Unusually High Selectivity of Guest Exchange in *tert*-Butylthiacalix[4]arene Clathrate Producing More Thermostable Inclusion and Memory of Guest

Shamil F. Galyaltdinov,[†] Marat A. Ziganshin,[†] Andriy B. Drapailo,[‡] and Valery V. Gorbatchuk*,[†]

[†]A.M. Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya, 18, 420008 Kazan, Russia
[‡]Institute of Organic Chemistry, NAS of Ukraine, Murmanskaya str., 5. Kiev, 02660 Ukraine

Ⓢ *Supporting Information*

ABSTRACT: New properties, earlier unknown for calixarenes, were found for *tert*-butylthiacalix[4]arene (**1**) clathrate with 1,2-dichloroethane (DCE). Guest exchange in **1**·1.90DCE for vapors of some organic compounds gives clathrates, which are more thermostable at 34−59 °C than those prepared by direct saturation of guest-free **1** with pure guests. Besides, guest exchange may produce clathrates that cannot be formed by direct saturation in binary host−guest systems. Some compounds, like water, toluene, and trichloroethylene, expel DCE from its clathrate with **1** but are not included above the trace level. Residual contents of DCE in clathrate may be controlled by variation of water and **1**·1.90DCE ratio in the studied system. Host **1** can remember methanol after its elimination from the guest exchange product. This memory can be read as an exoeffect by differential scanning calorimetry. Only methanol and only after guest exchange is remembered giving an example of a genuine molecular recognition.
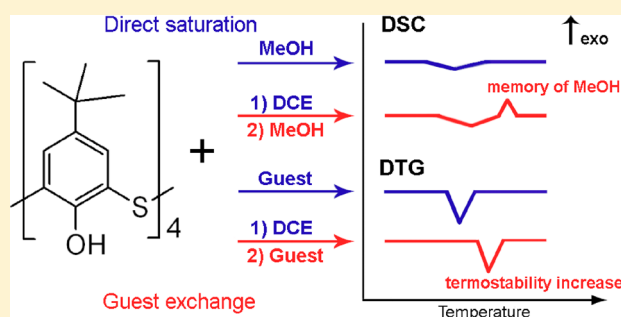
INTRODUCTION

Calixarenes are often studied as prospective receptors for molecular recognition[1,2] and encapsulation of volatiles and gases.[3,4] These studies look for enhanced selectivity, which helps to discriminate a target compound from others[5,6] or for enhanced stability of guest binding products.[7] A key to the success of such research is in an application of specific cooperative properties of calixarenes as clathrate-forming compounds. These are an ability to form polymorphs under thermal treatment[8−10] and a peculiar pseudopolymorphism in clathrate formation/decomposition.[11,12] So, a low-density (loose) polymorph of *tert*-butylcalix[4]arene can effectively bind gases, unlike its thermally stable form.[13] *tert*-Butylcalix[6]arene[9] and a *tert*-butylthiacalix[4]arene derivative[10] can remember previously bound guests after their elimination, forming guest-free polymorphs with guest-dependent properties, which may be used for unusually selective molecular recognition. Practically absolute selectivity may be reached using two-step pseudopolymorphism of guest binding with another *tert*-butylthiacalix[4]arene derivative.[11]

