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Thermodynamic Parameters of Sublimation of Calix[4]arenes

O. V. Surov[a], N. Zh. Mamardashvili[a], G. P. Shaposhnikov[b], and O. I. Koifman[a]

[a] *Institute of Solution Chemistry, Russian Academy of Sciences,*
ul. Akademicheskaya 1, Ivanovo, 153045 Russia
e-mail: ovs@isc-ras.ru
[b] *Ivanovo State University of Chemical Technology, Ivanovo, Russia*

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Abstract—The temperature dependences of the vapor pressure of calix[4]arenes were determined by the Knudsen effusion method. Some calix[4]arenes can form congruently subliming intramolecular compounds with a solvent. The thermodynamic parameters of the sublimation of the compounds were calculated. Molecules of organic solvents incorporated in the cavity of calix[4]arenes stabilize the crystal lattice, increasing the enthalpy of sublimation. The electrostatic interactions presumably make a significant contribution to stabilization of the crystal lattice of stoichiometric complexes of calix[4]arenes with solvents.

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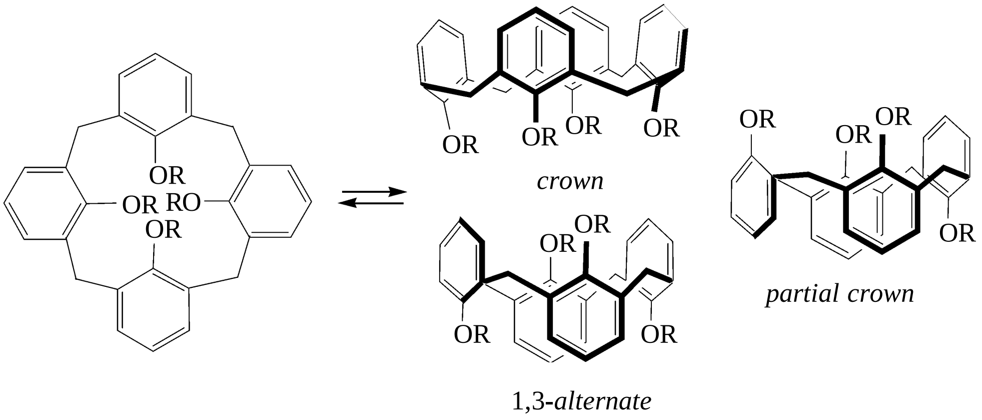
In the past two decades, much researchers' attention has been focused on the development of compounds containing large molecular cavities. The interest in these compounds is due to their capability to form inclusion complexes, i.e., to participate in receptor–substrate or host–guest interactions. Particular attention is given to calix[4]arenes, cyclic products of the condensation of phenols with aldehydes.



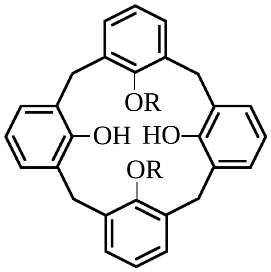
Chemical modification of the active reaction centers in these molecules allows adjustment of the geometry of the complexing cavity. The resulting molecules form inclusion compounds with cations, anions, and small organic molecules of various nature.

Despite active development of the chemistry of calix[4]arenes in the recent years, it is still difficult to unambiguously formulate any correlations between the structure and complexing power of calix[4]arenes because of the sophisticated relationships between the complexation constants and structures of both host and guest molecules. Studies of the crystal structures of calix[4]arene hosts with included guests, mass-spectrometric studies of the host–guest interactions in the gas phase, and data obtained by solution chemistry methods allow formulation of certain general relationships whose applicability, however, is restricted to specific systems [1].

