Pergamon

Tetrahedron 54 (1998) 14031–14040

TETRAHEDRON

The Complexes of Tetramethylresorc[4]arene with Amines, Amino Alcohols and Pyridine

Waldemar Iwanek [a*], Roland Fröhlich [b], Mariusz Urbaniak [a], Christian Näther [c] and Jochen Mattay [d+*]

a) *Pedagogical University, Institute of Chemistry, Checinska 5, PL-25020 Kielce, Poland*
b) *Institut für Organische Chemie, Universität Münster, Corrensstraße 40, D-48149 Münster, Germany*
c) *Institut für Anorganische Chemie, Universität Kiel, Olshausenstr. 40, D-24098 Kiel, Germany*
d) *Institut für Organische Chemie, Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany*
(E-mail: mattay@oc.uni-kiel.de; Fax: +49-431-880-7410)

Received 12 June 1998; revised 16 September 1998; accepted 18 September 1998

Abstract

The solid complexes of resorc[4]arenes with amines, amino alcohols, and pyridine were obtained. Their composition was determined by ^{1}H-NMR and spectrophotometric methods. For selected compounds, the composition was confirmed by the mass spectra. The crystallographic composition of the complex of calixresorcarene with pyridine was determined.

Keywords: *Resorc[4]arene-amine complexes; UV/VIS spectroscopy; NMR spectroscopy, MS-spectrometry.*

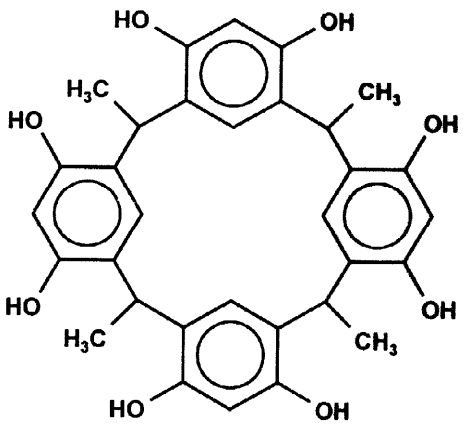
Introduction

The intermolecular interactions leading to the formation of supramolecular complexes are the base of the biological processes[1]. Calixarenes belong to the compounds frequently investigated in complexation studies[2] and, in special, tetramethylresorc[4]arene (**1**), due to the presence of eight hydroxy groups, has the unusually high ability for complexing of polar organic molecules. The complexing abilities do not restrict to neutral molecules only [1], but they involve also metal and ammonium cations[3]. Aoyama *et al.* for the first time investigated the complexation of **1** with the biologically important compounds such as sugars, amino acids, carboxylic acids and glucosides[4].

This paper concerns the complexation of the resorc[4]arene **1** with primary and secondary amines (including chiral amines), chiral amino alcohols and pyridine. Such complexes can be obtained in the solid form in high yields. These can be, in turn, used for partial functionalization of the calixarene platform, e.g. by the selective Mannich reactions[5].

+ New address: Fakultät für Chemie, Organische Chemie I, Universität Bielefeld, Postfach 10 01 31, D-33501 Bielefeld, Germany

0040-4020/98/$ - see front matter
PII: S0040-4020(98)00868-0



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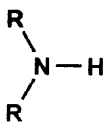

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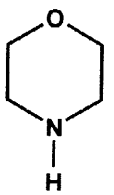
3: R = CH_2 CH_3
4: R = $CH(CH_3)_2$



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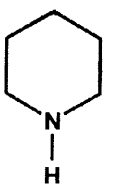

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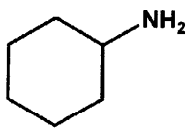
Primary amines:



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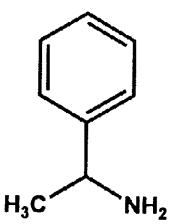
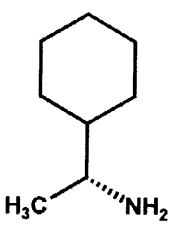


8: R(+), S(-)



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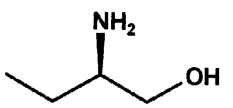

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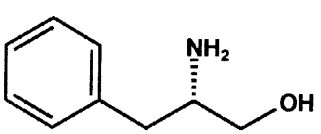

