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The complexes of tetramethylresorc[4]arene with amines. Effect of the amine concentration on the complex composition

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Abstract—The complexation of tetramethylresorc[4]arene with primary and secondary amines in acetonitrile was investigated spectrophotometrically. The stoichiometry of the complexes formed was shown to depend on the amine concentration. Based on the proposed complexation models, the formation constants of the complexes as well as their thermodynamical parameters were determined and discussed. Depending on the amine concentration, two types of solid complexes of tetramethylresorc[4]arene with amines were obtained. The composition of these complexes was confirmed by ^{1}H NMR. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Supramolecular chemistry belongs to the most rapidly developing areas of chemistry.[1] It concerns mainly the complementary, non-covalent molecular interactions such as hydrogen bonds, π-electron interactions, van der Waals forces. The resorcarenes are particularly useful for investigation of such interactions.[2] Because of their cylindrical structure, they tend to form host–guest complexes with the neutral organic molecules, ammonium cations[3] and metal cations.[4] The π-electron interactions also allow resorcarenes to form external complexes, e.g. with electron acceptors such as tetracyanoethylene.[5] The presence of hydroxy groups, which readily form hydrogen bonds, increases the complexing capabilities of resorcarenes further. Up to date, complexes with amines, amino alcohols and pyridine,[6] pyridils and phenanthroline,[7] saccharides and steroids,[8] amino acids,[9] chiral alcohols and glycosides[10] have been studied. This paper concerns the equilibria of complex formation by tetramethyl-resorc[4]arene (the resorcarene) with primary and secondary amines in acetonitrile, over a wide range of concentrations of the amines studied. This is a continuation of our studies into the synthesis and complex formation properties of resorcarenes.

2. The complex-formation equilibria in the resorcarene–amine system

Our previous studies proved that the reaction of the resorcarene with amines at moderate excess of the amine forms the complexes of the 1:2 stoichiometry.[6] These complexes have been obtained as solids and investigated by ^{1}H NMR. Our further experiments have shown that, at a several hundred-fold excess of amines, complexes of a 1:4 stoichiometry are formed. UV–VIS spectroscopy was used to determine the formation constants of the complexes formed by the resorcarene with selected amines. The investigated amines were: diethylamine, piperidine, cyclohexylamine, cyclohexylethylamine, and phenylethylamine. The effect of the added amine on the first long-wave absorption band of resorcarene was observed. Depending on the amine, two types of changes were noted, which are shown in Figs. 1 and 2. In case of the primary amines, i.e. cyclohexylamine (Fig. 1) and cyclohexylethylamine, two clear isosbestic points appear in the range of low and high concentrations of the amines. The first isosbestic point (λ=286.5 nm), for the several-fold excess of the amine, corresponds to formation of the 1:2 resorcarene–amine complex.

The second isosbestic point (λ=290.3 nm), for about 100–250-fold excess of the amine, corresponds to formation of the 1:4 resorcarene–amine complex. On the other hand, only one isosbestic point appears for the secondary amines such as diethylamine and piperidine (Fig. 2); the increase in the amine concentration results in monotonic long-wave shift of the absorption band of resorcarene. Such changes of the absorption band of resorcarene effected by the added amine were studied at several temperatures. It is characteristic that only one isosbestic point is observed in each case at 60°C; it appearsat the same wavelength as the first isosbestic point at 20°C. The solid 1:4 complexes of the resorcarene with the selected amines (piperidine, cyclohexylamine) were synthesized using a several hundred-fold excess of the amine. Their compositions were confirmed by ^{1}H