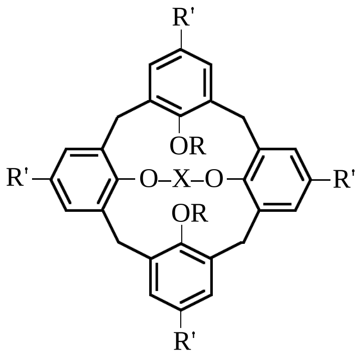
It is known that calix[4]arenes retain the solvent from which they are crystallized. For example, *p-tert-*

butylcalix[4]arene forms solid complexes with chloroform, toluene, xylene, and anisole [2]; *p-tert*-butylcalix[5]arene, with isopropyl alcohol [3] and acetone [2]; *p-tert*-butylcalix[6]arene, with chloroform and methanol; and *p-tert*-butylcalix[8]arene, with chloroform [4]. However, the guests are retained by these compounds differently. Whereas the cyclic octamer loses chloroform within several minutes at room temperature and atmospheric pressure, the cyclic hexamer does not completely lose chloroform even on keeping for 6 days at 237°C in a vacuum (1 mm Hg). The position of the guest in the complex is different and depends on the structures of both the guest and the host. According to [5], in the complex of *p-tert*-butylcalix[4]arene with toluene, the calixarene exists in the *crown* conformation, and toluene is located in the center of the cavity, i.e., an internal complex is formed. Similar complexes are formed with benzene, *p*-xylene, and anisole [2]. At the same time, *p*-(1,1,3,3-tetramethylbutyl)calix[4]arene forms with aromatic compounds external complexes, and calix[5]arene forms with acetone a 1 : 2 complex in which one acetone molecule is located in the cavity and the other, outside it [2]. According to [6], solvent-free *p*-(1,1,3,3-tetramethylbutyl)calix[4]arene exists in the *crown* conformation, and two 1,1,3,3-tetramethylbutyl groups are oriented inside, covering the cavity, i.e., intramolecular complexation takes place. Minor changes in the structures of the host and guest can exert a significant effect on the stability and structure of the molecular complex [2–6]. Some derivatives of calix[*n*]arenes can form ensembles in which the molecules are held together by intermolecular hydrogen bonds [7].

In this study, we attempted to experimentally estimate the enthalpy of sublimation of a series of calix[4]arenes with the aim to elucidate the structure–property relationships. We studied the following compounds: 25,26,27,28-tetrahydroxycalix[4]arene (**I**), 25,27-dimethoxy-26,28-dihydroxycalix[4]arene (**II**), 25,27-dimethoxycalix[4]arene-crown[6] (**III**), 25,27-dimethoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene-crown[5] (**IV**), 25,27-diethoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene-crown[5] (**V**), 25,27-dibenzyloxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene-crown[5] (**VI**), and 25,27-dimethoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene-crown[6] (**VII**).



I, II



III–VII

R = H (**I**), CH_3 (**II**); R = CH_3, R' = H, X = $CH_2CH_2(OCH_2CH_2)_4$ (**III**); R = CH_3, R' = *t*-Bu, X = $CH_2CH_2(OCH_2CH_2)_3$ (**IV**); R = C_2H_5, R' = *t*-Bu, X = $CH_2CH_2(OCH_2CH_2)_3$ (**V**); R = $CH_2C_6H_5$, R' = *t*-Bu, X = $CH_2CH_2(OCH_2CH_2)_3$ (**VI**); R = CH_3, R' = *t*-Bu, X = $CH_2CH_2(OCH_2CH_2)_4$ (**VII**).

The thermodynamic parameters of sublimation of **I**–**VII** were calculated by the well-known formulas

$$\Delta H_{\mathrm{sub}} = -Rd(\ln P)/d(1/T), \quad (1)$$

$$\Delta G_{\mathrm{sub}} = -RT\ln(P/P_0), \quad (2)$$

$$\Delta S_{\mathrm{sub}} = -d(\Delta G_{\mathrm{sub}})/dT, \quad (3)$$

where P is the partial pressure of the compound being sublimed, Pa; $P_0 = 1.013 \times 10^5$ Pa, atmospheric pressure; T, temperature, K; and $R = 8.314$ J mol^{-1} K^{-1}, gas constant.

Since the measurements were made within a relatively narrow temperature range and the plots of $\ln P$ vs. $1/T$ and ΔG_{sub} vs. T are well approximated by straight lines, in the subsequent comparative analysis we used the mean values of the thermodynamic functions without their recalculation to the standard temperature of 298.15 K.

