STUDIES ON RESORCINARENES AND THEIR ANALYTICAL APPLICATIONS

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1. INTRODUCTION

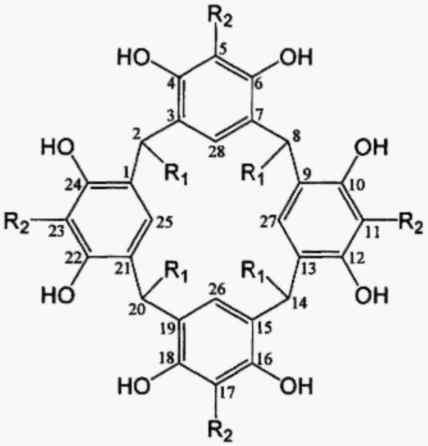
Resorcinarenes are analogs of calixarenes with two hydroxyl groups in benzene rings forming a macrocycle. Resorcinarenes belong to a class of [1n] metacyclophanes, In 1940, Niederl /1/ directed attention towards resorcinol-derived calixarenes. After that the chemistry of resorcinarenes was studied, in detail, by Högberg /2/, Erdtman /3/, Cram /4/, Reinhoudt /5/, Konovalov /6/, Śliwa /7/, and others /8-16/.

Resorcinarenes have been synthesized from acid-catalyzed condensation reaction of resorcinol or 2 – substituted resorcinol and an aliphatic aldehyde or aromatic aldehyde. In resorcinarenes, resorcinol units are linked by methylene bridges at their 4 and 6 positions.

Structure (1) was finally proved by Erdtman *et al.* /3/, in 1968, by a single crystal x-ray analysis.

Gutsche /8/ and Böhmer /9/ suggested to classify them as calixarenes by calling them calix[4]resorcinarenes or resorcinol-derived calixarenes. Totally different names like Högberg compounds /10/, or Octols /11/, or resorcinolarenes /12/, or resorcarenes /13/ also appeared in literature.

The official IUPAC name for compound (1) [Where, R_1 = aliphatic, R_2 = H] is 2,8,14,20-tetraalkyl pentacyclo $[19.3.1.1^{3,7}.1^{9\ 13}.1^{15,19}.]$octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4, 6, 10, 12, 6, 18, 22, 24-octol /14-18/.



(1) Where R_1 = Aliphatic or Aromatic groups
$R_2 = H$

Resorcinarenes are interesting for their receptor properties and as building blocks for large supramolecular assemblies of a fascinating architecture /5,19-21/. The bridging of hydroxyl groups of resorcinarenes leads to cavitands, bowl shaped species serving as synthetic receptors and able to assembly into capsules /22-27/.

In this review, selected examples of resorcinarenes are described, showing their synthetic approaches and reactivity as well as formation of complexes, host-guest systems and capsules. The preparation of mono- and multi-layers of resorcinarenes, promising for their applications, is also presented.

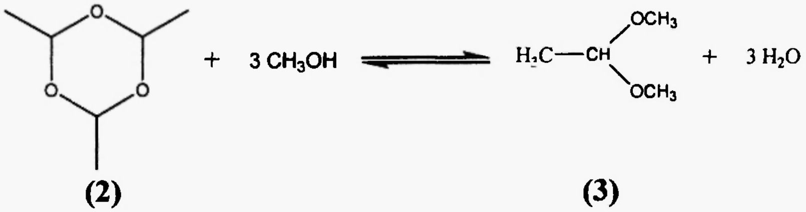
2. SYNTHESIS

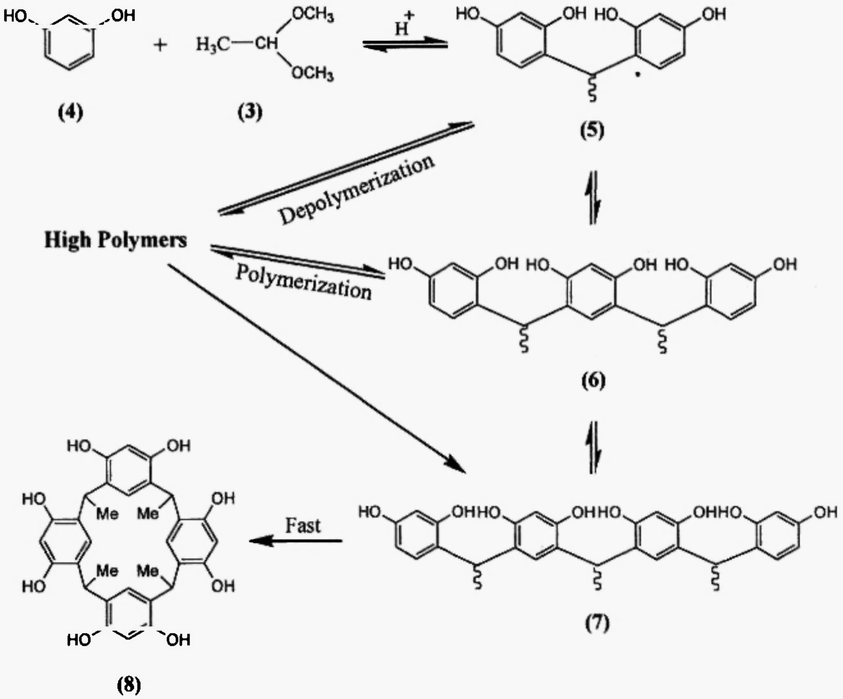
Resorcinarenes can be obtained in high yields via simple, one step procedures without using templates or high dilution techniques.

A) Most cases involve the acid-catalyzed condensation reaction between resorcinol and aliphatic or aromatic aldehydes /10,11,28/.