Keywords: tetramethylresorc[4]arene-amine complexes; UV–VIS spectroscopy; hydrogen bond.
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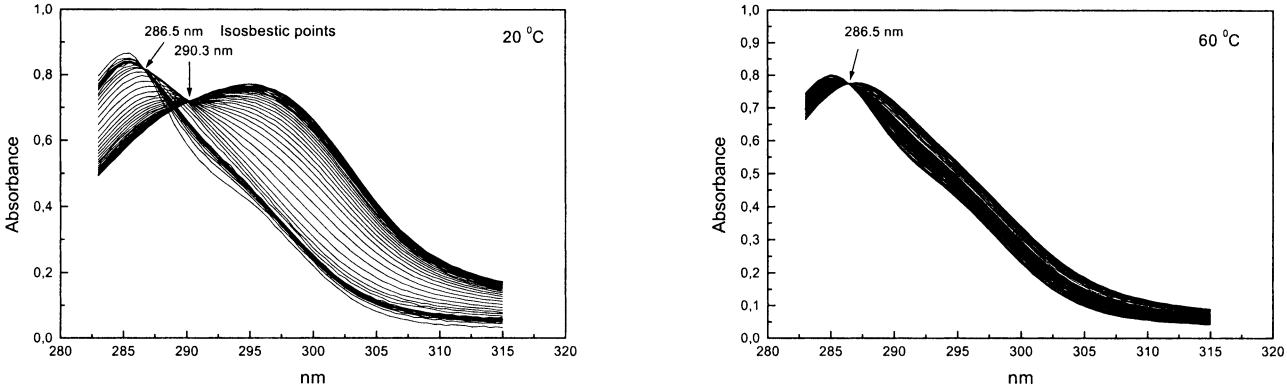


Figure 1. Effect of the added cyclohexylamine on the absorption band of the resorcarene. The resorcarene concentration is 7.35×10^{-5} M, the amine concentration varies from 7.51×10^{-5} to 1.95×10^{-2} M. The changes in the absorption spectrum are shown for 20 and 60°C.

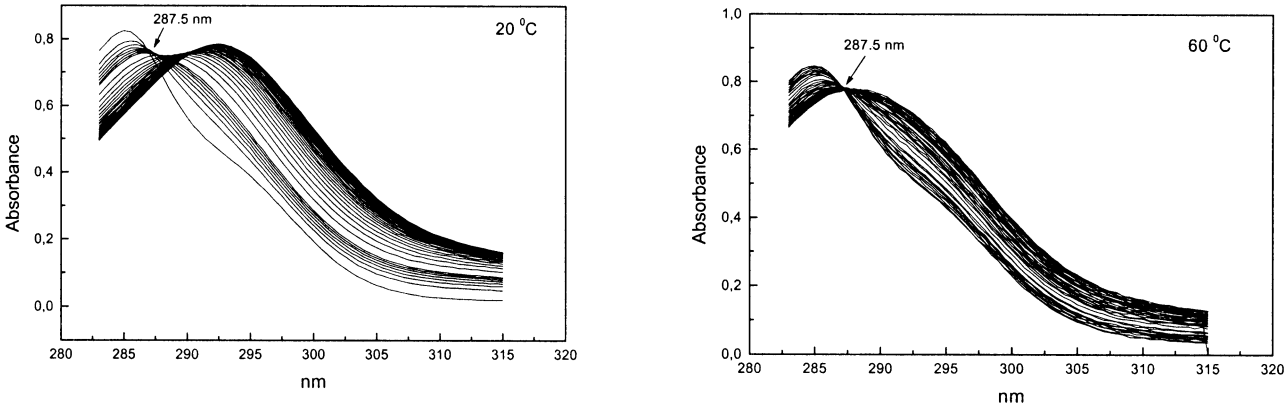


Figure 2. Effect of the added piperidine on the absorption band of the resorcarene. The resorcarene concentration is 7.35×10^{-5} M, the amine concentration varies from 7.51×10^{-5} to 1.95×10^{-2} M. The changes in the absorption spectrum are shown for 20 and 60°C.

NMR spectra. In these spectra, the OH···NH hydrogen bond signal of the 1:4 complex appears upfield in comparison to the 1:2 complex. For example, this signal appears at δ=4.62 for the 1:4 resorcarene–cyclohexylamine complex versus δ=6.02 for the 1:2 complex.