Figure 1 shows the dependences of $\ln P$ of **I**–**VII** on reciprocal temperature. The temperature dependence of the vapor pressure in the $\ln P–T^{-1}$ coordinates is linear:

$$\ln P = a + b/T. \quad (4)$$

The parameters of linear equation (4) and the mean values of the enthalpy and entropy of sublimation of **I**–**VII** are given in the table.

Coefficients of the linear equation $\ln P = a + b/T^a$ and mean values of the enthalpy and entropy of sublimation of **I**–**VII**

Comp. no.	a	$-b/100$	ΔH_{sub}, kJ mol^{-1}	ΔS_{sub}, J mol^{-1} K^{-1}
I	36.6 ± 0.9	15.7 ± 0.3	131 ± 3	208 ± 8
II	28 ± 1	14.7 ± 0.5	122 ± 4	134 ± 10
III	25 ± 1	11.7 ± 0.4	97 ± 3	118 ± 12
IV	28.0 ± 0.6	10.8 ± 0.2	90 ± 2	137 ± 5
V	19.2 ± 0.5	9.5 ± 0.2	79 ± 2	65 ± 4
VI	20.5 ± 0.8	9.3 ± 0.3	78 ± 3	74 ± 7
VII	24 ± 1.4	12.1 ± 0.5	100 ± 4	100 ± 12

[a] The regression coefficients of the linear dependences are within 0.995–0.999. The vapor pressure P is in Pa.

All the compounds studied can be subdivided into two groups. The elemental analysis and ^{1}H NMR spectra show that compounds **I**–**III** and **VII** form stable intramolecular complexes of the compositions $\mathbf{I} \cdot C_6H_{14} \cdot CH_2Cl_2$ $\mathbf{II} \cdot C_6H_{14}$, $\mathbf{III} \cdot C_6H_{14}$, and $\mathbf{VII} \cdot CH_3OH$, subliming congruently. Compounds **IV**–**VI** constituting the second group do not form stable complexes with solvents. The differences in the complexing power can be accounted for as follows. Apparently, in the complexes $\mathbf{I} \cdot C_6H_{14} \cdot CH_2Cl_2$, $\mathbf{II} \cdot C_6H_{14}$, and $\mathbf{III} \cdot C_6H_{14}$ calix[4]arene is in the *crown* conformation and hexane is located in the center of the complexing cavity, with the C–H–π interaction between the hydrogen atoms of the hexane molecule and the aromatic rings of calixarene. In contrast to the complexes $\mathbf{II} \cdot C_6H_{14}$ and $\mathbf{III} \cdot C_6H_{14}$, the complex $\mathbf{I} \cdot C_6H_{14} \cdot CH_2Cl_2$ contains, along with a hexane molecule, also a dichloromethane molecule. Apparently, the dichloromethane molecule coordinates with the hydroxy groups of the lower rim and is located under the complexing cavity of the calix[4]arene, with the C–H–π interaction between the hydrogen atoms of the dichloromethane molecule and two oxygen atoms of the adjacent hydroxy groups of tetrahydroxycalix[4]arene. Such an arrangement of the guest molecule was reported in [2] for the complex of calix[5]arene with acetone. The diametral arrangement of the two hydroxy groups on the lower rim of calixarenes **II** and **III** is apparently unfavorable for binding of the dichloromethane molecule, and the complexes $\mathbf{II} \cdot C_6H_{14}$ and $\mathbf{III} \cdot C_6H_{14}$ containing only the hexane molecule in the center of the complexing cavity are formed. Calix[4]arene **VII** with *tert*-butyl groups on the upper rim forms with methanol a stable complex in which the guest molecule is arranged inside the complexing cavity of the host, with the CH_3–π interaction between the methyl hydrogen atoms of the methanol molecule and aromatic rings of the calixarene. Presumably, the *tert*-butyl group also favors the complexation because of the CH_3–π interaction between its methyl groups and the oxygen atom of the methanol molecule. Along with the electronic factors, the so-called size effects are also essential in the formation of molecular complexes of this type. In particular, Ghidini et al. [8] examined the complexing power of calix[4]arene-crown[3] (**VIII**) and 5,11,17,23-tetra-*tert*-butylcalix[4]arene-crown[3] (**IX**) toward nitromethane and malonodinitrile; they showed that, although in malonodinitrile the C–H bonds are more polar, calix[4]arene **IX** containing bulky substituents binds more efficiently a smaller molecule of nitromethane. Therefore, it is quite natural that calix[4]arenes **I**–**III** containing no substituents on the upper rim bind a larger guest molecule (hexane), whereas *tert*-butyl-substituted calix[4]arene **VII** binds a smaller guest molecule (methanol).