Another property of calixarenes, which may be studied for its potential in molecular recognition, is a guest exchange in their clathrates. The possibility of exchange selectivity for calixarene clathrates had not been studied before the present work. Earlier, for several calixarenes, this exchange was observed to be successful irrespective of the guests studied.[4,14] So, the problem is to find a host that could have such a selectivity.
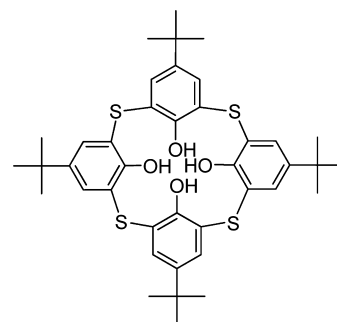
In the present work, the guest exchange selectivity of *tert*-butylthiacalix[4]arene (**1**) clathrate was studied. This host is very selective in the usual sense, with discrimination of close homologues, being able, for example, to bind methanol and to exclude ethanol.[6] For this host, a change in clathrate stability was studied as a result of sample preparation by guest exchange instead of direct saturation of the host with guest vapor. In addition, a host's ability to remember the guest participating in the exchange was analyzed. Both of these properties have not been reported before the present work, boosting the ways for development of new methods for effective encapsulation and genuine molecular recognition.
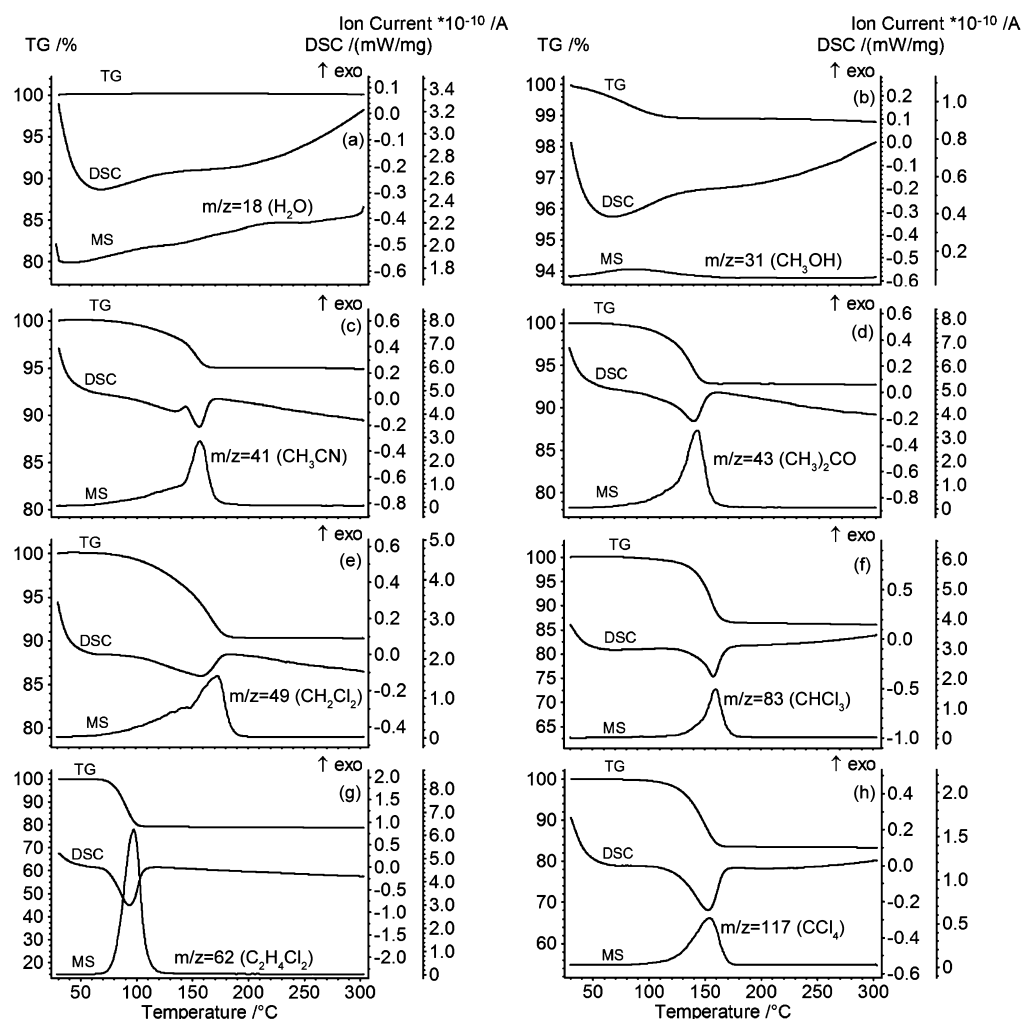
Figure 1. Thermal analysis data for clathrates prepared by saturation of calixarene **1** by guest vapors with $P/P_0 = 1$ at 25 °C: (a) **1**·0.24CH$_3$OH, (b) **1**·0.92CH$_3$CN, (c) **1**·0.96(CH$_3$)$_2$CO, (d) **1**·0.89CH$_2$Cl$_2$, (e) **1**·0.93CHCl$_3$, (f) **1**·1.90DCE, and (g) **1**·0.92CCl$_4$.

■ EXPERIMENTAL SECTION

Materials. *tert*-Butylthiacalix[4]arene (**1**)[15] was purified from nonvolatile impurities by recrystallization from chloroform. Enclathrated volatiles were removed by heating of **1** for 5 h at 200 °C in vacuum of 100 Pa. Dried calixarene did not change its initial white color in this drying process, which served as additional evidence of its purity. Besides, no mass loss and phase transitions were observed for dried calixarene up to 300 °C in thermoanalysis described below and in the Supporting Information (SI). The melting point of pure host **1** is 347 °C. Guest compounds were dried before experiments as described elsewhere[16] and had at least 99.5% of the main substance according to GC analysis. Polyethylene glycol (PEG-400, Merck Co.) was dried in vacuum of 100 Pa at 80 °C for 1 h.

Sample Preparation. Clathrate samples, 10−15 mg, were prepared in aluminum crucibles inside hermetically closed vials, 15 mL, by saturation of dried **1** or its clathrate with 1,2-dichloroethane (DCE) at 25 °C for 72 h by vapors of pure liquid guests (for 120 h by water vapors) taken in an amount of 100 μL, as described elsewhere.[2]

A sample of loose metastable **1** was prepared by saturation of its DCE clathrate with the vapor of liquid methanol as described above and by further heating of guest exchange product in argon flow inside thermoanalyzer (see below) at 100 °C for 30 min. Then the sample was cooled to room temperature.