This indicates that the hydrogen bond is stronger in the 1:2 complex than in the 1:4 complex. This may explain why it is more difficult to synthesize the 1:4 complexes. Fig. 3 shows a possible structure of the 1:4 resorcarene–cyclohexylamine complex, which was proposed taking into account the crystallographic structure of the 1:4 resorcarene–pyridine complex[6] as well as the reports on complexation of phenols with amines.[11,12]

The shift of the absorption band of the resorcarene resulting from the addition of the amine testifies that the excess of the primary or secondary amine can stabilize the proton-transferred species by hydrogen-bonding network formation, where the amines act as a hydrogen donor and form a hydrogen bond to the $O^{-\delta}$ anion.

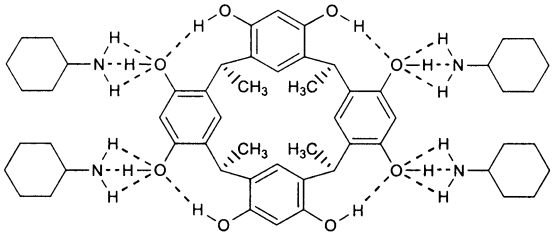
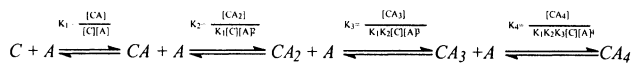


Figure 3.

3. Determination of the formation constants for the resorcarene–amine complexes

The literature data as well as the above-discussed spectrophotometric UV–VIS and ^{1}H NMR indicate that the highest number of the amine molecules which can be attached to the resorcarene molecule is 4, therefore our calculations were based on this model (Scheme 1).

In Scheme 1 C is a resorcarene molecule; A is an amine molecule; CA, CA_2, CA_3, and CA_4 are the individual types of complexes formed in the studied systems; K_1, K_2, K_3, and K_4 denote the formation constants of the individual complexes, respectively. The change of absorption, ΔD, in



Scheme 1.

such a system, (for l=1) is described by Eq. (1)

$$\Delta D = \varepsilon_{CA}[CA] + \varepsilon_{CA_2}[CA_2] + \varepsilon_{CA_3}[CA_3] + \varepsilon_{CA_4}[CA_4] \quad (1)$$

wherein $\Delta D = D - D_0$ is a difference between the absorption observed and the absorption of the resorcarene at given wavelength; $\varepsilon_{CA}, \varepsilon_{CA_2}, \varepsilon_{CA_3}, \varepsilon_{CA_4}$ are molar absorption coefficients for the individual complexes; $[CA_i]$ are the equilibrium concentrations of the formed complexes (i=1, 2, 3, 4). Using the expressions for the total concentration of the resorcarene (Eq. (2)) and the amine (Eq. (3)), one obtains the Eq. (4) for the theoretical change of absorption[13] in the studied system.

$$C_0 = [C] + K_1[C][A] + K_1K_2[C][A]^2 + K_1K_2K_3[C][A]^3 + K_1K_2K_3K_4[C][A]^4 \quad (2)$$

$$A_0 = [A] + K_1[C][A] + 2K_1K_2[C][A]^2 + 3K_1K_2K_3[C][A]^3 + 4K_1K_2K_3K_4[C][A]^4 \quad (3)$$

$$D - D_0 = \frac{C_0\{\varepsilon_1K_1[A] + \varepsilon_2K_1K_2[A]^2 + \varepsilon_3K_1K_2K_3[A]^3 + \varepsilon_4K_1K_2K_3K_4[A]^4\}}{1 + K_1[A] + K_1K_2[A]^2 + K_1K_2K_3[A]^3 + K_1K_2K_3K_4[A]^4} \quad (4)$$

wherein C_0 is the analytical concentration of resorcarene, [C] is the equilibrium concentration of resorcarene, A_0 and [A] are the analytical and equilibrium concentrations of the amine, respectively, K_i is the complex formation constant (i=1, 2, 3, 4). First, the Eqs. (2) and (3) were solved numerically for given values of the formation constants and the molar absorption coefficients. Then, using the equilibrium concentration of the amine for the given parameters, the theoretical absorbance was computed from Eq. (4). The values of K_1, K_2, K_3, K_4 as well as ε_{CA}, ε_{CA_2}, ε_{CA_3}, ε_{CA_4} were optimized iteratively.