As noted above, calix[4]arenes **IV**–**VI** do not form stable complexes with the examined solvents. Apparently, the crown[5] ether bridge at the lower rim of these compounds unfavorably affects the geometric parameters of the complexing cavity, so that the size matching between the host molecule cavity and the guest molecule is disturbed. It should also be noted that in calix[4]arenes **V** and **VI** the complexing cavi-

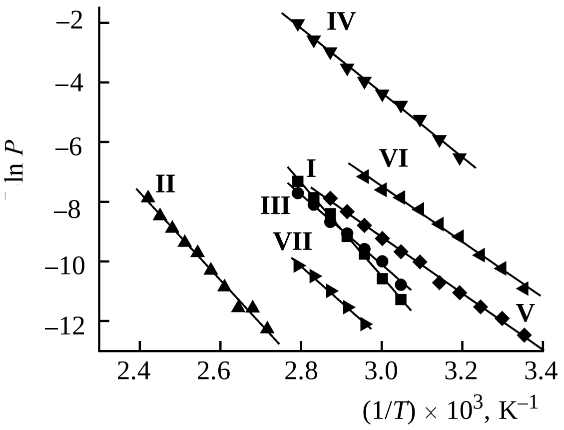


Fig. 1. Temperature dependences of the vapor pressures of **I**–**VII**.

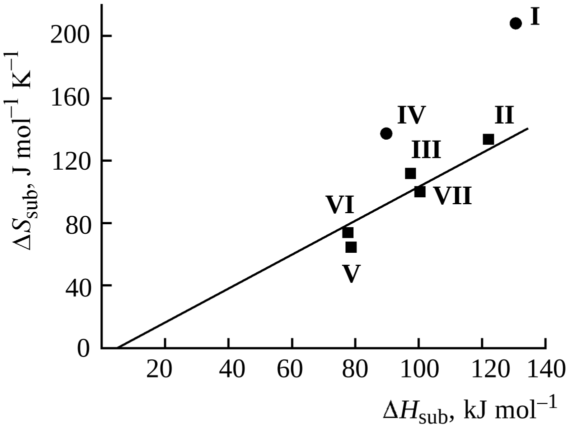


Fig. 2. Thermodynamic compensation effect in sublimation of calixarenes.

ties of the receptors are already occupied by one of the ethoxy or benzyloxy groups, respectively, i.e., the internal complexation is observed.

The structural differences between **IV** and **VII** are determined by the presence of an additional OCH_2CH_2 unit in the crown ether bridge of **VII**. As a result of increased length of the polyether bridge, compound **VII** forms a stable intramolecular compound with the solvent; the vapor pressure of complex **VII** is considerably lower than that of compound **IV**, and ΔH_{sub} is appreciably higher. Furthermore, in contrast to the other calixarenes studied, noticeable vaporization of **VII** starts only after melting at 53.3°C. A considerable increase in ΔH_{sub} with an appreciable decrease in the melting point seems at first glance unexpected. However, Klenke and Friederichsen [9] showed that the formation of stoichiometric solvates can lead to abnormally low melting points with simultaneous strengthening of the crystal lattice. Using solution calorimetry, they found that the stabilization gain in the energy in solvation of flurbiprophene in DMF is 9.8 kJ mol^{-1}, and the entropy of the process is 33 J mol^{-1} K^{-1}. For **IV** and **VII**, these quantities are 10 kJ mol^{-1} and 37 J mol^{-1} K^{-1}, respectively. A decrease in the melting point with simultaneous stabilization of the crystal lattice of the solvated phase is attributed in [9] to the absence of hydrogen bonds, which is well consistent with the concept [10] that the melting point correlates with the contribution of Coulomb forces to the crystal lattice energy. An important role of electrostatic interactions in stabilization of calixarene complexes is also noted in [1].