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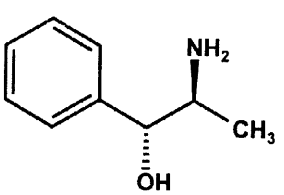

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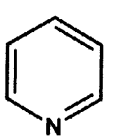

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Results

Complexation of tetramethylresorc[4]arene **1** with secondary aliphatic amines in ethanol results in formation of 1 : 2 complexes in 60-80% yield. The composition was calculated based on the ^1H NMR spectra. The amines used in complexation studies are: dimethylamine

(**2**), diethylamine (**3**), diisopropylamine (**4**), morpholine (**5**), and piperidine (**6**) (Scheme). Compared to pure **1** in DMSO, the ^{1}H NMR spectra of the complexes show a downfield shift of 0.2 to 0.4 ppm for the proton at the 2-position of the resorcinol ring. Moreover, in each case a broad signal characteristic for hydrogen bonding appears. Its position depends on the amine used, and it can be found in the range of about 5.3 to 7.1 ppm (Table 1). The other signals, both of **1** and of the amines practically do not change compared to the ^{1}H NMR spectra of the single starting molecules.

For the resorc[4]arene-diisopropylamine complex, the mass spectrum obtained by the DCI (NH_3) technique indicates formation of several types of complexes: with one NH_3 molecule ($M^+ + 1 = 562$), with one diisopropylamine molecule ($M^+ + 1 = 646$), with two diisopropylamine and two NH_3 molecules ($M^+ + 2 = 782$). Moreover, a complex consisting of two reorc[4]arene molecules and one NH_3 molecule ($M^+ + 3 = 1108$) can be observed. We assume a capsule structure of the complex with one molecule of NH_3 or the amine inside. Besides, application of the LSIMS technique for the resorc[4]arene-piperidine complex allowed observation of several types of complexes: with one piperidine molecule ($M^+ + 2 = 631$), with two piperidine molecules and one ethanol molecule ($M^+ + 3 = 763$). A complex consisting of two resorc[4]arene molecules and one piperidine molecule was also observed ($M^+ + 1.5 = 1174.5$). The mass-spectroscopic observations confirm the findings obtained from the ^{1}H NMR spectra.

Table 1: ^{1}H NMR shifts corresponding to the hydrogen bonding in the tetramethylresorc[4]-arene (**1**)-secondary amine complexes.

Secondary aliphatic amine	**Hydrogen bonding signal ^{1}H NMR, δ (ppm)**
Dimethylamine (**2**)	7.1
Diethylamine (**3**)	6.1
Diisopropylamine (**4**)	5.3
Morpholine (**5**)	5.6
Piperidine (**6**)	6.8

The 1:2 stoichiometry of the resorc[4]arene-amine complexes was confirmed by the UV/VIS spectrophotometry, too. Fig. 1 shows the typical changes of the absorption spectrum of **1** in acetonitrile occurring after addition of piperidine. A significant shift of the absorption band of **1** caused by piperidine should be noted. The absorption band of the resulting complex is shown in the differential spectrum in the inset of Fig. 1.