Thermoanalysis by Simultaneous TG/DSC/MS. Simultaneous thermogravimetry (TG), differential scanning calorimetry (DSC), and evolved gas analysis by mass-spectrometry (MS) of dried **1** and its clathrates was performed using thermoanalyzer STA 449C Jupiter with quadrupolar mass-spectrometer QMS 403 C Aëolos (Netzsch) in an argon flow of 75 mL/min and a heating rate of 10 K/min as described elsewhere.[2] Contents of DCE and traces of water in clathrates were determined using calibration of the mass-spectrometer with direct sampling of these liquids to its injection chamber. The error of guest contents determination is below 0.02 mol/mol for stable clathrates.

X-ray Powder Diffractograms. Powder diffractograms were determined using a D8 Advance (Bruker) device with linear detector PSD Vantec. Experimental conditions: Bragg−Brentano geometry, Cu Kα tube, and graphite monochromator were used with tube voltage of 40 kV and current of 40 mA, step of 0.0081°/2θ, exposure time of 0.5 s in each point without sample rotation. Host and clathrate powder samples were slightly pressed in a standard holder or on the quartz plate before experiment.

■ RESULTS AND DISCUSSION

Thermal Stability of Clathrates Formed in Binary Host−Guest Systems. To choose the calixarene **1** clathrate that may be used for guest exchange, a number of inclusion compounds of this host were prepared in its binary systems with vapors of various guests: methanol, acetonitrile, acetone, dichloromethane, chloroform, 1,2-dichloroethane (DCE), and tetrachloromethane. The composition and thermal stability of these clathrates was studied using simultaneous TG/DSC/MS analysis. The thermograms obtained are shown in Figure 1. Corresponding clathrate parameters, including mass loss Δm, %, guest/host molar ratio S, temperature of DTG (differential thermogravimetric) peak T_{DTG}, and enthalpy of guest elimination ΔH_e, are given in Table 1. The binding of ethanol,

Table 1. Thermal Analysis Data for Calixarene 1 Clathrates

guest	Δm, %	S	T_{DTG}, °C	ΔH_e, kJ/mol
CH$_3$OH	1.05	0.24	75	a
CH$_3$CN	4.96	0.92	153	27 ± 3
(CH$_3$)$_2$CO	7.17	0.96	138	26 ± 2
CH$_2$Cl$_2$	9.55	0.89	169	28 ± 2
CHCl$_3$	13.3	0.93	156	32 ± 2
C$_2$H$_4$Cl$_2$	20.7	1.90	91	41 ± 1
CCl$_4$	16.4	0.92	150	35 ± 1

^{a}Guest elimination enthalpy cannot be determined.

trichloroethylene, toluene, pyridine, and cyclohexane by host **1** is on the trace level, with a mass loss of 0.22÷0.74% and S = 0.01÷0.05, which is slightly above the sensitivity threshold of the used thermoanalyzer, SI. Still, corresponding saturation products have a noticeable guest elimination step on their TG curves with a DTG peaks from 69 °C for pyridine to 208 °C for cyclohexane, SI. No binding of water and benzene was observed, Figure 1a and SI.

All clathrates prepared by direct saturation of **1** with guest vapors lose the bound guest in one step, Figure 1. The values of guest contents S in the saturation products of **1** describe the composition of clathrates that are stable at room temperature (∼25 °C), which is the point of sample equilibration in argon flow before the thermal analysis. Composition of stable clathrates is close to the 1:1 host/guest molar ratio for all included guests except for methanol and DCE, Table 1. The same values of guest contents near S = 1 have been found from vapor sorption isotherms for systems of **1** with acetonitrile, acetone, dichloromethane, chloroform, and tetrachloromethane.[6] Close composition values, 1:1 or S = 1, were obtained earlier in X-ray studies of **1**·CHCl$_3$,[17] **1**·CH$_2$Cl$_2$,[17] **1**·CH$_3$CN,[18] and **1**·CH$_3$NO$_2$ monocrystals.[18]

The lower value of methanol contents S = 0.24 obtained in the present work, Table 1, than that in X-ray studies, S = 1,[17] is caused by the low stability of this clathrate, which can be seen in its thermogram, Figure 1b. This experiment shows the loss of guest just beginning from room temperature. So, the observed S value for methanol is a function of clathrate exposure to open air or inert gas flow before heating. The other studied clathrates with 1:1 stoichiometry are much more stable, showing DTG peaks in the range of T_{DTG} = 138÷169 °C, Table 1.

A single guest, which is included by **1** with a molar ratio higher than 1:1 in the present work, is DCE. The content of this guest in a saturated clathrate is S = 1.90, Table 1. This composition and XRPD diffractogram, SI, of the prepared clathrate are close to those of the **1**·2DCE single crystal.[19] This

clathrate is stable in the open air at room temperature but loses guest at much the lower temperature of T_{DTG} = 91 °C than the other clathrate-forming guests, except methanol.