Weinelt and Schneider studied the reaction mechanism of the acid-catalyzed condensation reaction between resorcinol and acetaldehyde in methanol / HCl /29/.

The electrophile stems not directly from the aldehyde but from its rapidly

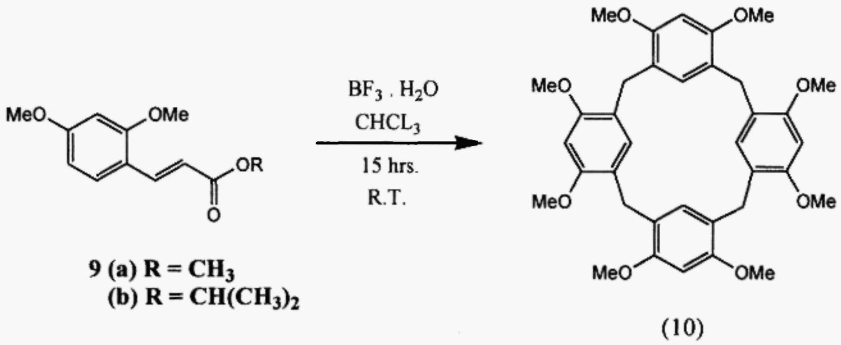




formed dimethylacetal (3). By high field ^{1}H NMR spectroscopy, they established that formation of cyclic tetramer (8) proceeds via sequential coupling of (3) with resorcinol units (4) to form intermediates (5), (6), (7) or higher oligomers containing more than four monomers. The dimmers (5) and trimmers (6) could be isolated, but the tetramers (7) cyclize too fast to accumulate in observable quantities. This fast cyclization is related to their conformation, which, according to molecular calculations, is folded rather then linear as a consequence of the ability to form stronger hydrogen bonds between phenolic hydroxyl groups of adjacent resorcinol units in the folded structure.

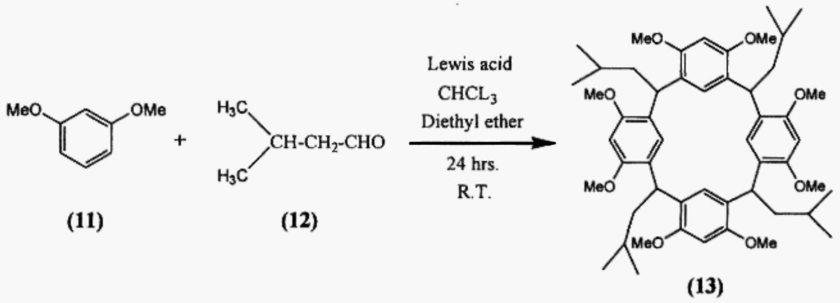
(B) Other types of condensation reactions

* Treatment of (E)-2,4-dimethoxy cinnamates (9) with BF_3 in chloroform at room temperature for 15 hrs. gave the related ocatmethylated resorcinarenes (10) in 75 % yield /17/.



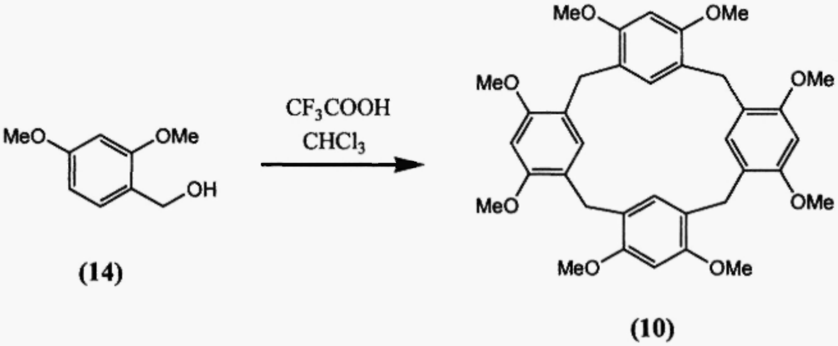
The ratio of the conformation of (10) is 3 : 2 mixture of boat isomer (all cis) : diamond isomer (cis.cis.trans).

* Another high yield synthesis of resorcinarenes (13) involves the lewis acid catalyzed condensation tetramerization of 1,3- dimethoxy benzene (11) with isovalaraldehyde (12) /30/.

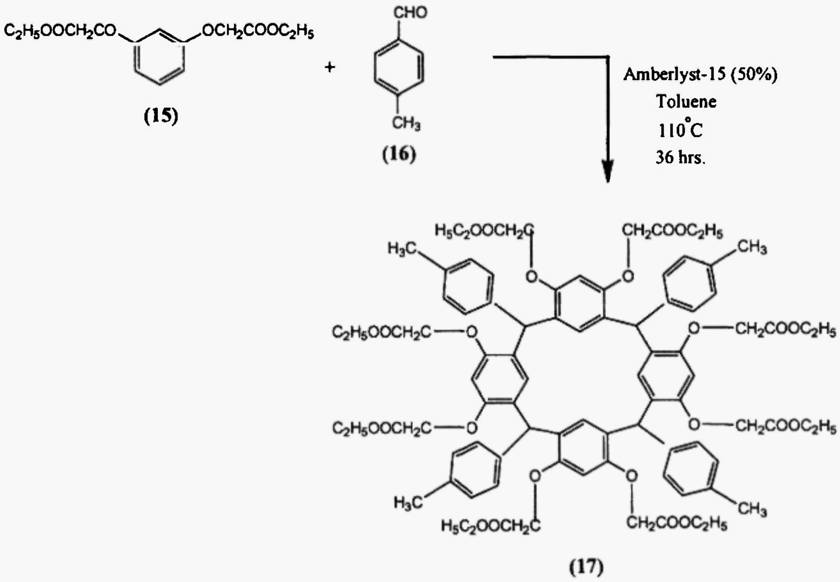


Different types of lewis acids like $SOCl_2$, $POCl_3$, $AlCl_3$, $SiCl_2Me_2$, $SiClMe_3$, $SnCl_4$ had been used. Amongst these lewis acids, only $SnCl_4$ catalyses this reaction selectively and promotes the formation of the crown conformer (rccc) in high yield (85%).