The heats of sublimation of compounds of the first group are higher than those of compounds of the second group by 10–40 kJ mol^{-1} on the average. ΔH_{sub} decreases in the order **I** > **II** > **III**, in parallel with a decrease in the number of hydroxy groups. The heats of sublimation of **III** and **VII** are close, since these compounds are structurally similar. For **V** and **VI** (second group of compounds), ΔH_{sub} differs insignificantly (by 1 kJ mol^{-1}), and the heat of sublimation of **IV** is appreciably higher.

Despite the differences in the complexing properties, compounds of the first and second groups demonstrate the thermodynamic compensation effect, except compounds **I** and **IV** whose ΔS_{sub} values lie above the linear correlation (Fig. 2). This fact may be due to the conformational mobility of compounds **I** and **IV**, although in the solid state compound **I** exists exclusively in the *crown* conformation because of strong intermolecular hydrogen bonding. Golubchikov and Perlovich [11] analyzed the thermodynamic parameters of the sublimation of crystalline porphyrins and suggested that their energy parameters correlate with the extent of “freezing” of the conformational mobility of their molecules. Indeed, compounds **I** and **IV** with within its group, have the maximal packing density of the unit cell and maximal ΔH_{sub}. Apparently, vaporization is accompanied by the maximal increase in the entropy.

Thus, the examined calix[4]arenes can form with solvents stable intramolecular compounds subliming congruently. Our results show that the thermodynamic parameters of the sublimation are very sensitive to the structural features of the calix[4]arenes. Organic solvent molecules incorporated in the cavities of calix[4]arenes stabilize the crystal lattice, increasing ΔH_{sub}. The complexing properties of the examined calix[4]arenes are determined by the conformational and steric factors, by the presence of functional groups capable of hydrogen bonding, and by the Coulomb contribution to the crystal lattice energy.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker-200 spectrometer (operating frequency 200.1 MHz, solvent $CDCl_3$, internal reference TMS).

The temperature dependence of the vapor pressure was determined by the effusion method. The experimental effusion installation was constructed on the basis of a VOU-1A vacuum unit ensuring the residual pressure in the system of no higher than 10^{-4} mm Hg. A ~4 cm^3 stainless steel effusion cell was placed in an electric oven. The cell temperature was controlled accurate to ±0.1 K with a battery of thermocouples and a TRM-34 two-loop heating control device. The effusion cell was also equipped with an electromagnetic valve hermetically closing the effusion orifice before reaching the required temperature. A glass ampule with a weighed portion of a sample (±0.05 mg) was placed in the effusion cell, the system was evacuated, and the cell heating was switched on. After reaching the required temperature, the orifice was opened, and measurement of the effusion time was started. After the lapse of the required time, the orifice was closed, the oven heating was switched off, and air was admitted. After cooling to room temperature, the ampule with the sample was weighed. The vapor pressure was calculated by Knudsen's equation (5):

$$P = [\Delta m/(\alpha\beta S_{\rm ef}\tau)](2\pi RT/M)^{1/2}, \qquad (5)$$

where Δm is the weight of the substance that effused from the cell; α, condensation coefficient; $S_{\rm ef}$, orifice area; β, Clausing coefficient characterizing the resistance of the orifice to the vapor flow; τ, evaporation time; R, gas constant; T, temperature; and M, molecular weight of the substance.

In accordance with the recommendations given in [12], for calibration we used naphthalene and benzoic acid. Benzoic acid (mp 395.5 K) and naphthalene of calorimetric grade (mp 353.43 K) were subjected to fractional sublimation, and the middle fraction was taken for the calibration.

Calibration with naphthalene was performed in the temperature range 298–318 K at effective orifice areas $\beta S_{\rm ef}$ of 2.21×10^{-7} and 2.7×10^{-8} m^2, and calibration with benzoic acid, in the temperature range 323–348 K with $S_{\rm ef}$ of 8.48×10^{-7} and 2.21×10^{-7} m^2. The heats of sublimation obtained, 72.4 kJ mol^{-1} for naphthalene and 89.8 kJ mol^{-1} for benzoic acid, are well consistent with the reference data [12].