The proposed model allowed computation of formation constants as well as the molar absorption coefficients for the individual complexes. Table 1 summarizes the logarithms of the formation constants for the investigated temperatures as well as the molar absorption coefficients of the formed complexes. In each case, the fitting of the theoretical parameters to the experimental data was performed for the same number of data points as well as the same range of concentrations of the amines, taking into accounts the equilibrium concentrations both of the resorcarene and of the amines. The goodness of fit was given by the following expression.[14]

$$\chi^2 = \frac{1}{n-p}\sum_{i=1}^{n}\frac{(D - D')^2}{D'} \quad (5)$$

wherein D is the observed absorption; D' is the computed absorption; $n-p$ is the number of degrees of freedom; n is the number of experimental data points, p is the number of fitted parameters. Fig. 4 shows an example of fitting the

Table 1. Logarithms of formation constants K (M^{-1}) for the complexes of resorcarene with amines and their molar absorption coefficients ε ($M^{-1}\,cm^{-1}$) at 300 nm computed from Eq. (4)

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	ε_1	ε_2	ε_3	ε_4	χ^2
Piperidine									
20°C	4.09	6.32	3.25	2.41	4260	615	1910	5640	1.94×10^{-5}
30°C	3.73	6.08	3.20	2.20	2460	446	1460	5220	5.86×10^{-6}
40°C	3.63	5.95	3.13	2.03	4490	363	1250	4770	2.04×10^{-5}
50°C	3.23	5.79	3.12	1.89	4480	304	1130	4910	5.30×10^{-5}
60°C	2.86	5.66	3.00	1.78	1137	183	1080	4410	8.10×10^{-5}
Diethylamine									
20°C	3.24	5.65	3.31	2.10	7450	287	1490	4540	2.57×10^{-5}
30°C	2.91	5.46	3.24	1.89	7080	173	1250	4250	2.56×10^{-5}
40°C	2.90	5.37	3.19	1.54	6000	144	1150	5170	5.38×10^{-5}
50°C	2.64	5.17	3.03	1.36	4900	143	958	5510	8.31×10^{-5}
60°C	2.52	5.06	2.98	1.22	4270	102	778	5970	4.23×10^{-5}
Phenylethylamine									
20°C	1.15	4.01	1.34	2.04	5400	187	1040	1210	1.95×10^{-4}
30°C	1.09	3.86	1.25	2.00	3390	158	597	1110	2.28×10^{-4}
40°C	0.97	3.63	1.15	1.98	3190	151	460	1003	3.52×10^{-4}
50°C	0.88	3.60	1.07	1.96	3450	91.8	504	914	6.55×10^{-4}
60°C	0.78	3.49	1.01	1.95	3430	67	613	811	3.00×10^{-4}
Cyclohexylethylamine									
20°C	2.02	5.16	0.96	3.57	14500	200	300	6800	5.18×10^{-4}
30°C	1.46	4.96	0.71	2.96	14100	449	669	6380	2.96×10^{-4}
40°C	1.26	4.73	1.57	2.48	13490	389	855	1820	3.73×10^{-4}
50°C	0.95	4.50	1.57	2.04	11330	377	750	2000	2.13×10^{-4}
60°C	0.95	4.49	1.57	1.63	14300	289	1020	2830	2.84×10^{-4}
Cyclohexylamine									
20°C	2.55	6.73	1.29	3.56	17700	247	304	6950	1.01×10^{-3}
30°C	1.12	6.10	0.82	3.09	15100	480	552	6370	3.96×10^{-4}
40°C	1.11	5.20	1.57	2.45	13800	464	960	2210	3.96×10^{-4}
50°C	1.14	4.57	1.66	2.28	15400	343	1080	1780	5.54×10^{-4}
60°C	1.02	4.41	1.40	1.50	15700	192	2820	2220	2.30×10^{-4}

