an isotherm shape is intrinsic to the sorption on porous sorbents.[2] The α-phase of **1** has a clear-cut threshold by guest activity on sorption isotherms of both guests, Fig. 4, ESI. Isotherms of guest vapor sorption by solid host powder were determined as described elsewhere.[3]

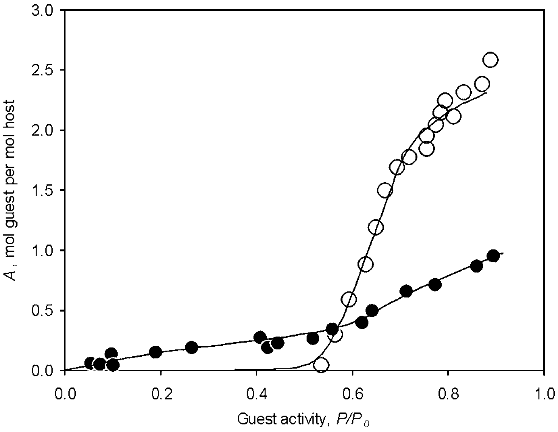

Fig. 4 Isotherms of cyclohexane vapor sorption at 298 K by powder of (○) α-phase of *tert*-butylcalix[6]arene (**1**), and (●) β_0-phase of **1** prepared by heating of $\mathbf{1}\cdot 3.5CCl_4$ clathrate under vacuum (0.1 kPa) at 150 °C for 8 h. The lines are drawn to guide the eye.

At high values of P/P_0, the binding capacity (guest uptake *A*) of β_0-phase for cyclohexane is less than a half of the corresponding value for the α-phase, Fig. 4, Table 1. The same was observed for the loose β_0-phase of *tert*-butylcalix[4]arene, which also binds gases mostly within its free volume.[10] Formation of a loose phase above the clathrate decomposition point may be caused by the specific pinched-cone shape of **1**, which enables self-inclusion of host molecules in clathrates by mutual hooking.[7] This may prevent the complete collapse of host upon guest removal. Thus, using a single calixarene host, by guest variation one can obtain different metastable materials with various free volume and thermostability. These materials may be used as sorbents for non-threshold encapsulation of volatiles and probably gases.

Acknowledgements

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Notes and references

‡ The α-phase of *tert*-butylcalix[6]arene (**1**) was prepared from this host sample purchased from Fluka by heating under vacuum (100 Pa) during 30 min at 230 °C and then 6 h at 200 °C. The purity of the calixarene powder was checked as described elsewhere.[3]

§ In several cases a slight mass change is observed corresponding to <0.02 mol of guest per 1 mol of host.

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