Each studied binary clathrate exhibits only one endothermic peak of guest elimination with clathrate-host pseudopolymorphic transition, and no polymorphic transitions without mass loss were observed. Corresponding elimination enthalpies ΔH_e are in the range of 27−41 kJ per 1 mol of guest, which are not much different from guest vaporization enthalpies ΔH_V at 25 °C: 33.4 (CH$_3$CN), 31.3 (CH$_3$)$_2$CO), 29.0 (CH$_2$Cl$_2$), 31.4 (CHCl$_3$), and 32 kJ/mol (CCl$_4$).[20] Only for DCE, its value of ΔH_e = 41 kJ/mol is a little higher than ΔH_V = 35.22 kJ/mol.[20] The small difference between ΔH_e and ΔH_V values may mean that calixarene **1** effectively collapses after guest elimination. The same conclusion may be made from the one-step shape of thermograms observed in all studied cases.

Guest Exchange in Calixarene 1 Clathrates. Formation of 2:1 (S = 1.90) clathrate by host **1** with DCE presents a good opportunity for guest exchange in this inclusion compound. This clathrate has rather loose packing with one DCE molecule included in the host molecular cavity and the other one kept in the interstitial space.[19] So, first, an interstitial DCE may be exchanged, and then a new guest may swap positions with neighboring encapsulated DCE. Both these processes should have a lower kinetic barrier than in 1:1 clathrates of **1**, where the only place for guests is inside its bowls forming columns of head-to-tail type.[17] A relatively low thermal stability of DCE clathrate may have the same explanation.

An exchange in **1**·1.90DCE clathrate was studied for vapors of 13 guests (**G**) mentioned above according to the next scheme 1:

$$1 \cdot 1.90(DCE) + x G_{(vap)}$$
$$\xrightarrow{25°C} 1 \cdot x G \cdot y DCE + (1.90 - y) DCE_{(vap)} \quad (1)$$
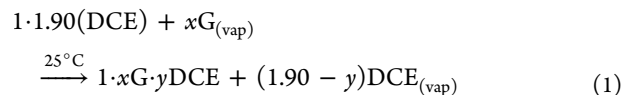
The guest exchange products were analyzed using simultaneous TG/DSC/MS method. Thermograms for each studied product are shown in Figure 2 and in the SI. Corresponding parameters are given in Table 2, including mass loss, contents of residual DCE, S_{DCE} and of the second bound guest per 1 mol of host, S_G, temperature of DTG peaks of guest release T_{DTG}, and enthalpy of guest release per 1 mol of released guests ΔH_1.

The data obtained show formation of clathrates with ethanol, benzene, cyclohexane, and pyridine, which are not bound through direct saturation of guest-free host. Respective contents of these guests are close to 1:1 for ethanol, pyridine, and cyclohexane and 1:2 for benzene, Figure 2 and Table 2. Residual contents of DCE in ethanol and benzene clathrates, S_{DCE}, are on the trace level: 0.01 and 0.02, respectively. The exchange for pyridine and cyclohexane leaves a significant amount of DCE in the clathrate: S_{DCE} = 0.10 and S_{DCE} = 0.17, respectively, Figure 2g,h. Despite the presence of a significant amount of DCE, the prepared pyridine clathrate has a XRPD diffractogram, SI, which is rather close to that simulated from X-ray single crystal data for **1**·C$_5$H$_5$N clathrate[21] but with several additional reflections of small intensity.