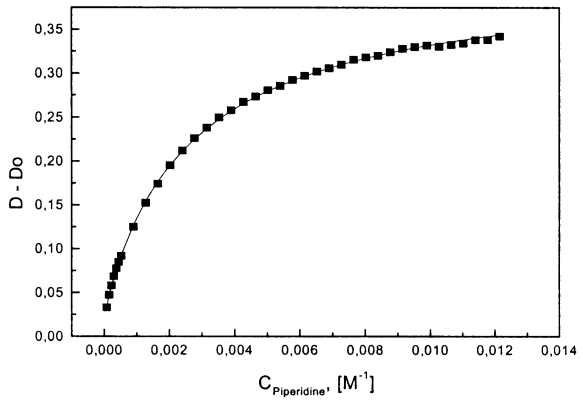


Figure 4. Example of fitting of the parameters of Eq. (4) to the changes of absorption of the first long-wavelength absorption band of the resorcarene depending on the concentration of piperidine at 300 nm.

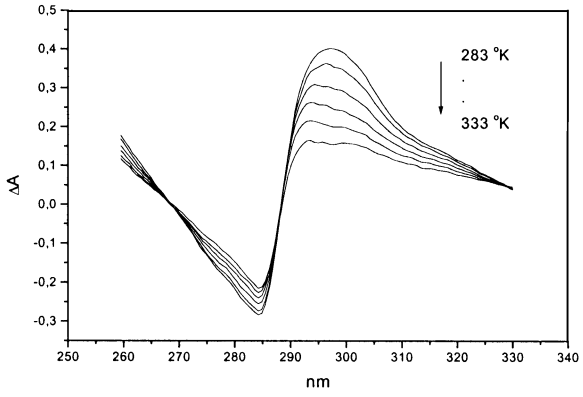


Figure 5. Differential spectra of the complexes formed between the resorcarene (7.35×10^{-5} M) and piperidine (10^{-2} M) in acetonitrile at increasing temperature.

theoretical curve resulting from Eq. (4) to the experimental data, taking into account the equilibrium concentrations of the resorcarene and the amine.

The data presented in Table 1 indicate that, in cases of cyclohexylamine, cyclohexylethylamine, and phenylethylamine, two formation constants, i.e. K_2 and K_4, outweigh the others at 20°C. This is reflected in the UV–VIS spectra, where two isosbestic points are observed. In cases of diethylamine and piperidine, the K_2 formation constant prevails, whereas the K_3 and K_4 constants are comparable. Therefore, no isosbestic point is observed in this concentration range, and the increasing concentration of the amine causes merely the monotonic shift of the absorption band of resorcarene towards longer wavelengths. At 60°C, in all cases, the K_2 formation constant clearly dominates the

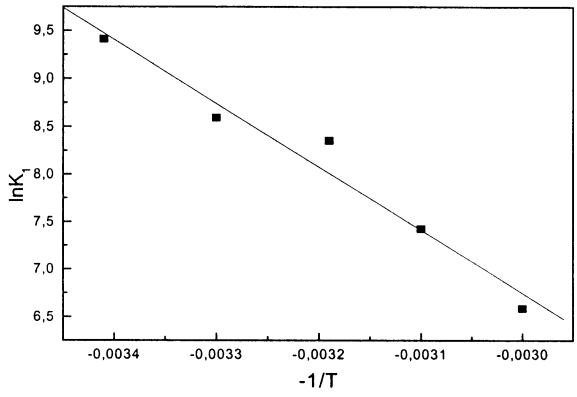


Figure 6. A plot of linear dependency of ln K_1 on the reciprocal temperature for the resorcarene–piperidine complex.

others. This is manifested in that only one isosbestic point is observed for all studied systems at this temperature. Such a strong temperature dependence is shown also in Fig. 5, which presents the change of differential absorption band of the complexes formed between the resorcarene and piperidine in relation to the resorcarene absorption band. For the piperidine concentration being about 140 times greater than the resorcarene concentration in acetonitrile, the increase of temperature results in the decreasing increment of absorption of the complexes formed as well as the change of shape of the absorption band of the complex.