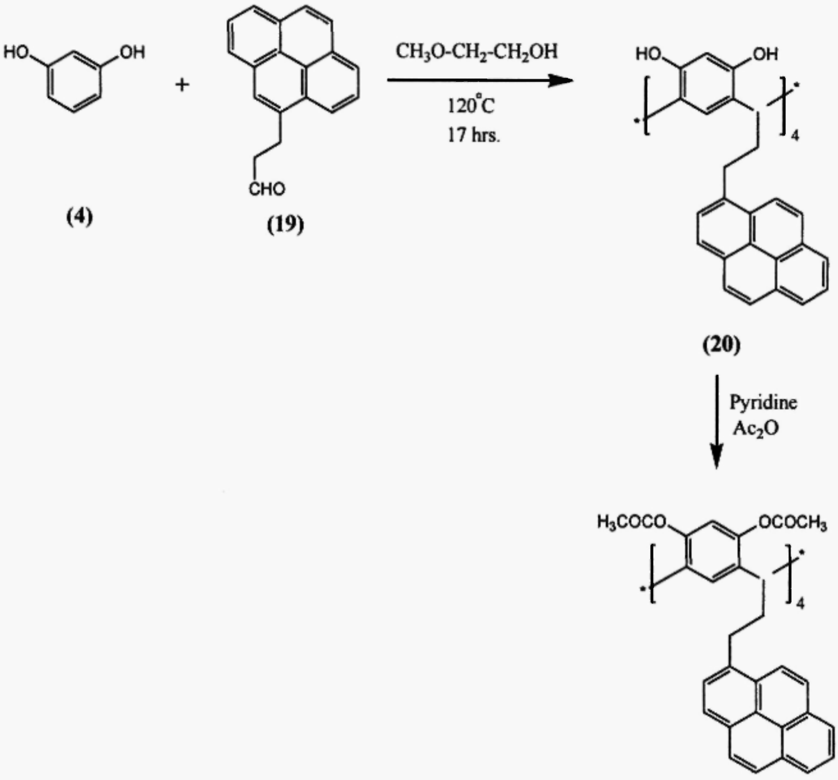
* When 2,4- dimethoxy benzyl alcohol (14) was treated with trifluoroacetic acid (5% in $CHCl_3$), resorcinarene (10) was obtained in 95 % yield /31/.



* Single step synthesis of O-functionalized resorcinarenes under heterogeneous catalytic conditions has been reported /32/. Cation-exchange resin (Amberlyst-15) induced condensation of diethyl benzene-1,3-diyldioxydiacetate (15) and p-methyl benzaldehyde (16) was reported as a novel synthesis of resorcinarene (17) in 34 % yield.



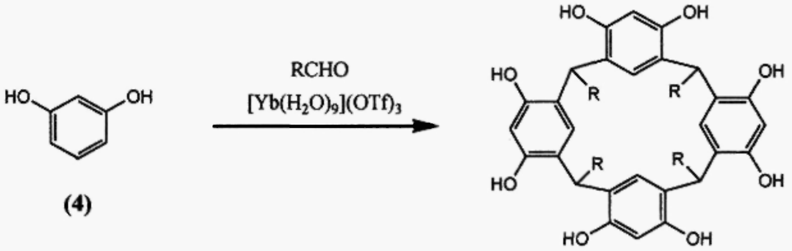
* A mixture of octaactylated calix[4]resorcinarenes with varying numbers of 2-(pyren-1-yl)ethyl residue is synthesized by acid-catalyzed condensation reaction of resorcinol (4) with 3-(pyren-1-yl)propanal (18), followed by acetylation /33/.



(4) **(19)** **(20)** **(21)**

The product is separated using reverse phase silica gel column HPLC. Measurements of steady state spectra and decay time of pyrene fluorescence of the (21) revealed that they form two types of excimer.

* The synthesis of resorcinarene (22) was carried out by acid-catalyzed condensation of resorcinol with aldehydes, catalyzed by ytterbium (III) triflate nonahydrate $\{[Yb(H_2O)_9](OTf)_3\}$ /34/.