The methanol content in the clathrate **1**·0.83CH$_3$OH·0.02DCE prepared by scheme 1 is 3.5 times higher than in clathrate prepared by direct saturation, Table 1. For comparison, methanol does not replace the more volatile guest, dichloromethane, in its more stable clathrate with **1**. This clathrate **1**·0.89CH$_2$Cl$_2$ equilibrated with headspace of liquid
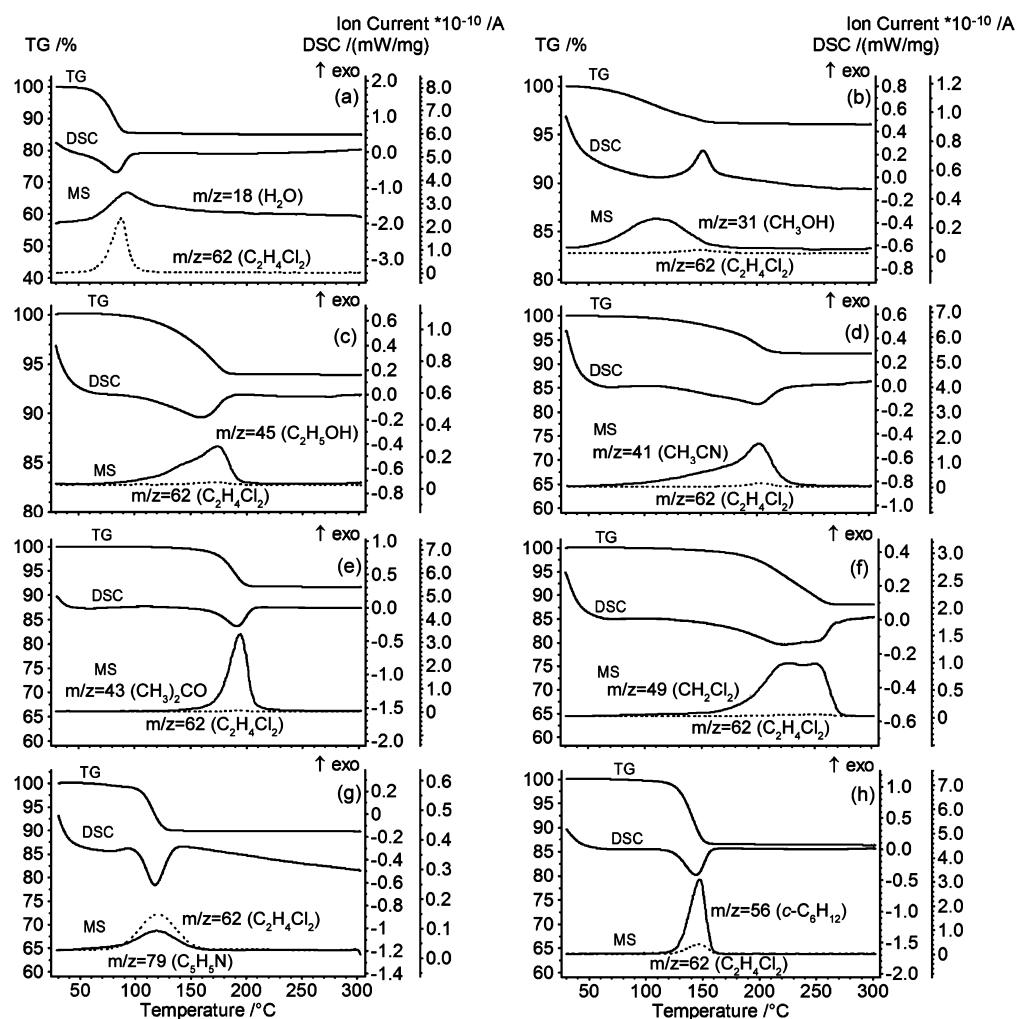
Figure 2. Thermograms of guest exchange products formed by equilibration of **1**·1.90DCE clathrate with headspace of liquid guests at $P/P_0 = 1$ and $T = 25$ °C: (a) H_2O (b) CH_3OH, (c) C_2H_5OH, (d) CH_3CN, (e) $(CH_3)_2CO$, (f) CH_2Cl_2, (g) C_5H_5N, and (h) c-C_6H_{12}.

Table 2. Thermal Analysis Data for Guest Exchange Products Formed by Equilibration of 1·1.90DCE Clathrate with Headspace of Liquid Guests at $P/P_0 = 1$ and $T = 25$°C[a]

guest	MR_D, cm^3/mol	Δm, %	S_G	S_{DCE}	T_{DTG}, °C	ΔH_1, kJ/mol
H_2O	3.7	14.6	<0.1	1.22	82[b]	39 ± 2[c]
CH_3OH	8.2	3.77	0.83	0.02	109;147[b]	−12 ± 2[d]
C_2H_5OH	13.0	6.02	0.98	0.01	169	39 ± 3[e]
CH_3CN	11.1	7.79	1.29	0.08	200	27 ± 4
$(CH_3)_2CO$	16.2	8.22	1.07	0.03	189	30 ± 3
CH_2Cl_2	16.4	11.9	1.10	0.04	228	39 ± 4
$CHCl_3$	21.3	14.2	0.98	0.02	161	27 ± 1
C_5H_5N	24.2	10.1	0.89	0.10	115	28 ± 2
C_6H_6	26.3	5.00	0.46	0.02	83	28 ± 2
CCl_4	26.4	17.7	0.91	0.14	146	35 ± 2
c-C_6H_{12}	27.7	13.4	1.12	0.17	142	32 ± 1

[a]Mass losses of guest exchange products for C_2HCl_3 and $C_6H_5CH_3$ are 0.70 and 0.74%, respectively, in the range of 120−280 °C. [b]DTG peak corresponds to DCE release from clathrate. [c]Enthalpy ΔH_1 of DCE release. [d]Enthalpy of exothermic peak of host collapse per 1 mol of host at 152 °C; the other ΔH_1 values are calculated per 1 mol of bound guests. [e]DSC peak is at 158 °C.

methanol for 72 h does not change its composition and thermograms, SI. The XRPD diffractogram of **1**·0.83CH$_3$OH·0.02DCE clathrate, SI, nearly coincides with diffractogram simulated from X-ray data for **1**·CH$_3$OH single crystal, which was grown by addition of liquid methanol to solution of **1** in p-xylene.[17]

A larger inclusion capacity of 24 and 40% than that in direct saturation was found also after exchange of DCE for dichloromethane and acetonitrile, respectively. Acetone and chloroform are included by **1** using direct and exchange methods with nearly the same composition of the resulting product, Figure 2, SI, and Tables 1 and 2. No difference in

inclusion capacity for tetrachloromethane was observed in its exchange product. However, the last one contains also some not exchanged DCE, $S_{DCE} = 0.14$.