These observations suggest that the equilibria in the resorcarene–amine system depend not only on the amine concentration, but they also strongly depend on temperature. The thermodynamic parameters for the individual complexes forming in the resorcarene–amine system were determined from the thermal dependencies using the van't Hoff equation:

$$\ln K = -\Delta H/RT + \Delta S/R \quad (6)$$

Fig. 6 shows an example of the thermal dependence of the logarithm of the K_1 formation constant for the resorcarene–piperidine system.

Table 2 summarizes the computed thermodynamical parameters of formation of individual types of complexes in the studied systems. In all cases, a negative enthalpy of formation is observed for the individual complexes, which results from formation of hydrogen bonds between the resorcarene and the amine. The calculation shows that, in all cases, the K_2 constant is greater than others.

However, the entropy of formation of such complex is positive only for the secondary amines. Moreover, the K_3 constant is greater than the K_4 constant only for the

Table 2. Thermodynamical parameters ΔH (kJ mol^{-1}) and ΔS (J mol^{-1} K^{-1}) for the individual complexes formed in the resorcarene–amine systems in acetonitrile

Amine	ΔH_1	ΔS_1	ΔH_2	ΔS_2	ΔH_3	ΔS_3	ΔH_4	ΔS_4
Piperidine	−55.10	−109.26	−30.40	16.81	−10.77	25.68	−29.34	−54.43
Diethylamine	−32.28	−48.93	−27.52	14.13	−15.96	9.24	−42.96	−106.50
Cyclohexylamine	−8.94	−6.95	−115.83	−267.40	–	–	−91.66	−244.15
Cyclohexylethylamine	−50.08	−134.89	−39.76	−36.67	–	–	−89.98	−239.53
Phenylethylamine	−17.54	−37.54	−24.62	−7.63	−16.11	−29.30	−4.2	24.50

secondary amines, reflected by the positive entropic effect, which, in consequence, increases the negative value of the free enthalpy (ΔG) of formation of such a complex. An enthalpic–entropic compensation is observed for all remaining complexes, i.e. the higher negative enthalpy corresponds to the higher negative entropy.

4. Determination of the formation constants of the 1:3 and 1:4 complexes from the 1:2 complex

As already mentioned, the 1:2 resorcarene–amine complexes can be readily synthesized, as described earlier.[6] By attaching the consecutive amine molecules, the complexes CA_3 and CA_4 are formed, as shown in Scheme 2. The values of K'_3 and K'_4 can be determined in a similar way to that for the process described in Scheme 1.

This independent method for computing the formation constants of the 1:3 and 1:4 complexes of resorcarene was used with piperidine as well as with diethylamine. It was intended to assess the correctness of the general model used for computing of the formation constants in the wide range of concentrations of the amines studied. This process can be observed by means of the UV–VIS spectroscopy. Fig. 7 shows the changes in the absorption bands of the acetonitrile solution of the 1:2 resorcarene–piperidine complex resulting from addition of piperidine.

As in Fig. 2, the isosbestic point is not clearly marked in this range of the amine concentrations, since none of the formation constants predominates. Using the modified Eq. (4) and the identical computing technique, the formation constants K'_3 and K'_4 as well as the molar absorption coefficients ε'_{CA_3}, ε'_{CA_4} were calculated. The results are given in Table 3. Table 4 shows the thermodynamic parameters for the complexes formed, which were calculated according to Eq. (5).

$$CA_2 + A \underset{}{\overset{K_3' = \frac{[CA_3]}{K_1K_2[C][A]^3}}{\rightleftharpoons}} CA_3 + A \underset{}{\overset{K_4' = \frac{[CA_4]}{K_1K_2K_3[C][A]^4}}{\rightleftharpoons}} CA_4$$

Scheme 2.