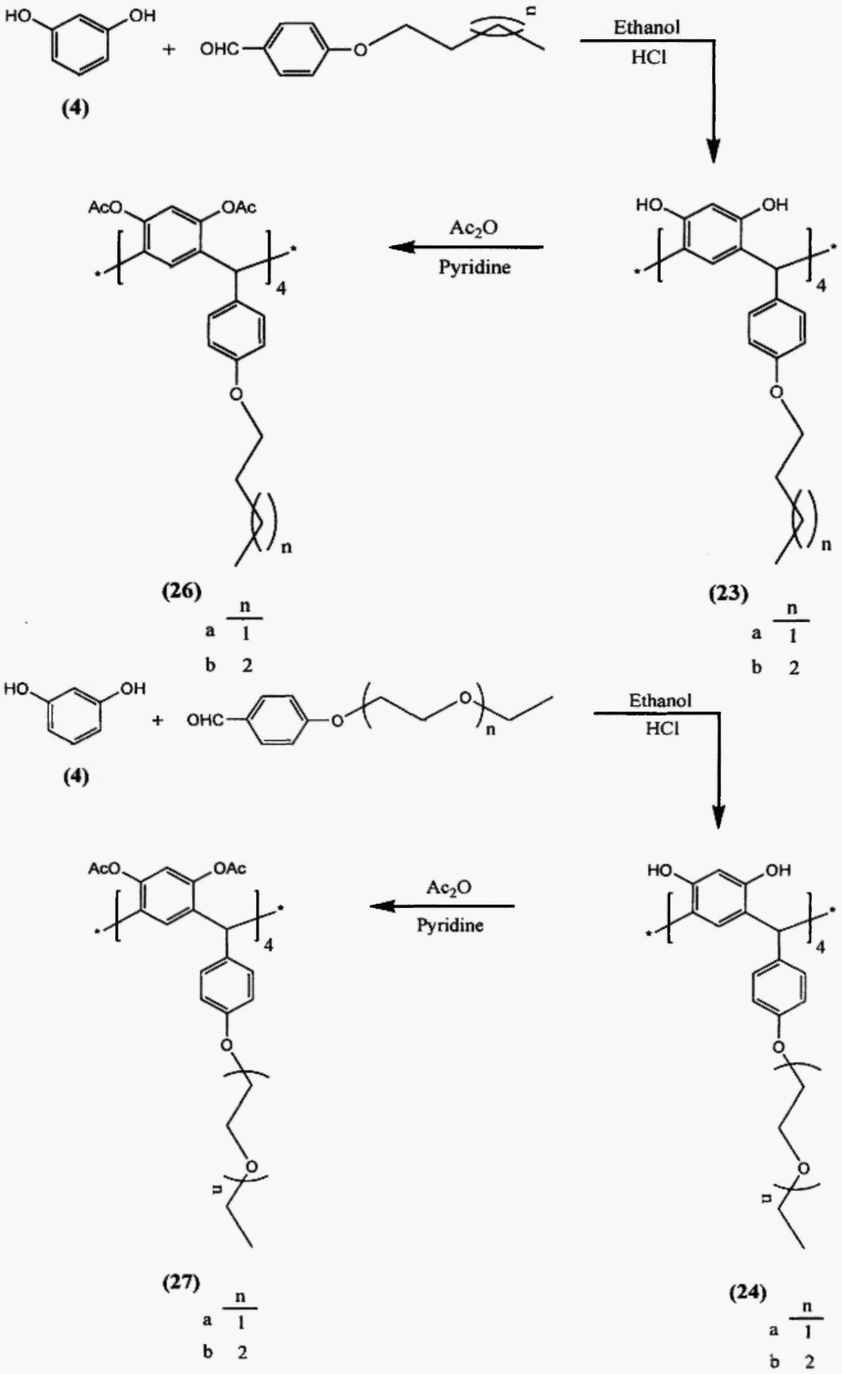
(4)

(22)

	R
a	C_2H_5
b	C_5H_{11}
c	C_9H_{19}
d	$C_{11}H_{23}$
e	C_6H_5

In the study of conformational properties of resorcinarenes, the relative stability of five extreme conformations of 22(a) and their intramolecular hydrogen bonding was investigated by ab initio calculations /35/. The structure of 22 (c,d) has been investigated by ^{1}H and 13C NMR spectroscopies. It was established that these compounds exist in CD_3CN in crown conformation, in $CDCl_3$ solutions. This conformation is violated by the intramolecular associations.

* The condensation of resorcinol with benzaldehyde derivatives affords resorcinarenes (23-25), which undergo acetylation to give acetyl resorcinarenes (26-28) /36/.



(4)

(26)

	n
a	1
b	2

(23)

	n
a	1
b	2

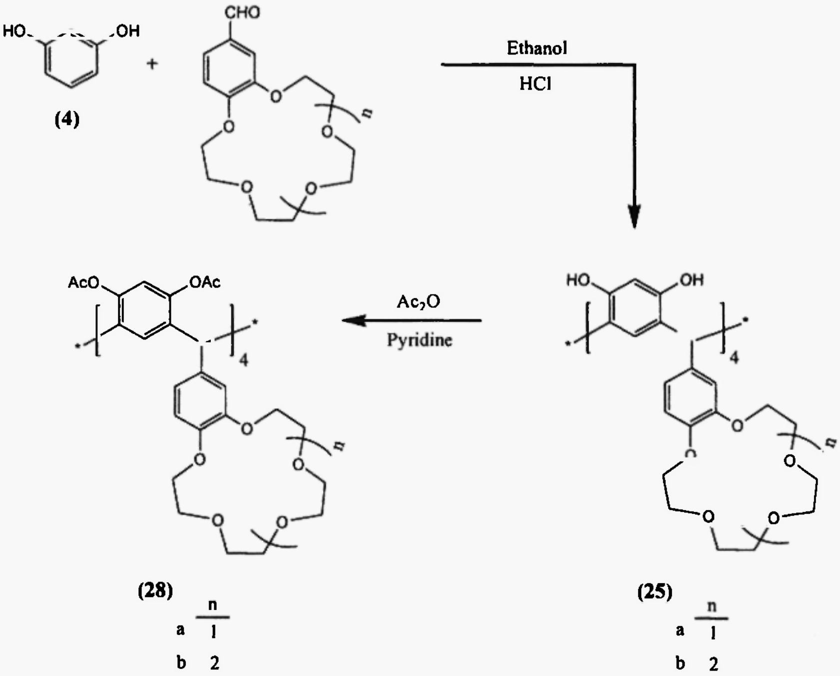
(4)

(27)

	n
a	1
b	2

(24)

	n
a	1
b	2



(4)

(28)

	n
a	1
b	2

(25)