Being bound in larger amounts in guest exchange, small guests CH_3OH, CH_3CN, $(CH_3)_2CO$, and CH_2Cl_2 also form more thermostable clathrates at 34−59 °C in this process than in direct saturation of guest-free **1**, as can be seen in comparison to the DTG peaks for clathrates prepared by these two methods, Tables 1 and 2. One can suppose that the initial structure of **1·1.90DCE** clathrate, when collapsing upon exchange with a smaller amount of entering guest, captures the last more efficiently. There is no influence of the preparation method on the thermal stability of clathrates formed by larger guests, chloroform and tetrachloromethane. Generally, a sinusoidal dependence of the DTG peak temperature on guest size parameter, MR_D, is observed with a maximum for dichloromethane and a minimum for benzene, Table 2. So, in guest exchange, host **1** is much more selective than in binary systems, Table 1.

Very different behavior in the guest exchange process was found for toluene, trichloroethylene, and water. Being not included by **1** above the trace level in the direct saturation process, these guests also repulse the bound DCE from its clathrate with **1**. So, with saturated vapors of toluene and trichloroethylene, practically pure calixarene **1** is formed, which practically does not lose mass and does not perform any MS peaks of bound guests above the noise level in thermal analysis, SI. With water, the exchange process according scheme 1 gives clathrate of **1** with DCE amount $S_{DCE} = 1.22$, Table 2, which is one-third less than its initial value of $S_{DCE} = 1.90$, Table 1. The resulting exchange product has a very small amount of water, $S_G < 0.1$. Probably, these three guests, H_2O, $C_6H_5CH_3$, and C_2HCl_3, behave as a catalyst, which removes a kinetic barrier of DCE elimination from clathrate.

The lower extent of DCE removal from its clathrate by water vapors may be caused by a lower solubility of DCE in liquid water than in toluene and trichloroethylene, which are present in the studied systems during guest exchange. For comparison, the limiting activity coefficient of DCE in water is $\gamma^\infty = 641$,[22] and in toluene this value is only $\gamma^\infty = 1.21$.[23] Respectively, when expelled from clathrate, DCE can form very dilute solutions (~1:60 v/v in the systems with 10 mg of clathrate and 100 μL of the second guest) in liquid $C_6H_5CH_3$ and C_2HCl_3 with very low thermodynamic activity, which shifts the equilibrium to the state of complete guest elimination. In water solution, DCE becomes saturated already at 1:150 v/v dilution. Hence, at least 60% of DCE should remain in the vapor and clathrate phases at the equilibrium. The increase of water amount to 0.50 and 1.50 mL in the studied systems reduces the resulting contents of bound DCE from 14.6 to 8.25 and 2.04% (w/w), respectively, Table 2 and SI. So, the residual DCE contents in the clathrate may be controlled by variation of the water/clathrate ratio.

Once the final activity of a leaving guest is important, one may wonder whether this factor is a single one defining DCE elimination from its clathrate in systems with H_2O, $C_6H_5CH_3$, and C_2HCl_3. To check this possibility, we made a blank experiment with only the desorption process in the studied system without competing vapors of a second guest. For this, **1·1.90DCE** clathrate was equilibrated under the same conditions with nonvolatile solvent polyethylene glycol (PEG 400) for 72 h. Thermoanalysis of the resulting product showed its composition as **1·1.79DCE**, SI. So, a very slow desorption process really occurs with guest loss slightly above experimental

errors. However, this loss is negligibly small compared with that caused by the studied nonbound guests. So, guests H_2O, $C_6H_5CH_3$, and C_2HCl_3 play the active role in elimination of DCE from its clathrate with **1**.

In most cases, thermal decomposition of clathrates prepared by guest exchange gives a normal endothermic effect with the enthalpy of guest release ΔH_1 in the range 26÷39 kJ/mol calculated per 1 average mol of both bound guests. These values are close to those of the samples prepared in binary host−guest systems, Table 1, except for dichloromethane, which, having replaced DCE in **1**, shows more endothermic ΔH_1 values.