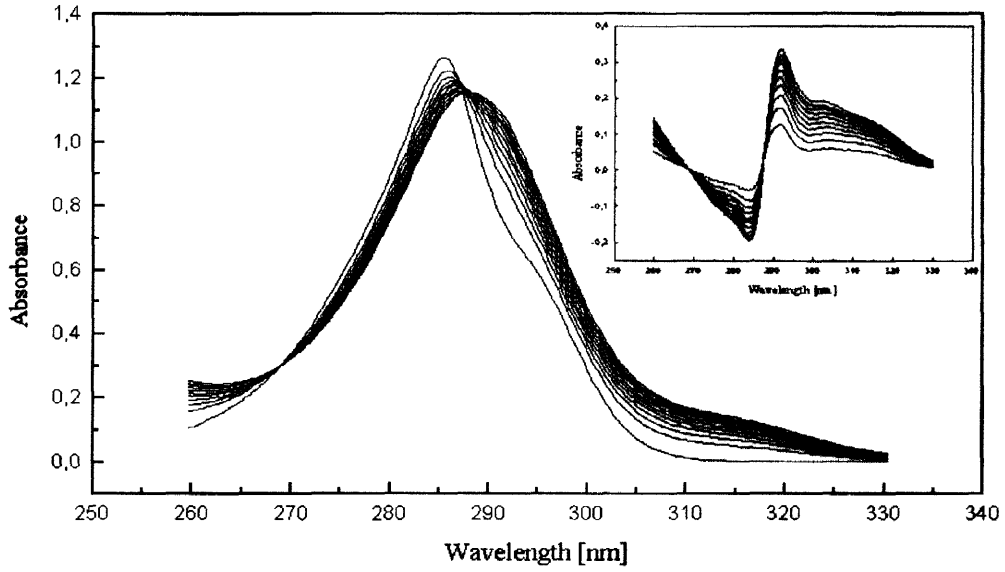


Fig. 1: Changes of the absorption spectrum of tetramethylresorc[4]arene (**1**) in acetonitrile resulting from addition of piperidine (**6**). Concentration of **1** is $1.8 \cdot 10^{-5}$ M; concentration of **6** ranges from $1 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ M. The inset at the right upper corner shows the differential spectrum of the resulting complex.

The equilibrium constants for complexation with selected amines were calculated by the Benesi-Hildebrand[4] method. Their values are given in Table 2.

Table 2: The equilibrium constants (K) for complexation of tetramethylresorc[4]arene (**1**) with the selected aliphatic amines[a].

Amine	K [M^{-2}]
Diethylamine (**3**)	$4.39 \cdot 10^{7}$
Piperidine (**6**)	$1.67 \cdot 10^{8}$
Cyclohexylamine (**7**)	$2.20 \cdot 10^{8}$

[a] The results of calculation for the assumed 1:1 composition depart completely from linearity.

In case of the optically active amines *S*(-)- and *R*(+)-1-phenylethylamine, *R*(-)-1-cyclohexylamine, the amino alcohols *R*(-)-2-aminobutanol (**10**) and L(-)-norephedrine (**12**) and in case of L-phenylalanine (**11**), the complexes with **1** precipitate readily from the ethanolic

solutions as well. Although they can be recrystallized easily from ethanol in high yields their composition is not strictly stoichiometric (Table 3).

Table 3: Complexes of tetramethylresorc[4]arene (**1**) with amines or amino alcohols. Composition and proton shifts in the ^{1}H NMR spectra.

Amine Amino alcohol	Composition[a)]	Hydrogen bonding signal ^{1}H NMR, δ (ppm)
S(-)-and *R*(+)-1-Phenylethylamine (**8**)	1 : 2.5	5.76
R(-)-1-Cyclohexylethylamine (**9**)	1 : 2.0	6.05
R(-)-2-Amino-1-butanol (**10**)	1 : 2.5	5.07
L(-)-Phenylalaninol (**11**)	1 : 2.6	5.12
L(-)-Norephedrine (**12**)	1 : 2.2	5.32