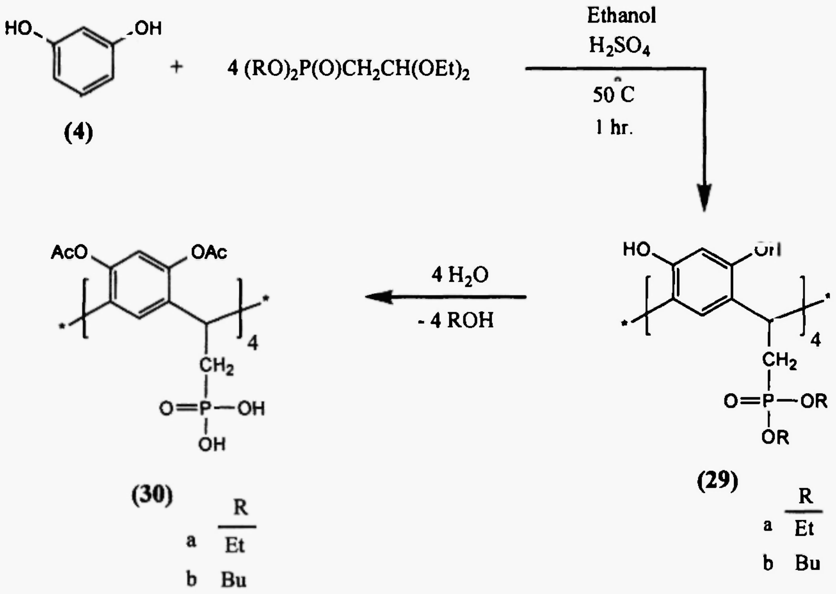
	n
a	1
b	2

It was found that these compounds (23-25), and among them especially 25 (a,b) are efficient carriers of K^+ ions across liquid membrane showing enhanced K^+/Na^+ selectivity.

* The synthesis of phosphorous-containing resorcinarene (29,30) was studied /37/.

The reaction between phosphorous-containing acetals with resorcinol under acid-catalyzed condition was studied. The first representatives of resorcinarene products (29) and (30) bearing phosphorous-containing fragments on the lower rim.

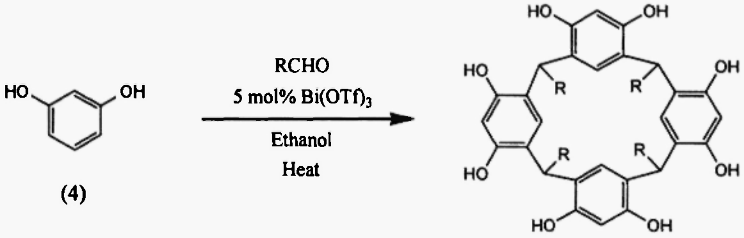
* $Bi(OTf)_3$ (5 mol%) catalyzes the condensation of aromatic and aliphatic aldehydes with resorcinol to give tetrameric cyclic products, resorcinarene (31) /38/.



(4)

(29)

(30)



(4)

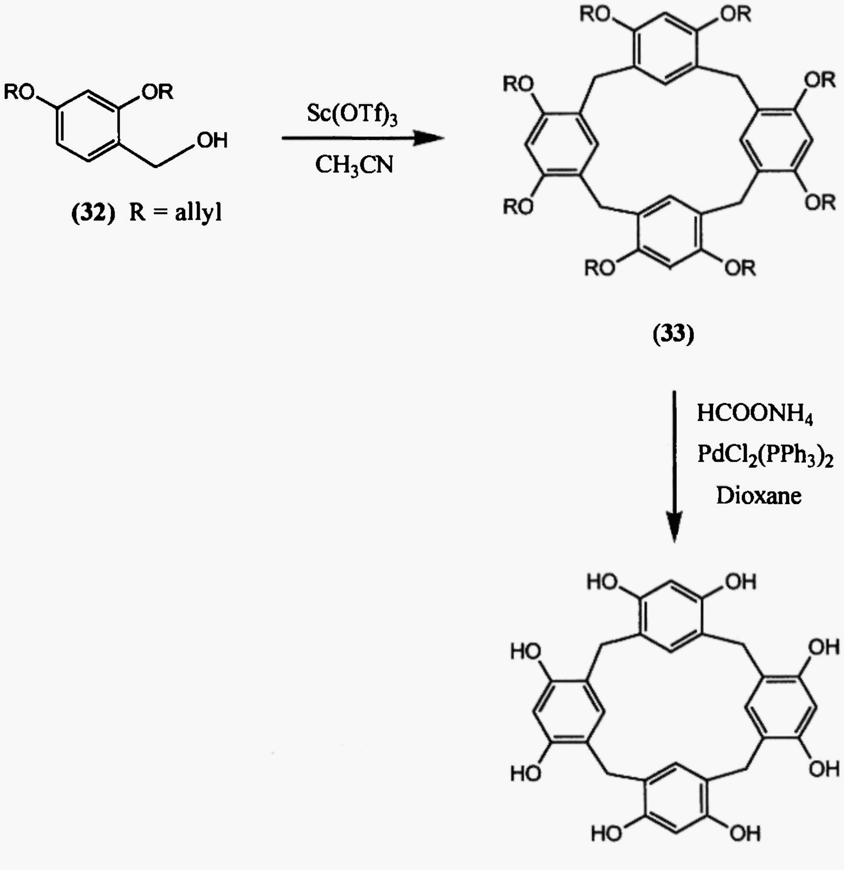
(31)

	R	Reacⁿ.time	Yield	Diastereomers ratio
a	C_6H_5	75 min.	66 %	0.78 : 1
	C_6H_5	8 days	89 %	1 : 0
b	C_9H_{19}	24 hrs.	91 %	1 : 0
c	C_5H_{11}	4 hrs.	84 %	1 : 0

With benzaldehyde, the product is obtained as a mixture of two diastereomers. The ratio of diastereomers depends on reaction time. When aliphatic aldehyde have been used, a single diastereomer is obtained.