More interesting is the exothermic host collapse with $\Delta H_1 = -12 \pm 2$ kJ/mol observed for the product of DCE exchange for methanol, **1·0.83CH_3OH·0.02DCE**, Figure 2b. This clathrate does not show a definite endothermic effect, as well as the product of direct saturation, **1·0.24CH_3OH**, Figure 1b, because of the very smooth release of methanol. However, above 130 °C, when most of the CH_3OH has already gone, the exothermic peak occurs on the DSC curve at 152 °C almost coinciding with the peak of the evolved traces of DCE on the ion thermogram at 150 °C. In this analysis, a delay of the DSC curve and ion thermogram at 3 and 5 °C, respectively, should be taken into account compared with the DTG curve. This exothermic effect may be regarded as a phase transition from the loose β_0-phase of **1** formed with elimination of methanol to the tightly packed guest-free α-phase of **1**. The phase transition from the β_0 to α-phase is confirmed by their XRPD patterns, which are essentially different, SI. The cause of the loose β_0-phase formation may be the traces of nonreplaced DCE in **1** along with its special guest exchange prehistory.

The size of the observed exoeffect does not depend much on the preliminary treatment of the initial **1·0.83CH_3OH·0.02DCE** sample. This sample heated at 100 °C inside the thermoanalyzer in argon flow for 30 min and then cooled to the room temperature has a thermogram, Figure 3,
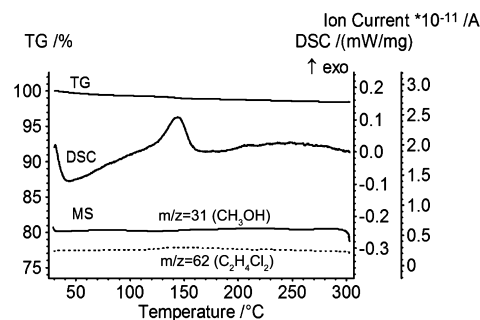

Figure 3. Data of TG/DSC/MS analysis of the metastable porous phase of **1** prepared by heating of **1·0.83CH_3OH·0.02DCE** clathrate at 100 °C in argon flow for 30 min and cooling to room temperature.

corresponding to **1·0.2CH_3OH·0.01DCE** composition with enthalpy of $\Delta H_1 = -10 \pm 1$ kJ/mol. This exothermic effect takes place from 111 to 169 °C with only 0.42% of mass loss, which is slightly above the baseline drift level. So, this transition may be regarded as a polymorphic one. Still, the packing of loose β_0 phase is not much different from that of the initial guest-exchange product **1·0.83CH_3OH·0.02DCE** (β phase). The XRPD diffractogram determined for the **1·0.2CH_3OH·0.01DCE** sample (loose β_0 phase) is rather similar to the diffractogram of the β phase with the same

position of main reflexes but indicating the more amorphous nature of β_0 phase, SI.

Being stable at room temperature, the loose phase of **1** is similar to the β_0 phases of *tert*-butylcalix[6]arene[9] or the derivative of *tert*-butylthiacalix[4]arene.[10] However, the ability of calixarene **1** definitely to remember a guest that has gone from the clathrate formed only in guest exchange is a new property, which has not been known yet.

Something like an implicit contribution of the *exo*-effect can be supposed also for decomposition of ethanol clathrate prepared by guest exchange, Figure 2c and Table 2. This clathrate has a DSC peak, which is lower by 11 °C than the corresponding DTG peak, whereas normally the DSC signal has a delay of ~3 °C compared with that for the DTG curve, which is observed in all other studied cases except methanol clathrate. This may be a result of exothermic contribution to DSC data near the end of ethanol elimination, which is subtracted from the *endo*-peak of this guest release.

CONCLUSIONS

New properties of *tert*-butylthiacalix[4]arene (**1**) clathrates in guest exchange were found, which have not been previously known for any other calixarene and can be a good basis for practical applications related to vapor encapsulation or recognition. This exchange can give clathrates of **1** with much higher thermal stability than those prepared by direct saturation of guest-free calixarene **1** with vapors of the same guests. In several cases, these clathrates can be prepared only by guest exchange. Otherwise, the saturation of the initial **1**·1.90DCE clathrate with a second guest gives a guest-free host. When headspace of liquid water is used in the exchange, the resulting contents of 1,2-dichloroethane in clathrate may be controlled by variation of the clathrate/water ratio, whereas water does not enter the solid phase above the trace level. For water and two organic guests, this level is still enough to catalyze decomposition at 25 °C of the clathrate, which otherwise is stable up to 91 °C.

A genuine molecular recognition of methanol by **1** was observed in the formation of a metastable loose polymorph of **1** that remembers this compound after its release from a guest-exchange product. The written memory of methanol can be read in the DSC experiment. No other guest studied can be thus remembered by **1**. This is a first example where methanol can be remembered by the host and the first one where memory of a released guest was found to be possible only after guest exchange.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Powder X-ray diffraction data and data of simultaneous TG/DSC/MS analysis for *tert*-butylthiacalix[4]arene and its clathrates. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Fax: +7 843 2927418. Tel: +7 843 2337309. E-mail: Valery.Gorbatchuk@ksu.ru.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Ripmeester, J. A.; Enright, G. D.; Ratcliffe, C. I.; Udachin, K. A.; Moudrakovski, I. L. *Chem. Commun.* **2006**, 4986−4996.