Effusion orifices were made in 0.1-mm-thick aluminum foil with a specially designed device allowing formation of orifices of a regular round shape with a diameter of down to 0.01 mm. The orifice areas $S_{\rm ef}$ were measured with a microscope (×200 magnification); the Clausing coefficient β was calculated as recommended in [13].

To estimate the condensation coefficient α, we performed an experiment with two different orifices with the effective areas $\beta S_{\rm ef}$ of 2.21×10^{-7} and 8.48×10^{-7} m^2, and also an experiment on evaporation from the open surface (area 7.088×10^{-5} m^2, Langmuir method). The ratio of the geometric surface area of the sample to the orifice area was 80–300. We found that the rate of the vapor effusion from the Knudsen cell was independent of the orifice area and that the sublimation rates measured by the Knudsen and effusion methods were equal. This fact indicates that the condensation coefficient α is unity for all the examined compounds [13].

Compounds **II**–**VII** were prepared from commercially available calix[4]arene **I** (Aldrich) by previously described procedures [14–17]. All the compounds after chromatographic purification were precipitated with methanol from their solutions in dichloromethane–hexane, 1 : 1.

I · C_6H_{14} · CH_2Cl_2. ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 7.95 s (4H, OH), 7.41 d (8H, ArH$_m$), 6.71 t (4H, ArH$_p$), 5.68 s (2H, $_C$H2Cl2), 4.31 d (4H, ArCH$_2$Ar), 3.40 d (4H, ArCH$_2$Ar), 0.98 m (8H, C_6H_{14}), 0.58 t (6H, C_6H_{14}). Found, %: C 70.59; H 6.72; Cl 11.93. $C_{28}H_{24}O_4 \cdot C_6H_{14} \cdot CH_2Cl_2$. Calculated, %: C 70.56; H 6.70; Cl 11.91.

II · C_6H_{14}. ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 7.82 d (4H, ArH$_m$), 7.71 s (2H, OH), 6.83 d (4H, ArH$_m$), 6.74 t (2H, ArH$_p$), 6.43 t (2H, ArH$_p$), 4.35 d (4H, ArCH$_2$Ar), 3.82 s (6H, OCH$_3$), 3.41 d (4H, ArCH$_2$Ar), 0.97 m (8H, C_6H_{14}), 0.55 t (6H, C_6H_{14}). Found, %: C 80.30; H 7.80. $C_{30}H_{28}O_4 \cdot C_6H_{14}$. Calculated, %: C 80.27; H 7.78.

III · C_6H_{14}. ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 7.80 d (4H, ArH$_m$), 7.41 d (4H, ArH$_m$), 6.89 t (2H, ArH$_p$), 6.62 t (2H, ArH$_p$), 4.41 d (4H, ArCH$_2$Ar), 4.10, 4.02, 3.92, 3.85 all m (16H, OCH$_2$CH$_2$O), 3.71 s (4H, OCH$_2$CH$_2$O), 3.12 s (6H, OCH$_3$), 3.38 d (4H, ArCH$_2$Ar), 0.95 m (8H, C_6H_{14}), 0.52 t (6H, C_6H_{14}). Found, %: C 74.59; H 8.11. $C_{40}H_{46}O_8 \cdot C_6H_{14}$. Calculated, %: C 74.56; H 8.08.

VII · CH_3OH. ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 7.78 d (4H, ArH$_m$), 7.39 d (4H, ArH$_m$), 4.44 d (4H, ArCH$_2$Ar), 4.15, 4.06, 3.93, 3.81 all m (16H, OCH$_2$CH$_2$O), 3.64 s (4H, OCH$_2$CH$_2$O), 3.25 s (3H, CH$_3$OH), 3.10 s (6H, OCH$_3$), 3.40 d (4H, ArCH$_2$Ar), 1.31 s [36H, C(CH$_3$)$_3$], 1.17 s (1H, CH$_3$OH). Found, %: C 75.16; H 9.01. $C_{56}H_{78}O_8 \cdot CH_3OH$. Calculated, %: C 75.13; H 8.97.

Before effusion experiments, compounds **I**–**VII** were subjected to fractional sublimation in a high vacuum, and the middle fraction was taken for the experiment. The absence of degradation and the purity were checked by ^{1}H NMR spectroscopy.

ACKNOWLEDGMENTS

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