The low toxicity, low costing and ease of handling of bismuth compounds coupled with fast reaction time make this method attractive as an alternative to the existing methods for resorcinarene formation.

* Another example involves the cyclocondensation of 2,4-bis(allyloxy)benzyl alcohol (32) catalyzed by Sc(OTf)$_3$, leading to compound (33). The subsequent deallylation of (33) by treating with ammonium formate and PdCl$_2$(PPh$_3$)$_2$ affords the parent resorcinarene (34) existing in 1,3-alternate conformation /39/.



(32) R = allyl

(33)

(34)

* The synthesis of resorcinarenes was carried out with formaldehyde and unsubstituted resorcinol; the products were polymers /8/. The reason is that formaldehyde has no alkyl chains at the methylene bridges. In certain cases, formaldehyde and 2-methyl resorcinol or pyrogallol yield isolable amounts of tetrameric products /40/.

Resorcinol derivatives with electron withdrawing substituents like $-NO_2$ or –Br /11/ at the 2-position or in which the hydroxyl groups are (partially) alkylated /29/, do not give cyclic products.

Throughout the years, a variety of resorcinarenes have been synthesized. Most of these are listed in the following Table 1.

Table 1

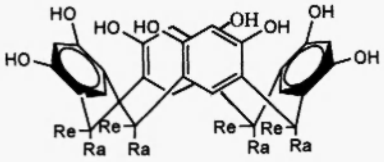
Yield of resorcinarene (1) synthesized from unsubstituted or 2-substituted resorcinol with aliphatic or aromatic aldehydes.

R_1 in 1	**R_2 in 1**	**% yield**
$-CH_3$	-H	73%
$-CH_2CH_3$	-H	88%
$-(CH_2)_2CH_3$	-H	92%
$-(CH_2)_3CH_3$	-H	89%
$-(CH_2)_4CH_3$	-H	77%
$-(CH_2)_{11}CH_3$	-H	69%
$-CH_2CH(CH_3)_2$	-H	95%
$-(CH_2)_4OH$	-H	80%
$-(CH_2)_5Cl$	-H	67%
$-CH_2C_6H_5$	-H	70%
$-(CH_2)_2C_6H_5$	-H	69%
$-(CH_2)_2SO_3Na$	-H	40%
$-(CH_2)_8CH=CH_2$	-H	20%
C_6H_5-	-H	83%
$2-OHC_6H_4-$	-H	78%
$3-NO_2C_6H_4-$	-H	72%
$3-H_3CSC_6H_4-$	-H	77%
$4-BrC_6H_4-$	-H	43%
$4-(CH_3)_3CC_6H_4-$	-H	28%
$4-C_6H_5C_6H_4-$	-H	99%
$4-NCC_6H_4-$	-H	52%
$4-HOOCC_6H_4-$	-H	79%
$4-H_2NC_6H_4-$	-H	Not reported
$4-AcHNC_6H_4-$	-H	82%
$4-H_3COC_6H_4-$	-H	93%
$4-C_6H_5OC_6H_4-$	-H	76%
$4-HO\ C_6H_4-$	-H	91%
$3,4-[(OCH_2CH_2)_4O]C_6H_3-$	-H	43%
$[(CH_3)_3S]C-$	-H	34%
$(C_5H_5)Fe(C_5H_4)-$	-H	10%
-H	$-CH_3$	90%
-H	$-CH_3$	53%
$-CH_3$	-OH	72%

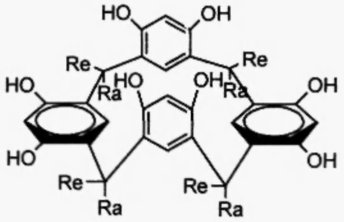
3. CONFORMATIONAL PROPERTIES

Resorcinarenes can exist in different isomeric forms. The stereochemistry of resorcinarenes is defined as a combination of the following three stereochemical elements.

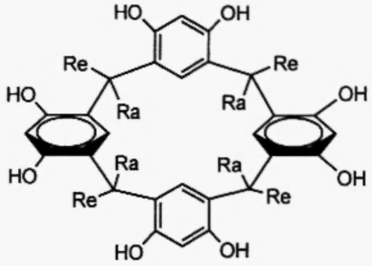
(1) The conformation of the macrocyclic ring. A total of five symmetrical arrangements may be possible.



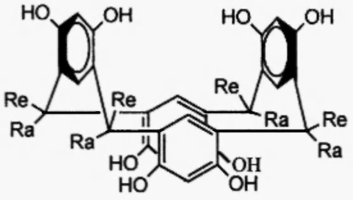
Crown (C_{4v})



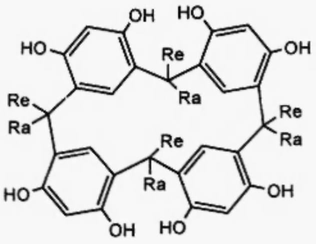
Boat (C_{2v})



Chair (C_{2h})

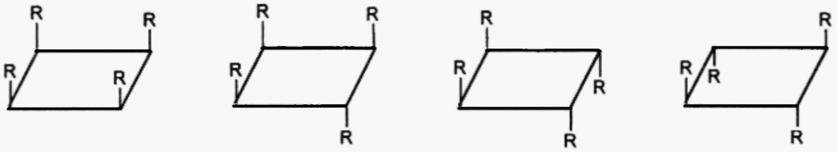


Saddle (D_{2d})



Diamond (Cs)

(2) The relative configuration of the substituents at the methylene bridges. Four types of arrangements are possible.