(2) Yakimova, L. S.; Ziganshin, M. A.; Sidorov, V. A.; Kovalev, V. V.; Shokova, E. A.; Tafeenko, V. A.; Gorbatchuk, V. V. *J. Phys. Chem. B* **2008**, *112*, 15569−15575.

(3) Xu, H.; Rudkevich, D. M. *Chem.—Eur. J.* **2004**, *10*, 5432−5442.

(4) Ziganshin, M. A.; Yakimova, L. S.; Khayarov, K. R.; Gorbatchuk, V. V.; Vysotsky, M. O.; Böhmer, V. *Chem. Commun.* **2006**, 3897−3899.

(5) Ramon, G.; Jacobs, A.; Nassimbeni, L. R.; Yav-Kabwit, R. *Cryst. Growth Des.* **2011**, *11*, 3172−3182.

(6) Gorbatchuk, V. V.; Tsifarkin, A. G.; Antipin, I. S.; Solomonov, B. N.; Konovalov, A. I.; Lhotak, P.; Stibor, I. *J. Phys. Chem. B* **2002**, *106*, 5845−5851.

(7) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Science* **2002**, *296*, 2367−2369.

(8) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Chem. Commun.* **2002**, 2952−2953.

(9) Yakimov, A. V.; Ziganshin, M. A.; Gubaidullin, A. T.; Gorbatchuk, V. V. *Org. Biomol. Chem.* **2008**, *6*, 982−985.

(10) Safina, G. D.; Gavrilova, O. M.; Ziganshin, M. A.; Stoikov, I. I.; Antipin, I. S.; Gorbatchuk, V. V. *Mendeleev Commun.* **2011**, *21*, 291−292.

(11) Safina, G. D.; Validova, L. R.; Ziganshin, M. A.; Stoikov, I. I.; Antipin, I. S.; Gorbatchuk, V. V. *Sens. Actuators, B* **2010**, *148*, 264−268.

(12) Ziganshin, M. A.; Yakimov, A. V.; Safina, G. D.; Solovieva, S. E.; Antipin, I. S.; Gorbatchuk, V. V. *Org. Biomol. Chem.* **2007**, *5*, 1472−1478.

(13) Atwood, J. L.; Barbour, L. J.; Lloyd, G. O.; Thallapally, P. K. *Chem. Commun.* **2004**, 922−923.

(14) Ananchenko, G. S.; Udachin, K. A.; Dubes, A.; Ripmeester, J. A.; Perrier, T.; Coleman, A. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 1615−1618.

(15) Sone, T.; Ohba, Y.; Moriya, K.; Kumada, H.; Ito, K. *Tetrahedron* **1997**, *53*, 10689−10698.

(16) Armarego, W. L. F.; Chai, C. L. L. *Purification of laboratory chemicals*; Butterworth-Heinemann: Oxford, U.K., 2009.

(17) Akdas, H.; Bringel, L.; Graf, E.; Hosseini, M. W.; Mislin, G.; Pansanel, J.; de Cian, A.; Fischer, J. *Tetrahedron Lett.* **1998**, *39*, 2311−2314.

(18) Arduini, A.; Nachtigall, F. F.; Pochini, A.; Secchi, A.; Ugozzoli, F. *Supramol. Chem.* **2000**, *12*, 273−291.

(19) Iki, N.; Kabuto, C.; Fukushima, T.; Kumagai, H.; Takeya, H.; Miyanari, S.; Miyashi, T.; Miyano, S. *Tetrahedron* **2000**, *56*, 1437−1443.

(20) *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; Linstrom, P.J., Mallard, W.G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2012; http://webbook.nist.gov; retrieved June 27, 2012.

(21) Bilyk, A.; Hall, A. K.; Harrowfield, J. M.; Hosseini, M. W.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **2001**, *40*, 672−686.

(22) Sherman, S. R.; Trampe, D. B.; Bush, D. M.; Schiller, M.; Eckert, Ch. A.; Dallas, A. J.; Li, J.; Carr, P. W. *Ind. Eng. Chem. Res.* **1996**, *35*, 1044−1058.

(23) Gerasimov, A. V.; Ziganshin, M. A.; Vandyukov, A. E.; Kovalenko, V. I.; Gorbatchuk, V. V.; Caminade, A.-M.; Majoral, J.-P. *J. Colloid Interface Sci.* **2011**, *360*, 204−210.

11385

dx.doi.org/10.1021/jp3065739 | *J. Phys. Chem. B* 2012, 116, 11379−11385