[a)] Calculated from ^{1}H NMR spectra

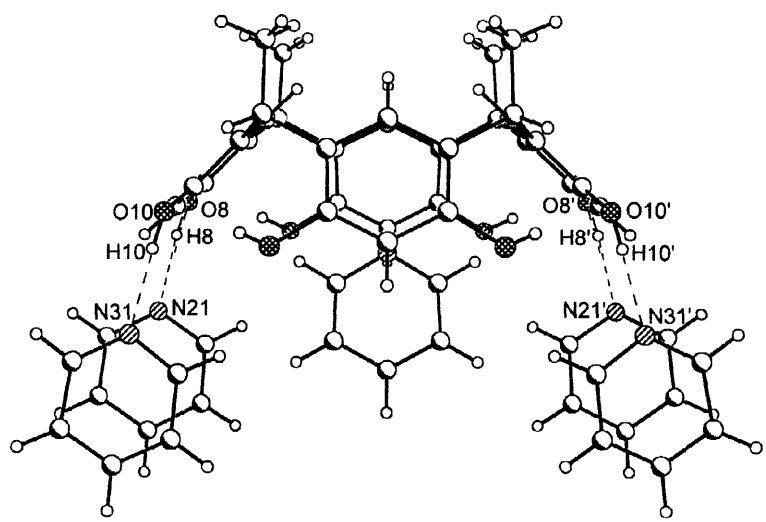
Similar to the complexes with secondary aliphatic amines, the complexes of **1** with chiral amines and amino alcohols exhibit a downfield shift for the proton at the 2-position in the resorcinol ring by 0.2 - 0.3 ppm in their ^{1}H NMR spectra, when compared with the spectrum of **1** alone in DMSO. A broad signal of hydrogen bond forming groups can also be observed, with the maximum in the range of 5 to 6.8 ppm, depending on the component (Table 3). Except for the NH_2 group, which participates in the hydrogen bonding, no other proton shifts corresponding to the investigated chiral amines and amino alcohols are observed. Satisfactory elemental analyses were obtained for the selected complexes. In order to confirm the composition of complex by an independent method, the mass spectra were measured for the **1**/S(-)-**8** complex using the DCI (NH_3) technique. In the mass spectrum, there are the molecular peaks corresponding to the calixresorcarene complexes with one NH_3 molecule ($M^+ + 1 = 562$), with one S(-)-1-phenylethylamine molecule ($M^+ + 1 = 666$), with two S(-)-1-phenylethylamine and two NH_3 molecules ($M^+ + 1 = 821$). As in to the case of **1/3** complex, here a molecular peak corresponding to the complex of two resorc[4]arrene molecules and one NH_3 molecule ($M^+ = 1108$) can be observed.

The resorc[4]arene (**1**)-pyridine (**13**) complex can be obtained as a solid by recrystallization of **1** from pyridine (molecular composition 1:6). Moreover, a precipitate appears when pyridine is added to the solution of **1** in acetone, to give a complex of molecular composition 1:2 (**1** : **13**). The solid state structure of the former complex is shown in Fig. 2. It also explains the appearance of two broad signals at $\delta = 8.8$ and $\delta = 3.45$ in the ^{1}H NMR spectrum. The first one reflects the presence of a hydrogen bond between OH groups in **1**, the other one is a symptom

of forming of hydrogen bonds between four OH groups of two resorcine rings and four molecules of pyridine. When decreasing the temperature up to 223 K both groups of signals become distinctly sharper and shift to the lower magnetic field. These shifts are remarkably large, i. e. they reach $\delta = 9.35$ in the first case and $\delta = 4.35$ in the second one.

The title compound **1** crystallizes in the orthorhombic space group Pnma with four molecules in the unit cell. The resorc[4]arene molecule is located around a crystallographic mirror plane, which passes through two opposite benzene rings. Altogether there are four crystallographically independent pyridine molecules in the asymmetric unit, of which two are located around a crystallographic mirror plane. Altogether a 1 : 6 complex is formed. Four of them are involved in intermolecular O-H···N hydrogen bonding between the nitrogen atoms of the pyridine molecule and the hydrogen atoms of the hydroxyl groups. One pyridine molecule is pointed into the resorc[4]arene molecule and one is located between the molecular complexes in holes of the crystal structure.

All four hydroxyl groups bound to the two opposite symmetry equivalent benzene rings which are located around the mirror plane form intramolecular O-H···O hydrogen bonds to the hydroxyl group of the neighboured benzene rings. The O···H bond lengths amount to 1.83 and 1.93 Å and the O-H···O angles to 169.6 and 171.0°. The four remaining hydroxyl groups form intermolecular O-H···N hydrogen bonds to the pyridine molecules. The N···H bond lengths (H8···N21: 1.84 Å and H10···N31: 1.85 Å) as well as the O-H···N angles (O8-H8···N21: 172.7° and O10-H10···N31: 172.3°) indicate strong hydrogen bonding. In the crystal structure the molecular complexes are well separated. Due to the hydrogen bonding to the solvent molecules there are no short contacts between the calixarene molecules.