(3) The individual configuration of the substituents at the methylene bridges which, in conformations of the macrocycles with C-symmetry, may be either axial or equatorial.

Combination of these three elements gives rise to a number of possible stereoisomers. Only four have been found experimentally. The ratio in which all diastereomers are formed during the reaction is dependent strongly on the conditions used. There are many factors that can account for the presence or absence of a certain isomer.

Under homogeneous acidic reaction conditions the product ratio at equilibrium mainly reflects the thermodynamic stability of the different isomers, since the condensation reaction is reversible. Weinelt and Schneider studied the thermodynamic stability of the different isomer of C-methyl calix[4]resorcinarenes /29/.

When the reaction is carried out under heterogeneous conditions, the product ratio at equilibrium is determined by the relative solubilities of the different isomers in the reaction solvent. Högberg studied the reaction between resorcinol and benzaldehyde in heterogeneous conditions /2/.

Thus, the preference for a certain conformation in resorcinarene is governed by two effects.

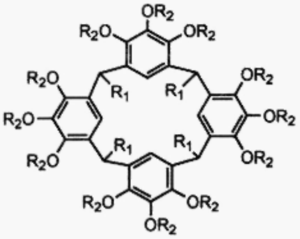
(i) all conformations with the maximum number of hydrogen bonds are preferred.

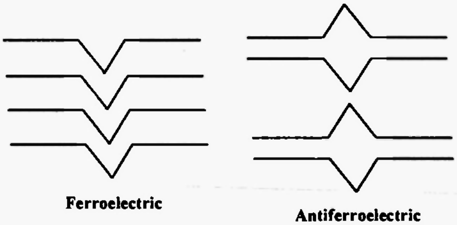
(ii) axial orientations of substituents are strongly favored over equatorial orientations.

4. LIQUID CRYCTALLINE BEHAVIOR

Resorcinarenes, which are fixed in the boat conformation, have a three dimensional bowl-like shape. They have ability to self-organize in ferroelectric (head-to-tail) or antiferroelectric (head-to-head, tail-to-tail) columnar arrangements /41/. Their liquid crystalline properties have been studied in detail /42,43/. Particular interest in such columnar mesophases originates from their potential ferroelectricity when all the columns are oriented in the same direction.

When the following requirements are possible, resorcinarenes become liquid crystalline /44/.





	R_1	R_2
(35)	CH_3	COC_3H_7
(36)	H	COC_nH_{2n+1}

(i) R_1 groups must be small enough to allow an optimal core stacking [maximum $R_1 = CH_3$].

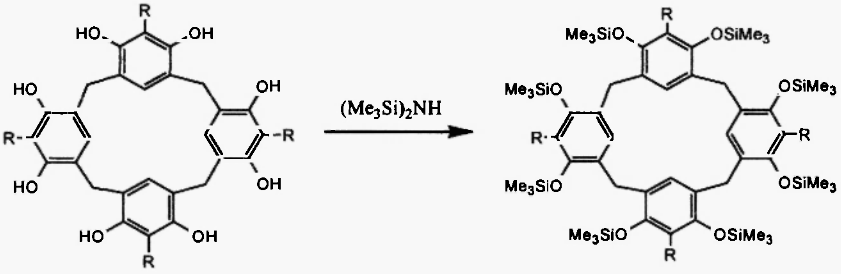
(ii) The presence of at least twelve linear R2 side chains, having 12 to 17 carbon atoms each, to cover the periphery of the core in a homogeneous manner.

(iii) Without bulky substituents close to the macrocycle core, ester groups are favorable to connect the side chains to the periphery.

Single crystal x-ray data of (35) reveal that the molecules are oriented in an antiferroelectric arrangement, most probably as a result of the large dipole moment, which is calculated as 10.3 D for the monomer and almost zero for the antiferroelectric pair /41/. Compound (36) having a conformationally mobile macrocyclic core, already exhibits liquid crystalline behavior with 9-12 carbon atoms in the R_2 side chains /45/. In this case, the presence of a fast ring-inversion process overcomes the constrant for antiferroelectric coupling of the molecules within the columns. In this way, the mesogens should be able to align their dipoles freely under the influence of an electric field.

5. REACTIVITY OF RESORCINARENE

* In the study of reactivity of resorcinarenes /39/, 37 (a,b) were treated with hexamethyldisilazane to give octasubstituted resorcinarenes 38 (a,b) /46/.



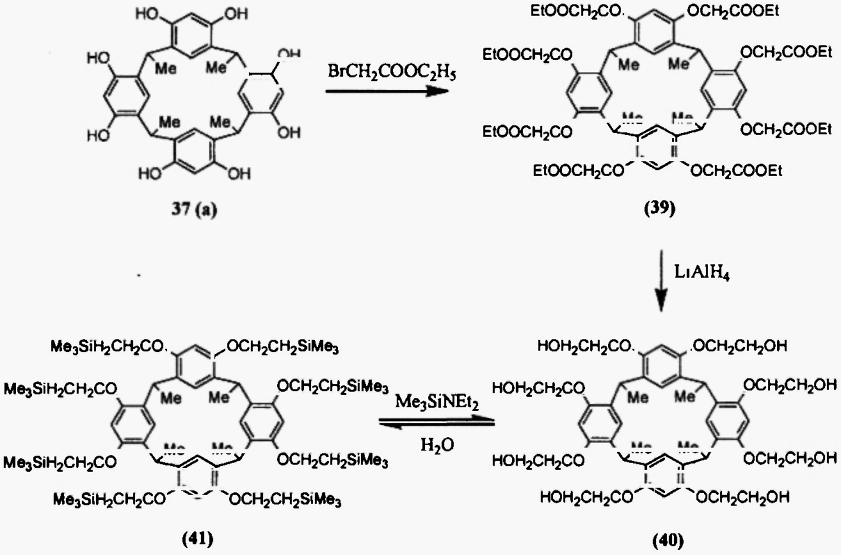
(37)

	R
a	H
b	Br

(38)

	R
a	H
b	Br

* The reaction of 37 (a) with ethylbromoacetate leads to the ester (39), which was reduced with $LiAlH_4$ to yield hydroxymethyl derivative (40). Since (40) could not be obtained in the pure state, this compound as the crude substance was treated with diethyl aminotrimethyl silane affording (41), which by hydrolysis yielded pure (40) /46/.