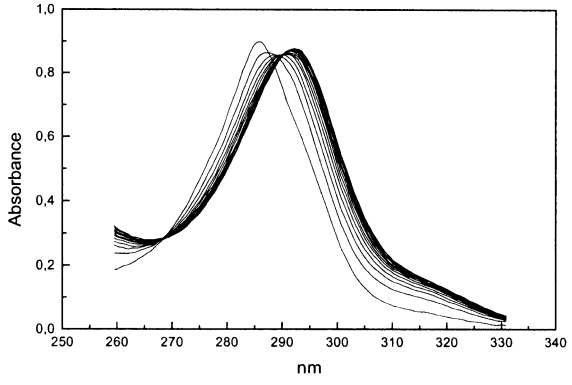


Figure 7. Effect of the addition of piperidine on the absorption spectrum of the 1:2 resorcarene–piperidine complex in acetonitrile. The complex concentration is 7.27×10^{-5} M, the amine concentration varies from 5.58×10^{-4} to 7.25×10^{-3} M. All spectra were taken at 20°C.

Table 3. Logarithms of the K'_3 and K'_4 formation constants (M^{-1}) and the molar absorption coefficients ε' (M^{-1} cm^{-1}) for the complexes formed between the 1:2 resorcarene–amine complex and the amine in acetonitrile

	$\log K'_3$	$\log K'_4$	ε'_3	ε'_4	χ^2
Piperidine					
20°C	3.18	2.44	1660	5460	3.27×10^{-5}
30°C	3.15	2.20	1420	5180	2.14×10^{-5}
40°C	3.13	2.05	1040	5370	1.22×10^{-4}
50°C	3.12	1.85	990	5250	5.10×10^{-5}
60°C	3.03	1.68	956	5360	7.12×10^{-5}
Diethylamine					
20°C	3.29	2.21	1340	5670	2.60×10^{-5}
30°C	3.24	1.88	1320	5600	2.07×10^{-5}
40°C	3.21	1.52	1350	6280	4.71×10^{-5}
50°C	3.03	1.36	1478	6840	8.55×10^{-5}
60°C	3.03	1.24	1418	7250	8.59×10^{-5}

Table 4. Thermodynamical parameters $\Delta H'$ (kJ mol^{-1}) and $\Delta S'$ (J mol^{-1} K^{-1}) for the complexes formed by the 1:2 resorcarene–amine complex and the amine in acetonitrile

	$\Delta H'_3$	$\Delta S'_3$	$\Delta H'_4$	$\Delta S'_4$
Piperidine	−6.16	40.06	−34.94	−72.70
Diethylamine	−13.78	16.40	−42.53	−105.2

In general, one can note a good agreement between the formation constants and the molar absorption coefficients with the results in Table 1. The calculated thermodynamic parameters of the complexes formed also reproduce the previously observed tendency for the positive entropic effect in the case of the 1:3 complexes as well as the enthalpic–entropic compensation in the case of the 1:4 complexes.

In summary, the complexation of the resorcarene with the primary and secondary amines in acetonitrile was followed spectrophotometrically across a wide range of the amine concentrations. The dependence of complex stoichiometry on the amine concentration was demonstrated. Two types of solid resorcarene–amine complexes were obtained. The thermodynamic parameters of the formed complexes were determined.

5. Experimental

^{1}H NMR spectra (500 MHz) and ^{13}C NMR (125 MHz) were recorded on a Bruker AM 500 spectrometer. The coupling constants (J) are given in Hz. UV–VIS spectra were taken on an Specord 500 spectrophotometer. IR spectra were taken on an Specord M80 spectrophotometer. The melting points are generally >300°C.

5.1. General procedure for the preparation of complexes of resorcarene with selected amines

The 1:2 complexes were synthesized as previously described,[6] but acetonitrile was used instead of ethanol. In case of the 1:4 complexes, in a typical experiment, calixresorcarene (0.5 g) was dissolved in acetonitrile (5 ml) followed by addition of the amine (100 equiv.). The solution was heated until the precipitate dissolved, and then left apart to crystallize. Yield 50%.