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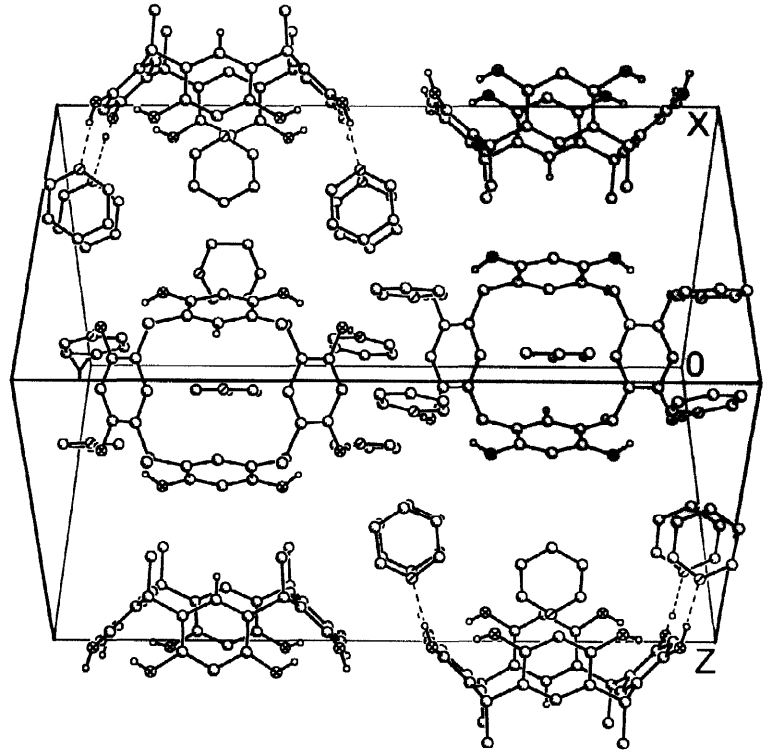

Fig.2: Crystallographic structure of complex of the resorc[4]arene-pyridine complex (recrystallized from pyridine):
(A) View from hydrogen bonding between the resorc[4]arene hydroxyl groups and the pyridine nitrogens with labelling
(B) View on (101)
Hydrogen bondings is shown as dotted lines; ◎: O, ○: C, ◎: N.

Experimental Part

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AM 300 spectrometer at room temperaure. Coupling constants (J) are given in Hz. Mass spectra were recorded with a LAZARUS II (performed by H. Luftmann, Organisch Chemisches Institut, University of Münster, Germany) and a AMD 604 spectrometer. Only selected examples of the ^{13}C NMR and MS spectra are given in the following. The elemental analysis were determined for the selected complexes using Foss Heraeus CHNO-Rapid Elemental Analyser. The melting points are generally > 300 °C.

*General procedure for the preparation of complexes of tetramethylresorc[4]arene (**1**) with amines and amino alcohols.*

In a typical experiment, **1** (1 g) was dissolved in ethanol (10 ml), then the amine or amino alcohol (4 equiv.) was added. After some seconds, a precipitate fell out; its color depended on

the amine or amino alcohol used: In general, the color of the complexes appears cream or pale pink directly after precipitation. After exposing to air it turns deeper. The IR spectra show the typical broad signals between ca. 2000 and 3600 cm^{-1} indicating H bonding and protonated amino groups. In case of the optically active amines and amino alcohols, the complexes were crystallized from ethanol. In general, the yields were 60-80%.

Complex of 1 and dimethylamine (2): ^{1}H NMR (DMSO): δ 1.73 (d, J=7.15Hz, 12H, CH3), 2.55 (s, 12H, CH3), 4.68 (q, J=7.15Hz, 4H, CH), 6.34 (s, 4H, ArH), 7.13 (s, 10H, ArOH··NH), 7.29 (s, 4H, ArH). ^{13}C NMR (DMSO): δ 21.05, 28.53, 37.59, 102.97, 124.19, 124.62, 152.60.

Complex of 1 and diethylamine(3): ^{1}H NMR (DMSO): δ 1.01 (t, J=7.15Hz, 12H, CH_3), 1.43 (d, J=7.4Hz, 12H, CH_3), 2.57 (q, J=7.15Hz, 8H, CH_2), 4.41 (q, J=7.4Hz, 4H, CH), 6.07 (s, 14H, ArH, ArOH··NH), 6.99 (s, 4H, ArH). ^{13}C NMR (DMSO): δ = 14.68, 21.35, 28.66, 43.24, 102.80, 123.93, 124.99, 152.43.

Complex of 1 and diisopropylamine (4): ^{1}H NMR (DMSO): δ = 1.12 (d, J=6.2Hz, 24H, CH_3), 1.56 (d, J=7.15Hz, 12H, CH_3), 3.02 (m, J=6.2Hz, 4H, CH), 4.57 (q, J=7.15Hz, 4H, CH), 5.29 (s, 10H, ArOH··NH), 6.25 (s, 4H, ArH), 7.10 (s, 4H, ArH). ^{13}C NMR (DMSO): δ = 21.35, 22.86, 28.65, 45.10, 102.82, 123.96, 124.97, 152.42. MS (DCI) m/z = 782 [M^+ + 2 of **1**, 2 x **4**, 2 x NH_3].

Complex of 1 and morpholine (5): ^{1}H NMR (DMSO): δ = 1.32 (d, J=7.15Hz, 12H, CH_3), 2.67 (d, J=4.53Hz, 8H, CH_2), 3.49 (t, J=4.53Hz, 8H, CH_2), 4.44 (q, J=7.15Hz, 4H, CH), 5.60 (br s, 10H, ArOH··NH), 6.13 (s, 4H, ArH), 6.82 (s, 4H, ArH). ^{13}C NMR (DMSO): δ = 21.79, 28.86, 30.99, 46.16, 58.99, 67.44, 102.59, 132.65, 125.54, 152.24.

Complex of 1 and piperidine (6): ^{1}H NMR (DMSO): δ = 1.47 (m, 24H, CH_3, CH_2), 2.70 (s, 8H, CH_2), 4.41 (q, J=7.15Hz, 4H, CH), 6.04 (s, 4H, ArH), 6.81 (s, 10H, ArOH··NH), 7.05 (s, 4H, ArH). ^{13}C NMR (DMSO): 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 (LSIMS(+)) m/z 763 [M^+ + 3 of **1**, 2 x **6**, EtOH].

Complex of 1 and S(-)-and R(+)-phenylethylamine (8): ^{1}H NMR (DMSO): δ = 1.24 (d, J=6.44Hz, 7.5H, CH_3), 1.39 (d, J=7.40Hz, 12H, CH_3), 3.98(q, J=6.44Hz, 2.5H, CH), 4.44 (q, J=7.40Hz, 4H, CH), 5.76 (s, 13H, ArOH··NH_2), 6.12 (s, 4H, ArH), 6.91 (m, 4H, ArH), 7.14-7.36 (m, 12.5H, ArH). MS (DCI) m/z 821 [M^+ + 1 of **1**, 2 x **8**, 2 x NH_3]. Anal. Calcd. for $C_{54}H_{65.5}N_{2.5}O_9$ (M.W.= 893.0) : C, 72.58; H, 7.39; N, 3.92; found: C, 72.29; H, 7.40; N, 4.57.

Complex of 1 and R(-)-1-cyclohexylethylamine (9): ^{1}H NMR (DMSO): δ = 0.85-1.71 (m, 40H, CH_3, Cyclohexyl), 3.43 (q, J=6.9Hz, 2H, CH), 4.41 (q, J=7.15Hz, 4H, CH), 6.05 (s, 16H, ArH, ArOH··NH_2), 7.04 (s, 4H, ArH). ^{13}C NMR (DMSO): δ = 18.90, 19.58, 20.98, 26.25, 26.50, 28.46, 28.91, 44.20, 51.31, 56.39, 103.03, 124.20, 124.80, 152.63. Anal. Calcd. for $C_{48}H_{66}N_2O_8$ (M.W.=798.5) : C, 72.15; H, 8.33; N, 3.51; found: C, 69.63; H, 8.66; N, 3.62.

Complex of 1 and R(-)-2-amino-1-butanol (10): ^{1}H NMR (DMSO): δ = 0.85 (t, J=7.39Hz, 7.5H, CH_3), 1.06-1.46 (m, 17H, CH_3, CH), 2.57 (m, 2.5H, CH), 3.16 (dd, 2.5H, CH_2), 3.32 (dd, 2.5H, CH_2), 4.41 (q, J=7.15Hz, 4H, CH), 5.07 (s, 15.5H, ArOH··NH_2, ArOH··OH), 6.07 (s, 4H, ArH), 7.00 (s, 4H, ArH). ^{13}C NMR (DMSO): δ = 10.70, 21.14, 26.05, 28.56, 54.51, 65.59, 102.93, 124.11, 124.71, 152.53.