5.1.1. 1:2 Resorcarene–piperidine complex. IR (KBr) ν: 3700–3100 cm^{-1} (max. 3176 cm^{-1}; >NH···OH), 2800–2300 cm^{-1} (max. 2536 cm^{-1}; $>NH_2^+$); ^1H NMR (500 MHz, DMSO-d_6, RT): δ=1.47 (m, 24H, CH_3, CH_2), 2.70 (s, 8H, CH_2), 4.41 (q, J=7.20 Hz, 4H, CH), 6.04 (s, 4H, ArH), 6.81 (s, 10H, ArOH···NH), 7.05 (s, 4H, ArH); ^{13}C NMR (125 MHz, DMSO, RT): δ=18.90, 20.88, 22.76, 24.31, 25.65, 28.49, 46.08, 56.40, 103.07, 124.29, 124.41, 152.68; MS-FAB (NBA, 30°C): 629.6 ($M^+-C_5H_{11}N$), 544.1 ($M^+-2\times C_6H_{13}N$).

5.1.2. 1:4 Resorcarene–piperidine complex. IR (KBr) ν: 3700–3100 cm^{-1} (max. 3280 cm^{-1}; >NH···OH), 2800–2300 cm^{-1} (max. 2527 cm^{-1}; $>NH_2^+$); ^1H NMR (500 MHz, DMSO-d_6, RT): δ=1.44 (d, J=7.20 Hz, 12H, CH_3), 1.49 (m., 24H, CH_2), 2.56 (s, 16H, CH_2), 3.80 (s, 12H, ArOH···NH), 4.46 (q, J=7.20 Hz, 4H, CH), 6.13 (s, 4H, ArH), 6.97 (s, 4H, ArH); ^{13}C NMR (125 MHz, DMSO, RT): δ=18.90, 20.88, 22.76, 24.31, 25.65, 28.49, 46.08, 56.40, 103.07, 124.29, 124.41, 152.68; MS-FAB (NBA, 30°C): 796.2 ($M^+-C_5H_{11}N-4H$), 735.3 ($M+Na^+-2\times C_5H_1N$), 655.1 ($M^+-3\times C_5H_{11}N+3H$).

5.1.3. 1:2 Resorcarene–cyclohexylamine complex. IR (KBr) ν: 3700–3100 cm^{-1} (max. 3192 cm^{-1}; $-NH_2$···OH), 2800–2300 cm^{-1} (max. 2576 cm^{-1}; $-NH_3^+$); ^1H NMR (500 MHz, DMSO-d_6, RT): δ=1.21 (m, 4H, CH_2), 1.50 (d, J=7.20 Hz, 12H, CH_2), 1.64 (m., 4H, CH_2), 1.74 (m., 4H, CH_2), 2.59 (m., 2H, CH), 4.4 (q, J=7.20 Hz, 4H, CH), 6.02 (s, 10H, ArOH···NH), 6.04 (s, 4H, ArH), 7.08 (s, 4H, ArH); ^{13}C NMR (125 MHz, DMSO, rt): δ=18.50, 20.03, 24.40, 25.19, 27.75, 34.50, 49.67, 56.00, 102.79, 123.70, 123.99, 152.43; MS-FAB (NBA, 30°C): 544.2 ($M^+-2\times C_6H_{13}N$).

5.1.4. 1:4 Resorcarene–cyclohexylamine complex. IR (KBr) ν: 3700–3100 cm^{-1} (max. 3178 cm^{-1}; $-NH_2$···OH), 2800–2300 cm^{-1} (max. 2544 cm^{-1}; $-NH_3^+$); ^1H NMR (500 MHz, DMSO-d_6, rt): δ=1.01 (m, 16H, CH_2), 1.20 (m, 8H, CH_2), 1.53 (d, J=7.20 Hz, 12H, CH_3), 1.63 (m, 8H, CH_2), 1.72 (m, 8H, CH_2), 2.51 (m, 4H, CH), 4.38 (q, J=7.20 Hz, 4H, CH), 4.62 (s, 12H, ArOH···NH), 5.97 (s, 4H, ArH), 7.15 (s, 4H, ArH); ^{13}C NMR (125 MHz, DMSO, RT): δ=20.04, 24.46, 25.25, 27.87, 35.34, 49.74, 102.82, 123.27, 123.98, 152.64; MS-FAB (NBA, 30°C): 643.5 ($M^+-3\times C_6H_{13}N$).

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