Complex of 1 and L(-)-phenylalanine (11): ^{1}H NMR (DMSO): δ = 1.32 (d, J=7.15Hz, 12H, CH_3), 2.36 (dd, 2.6H, CH), 2.62 (dd, 2.6H CH), 2.82 (m, 2.6H, CH), 3.13 (dd, 2.6H, CH), 3.23 (dd, 2.6H, CH), 4.39 (q, J=7.15Hz, 4H, CH), 5.12 (s, 15.8H, ArOH··NH_2, ArOH··OH), 6.07 (s, 4H, ArH), 6.84 (s, 4H, ArH), 7.08-7.24 (m, 13H, ArH). ^{13}C NMR (DMSO): δ = 18.90, 21.58, 28.76, 54.78, 56.40, 65.93, 102.70, 123.82, 125.27, 126.15, 128.47, 129.55, 140.07, 152.33.

Complex of 1 and L(-)-norephedrine (12): ^{1}H NMR (DMSO, RT): δ = 0.78 (d, J=6.4Hz, 6.6H, CH_3), 1.39 (d, 7.15, 12H, CH_3), 2.91 (m, 2.2H, CH), 4.35 (d, J=4.77Hz, 2.2H, CH), 4.41 (q, J=7.15Hz, 4H, CH), 5.31 (s, 14.6H, ArOH··NH_2, ArOH··OH), 6.11 (s, 4H, ArH), 6.92 (s, 4H, ArH), 7.19 (m, 2.2H, CH), 7.30 (m, 11H, ArH). ^{13}C NMR (DMSO): δ = 17.91, 18.90, 21.49, 28.72, 52.62, 56.40, 77.35, 102.75, 123.89, 125.16, 126.91, 127.03, 128.07, 143.71, 152.37.

Complex of 1 and pyridine (13)

Tetramethylresorc[4]arene (**1**) (1 g) was dissolved in acetone (10 ml), then pyridine (**13**) (4 equiv.) was added. After some minutes a precipitate fell out. Stirring was continued for 3 hours. The precipitate was separated by filtration and recrystallized from acetone. Yield of 60%: ^{1}H NMR (DMSO): δ = 1.76 (d, J=7.3Hz, 12H, CH_3), 3.08 (s,broad, 4H, OH··N), 4.53 (q, J=7.2Hz, 4H), 6.22 (s, 4H, ArH), 7.35 (m, 4H, CH), 7.65 (s, 4H, ArH), 7.75 (m, 2H, CH), 8.57 (m, 4H, CH), 8.68 (s, broad, 4H, OH··OH).

X-ray crystal structure analysis

Formula $C_{32}H_{32}O_8$ * $4C_5H_5N$ * 4/2 C_5H_5N, M = 1019.18, 0.5 x 0.4 x 0.2 mm, a = 14.440(2), b = 25.346(2), c = 14.836(2) Å, V = 5429.9(11) Å^3, ρ_{calc} = 1.247 g cm^{-3}, μ = 6.69 cm^{-1}, Z = 4, orthorhombic, space group *Pnma* (No. 62), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 8691 reflections collected (-h, +k, ±l), [(sinθ)/λ] = 0.54 Å^{-1}, 4443 independent and 2964 observed reflections [$I \geq 2\ \sigma(I)$], 368 refined parameters, R = 0.075, wR^2 = 0.193, max. residual electron density 0.32 (-0.44) e Å^{-3}, hydrogens calculated and riding. Further details of the structural investigations have been deposited [6].

Data sets was collected with an Enraf Nonius CAD4 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92.

Acknowledgement

This work was supported by the State Committee for Scientific Research, Poland (Project 3T09A00613) and by the Volkswagen-Stiftung, Hannover, Germany (Osteuropa-Programm). JM acknowledges support by the Fonds der Chemischen Industrie, Frankfurt. We are also grateful to Dr. H. Luftmann (Münster) for measuring the mass spectra.

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[6] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].