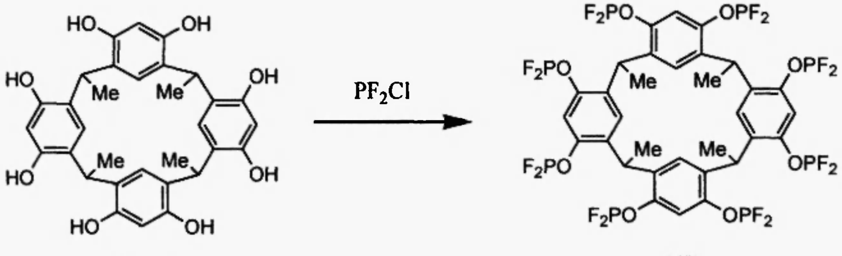
37 (a)

(39)

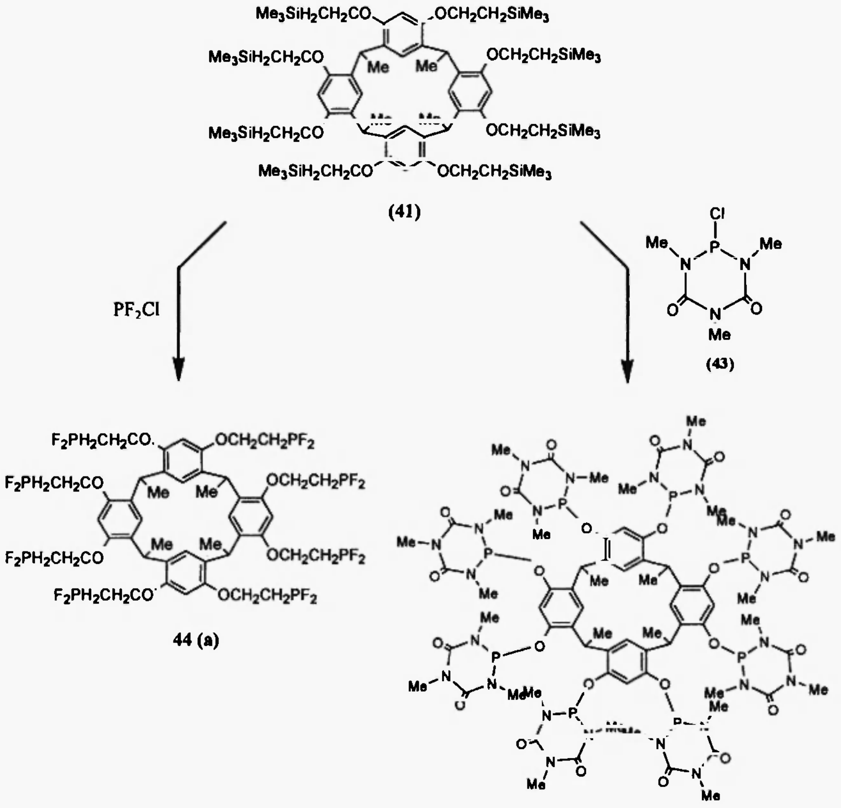
(41)

(40)

* The reaction of 37 (a) with chlorofluorophosphine leads to the unstable derivative (42). When reaction of (41) with chlorodifluorophosphine and with chlorotriazaphosphoridine (43) afford stable compounds 44 (a,b) /47/.



37 (a) **(42)**



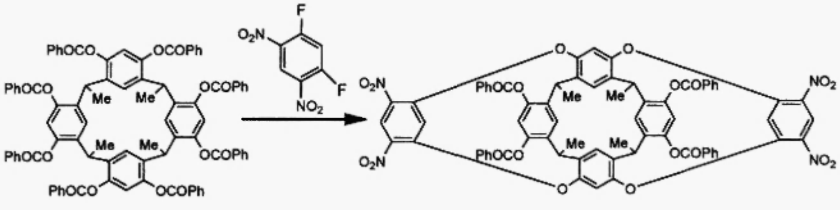
(41)

(43)

44 (a)

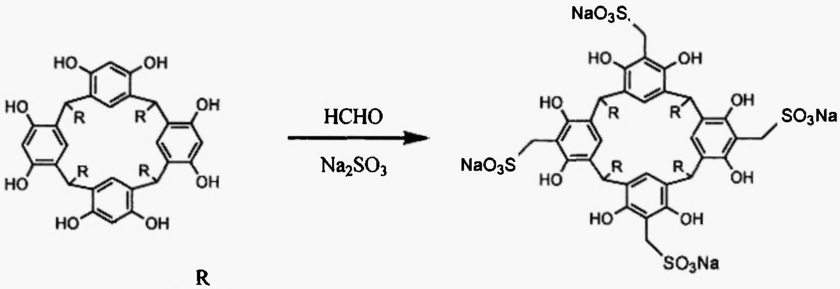
44 (b)

* Resorcinarene derivative (45) reacts with 1,3-difluoro-4,6-dinitrobenzene to give the rigid tetranitro resorcinarene (46) /48/.



(45) **(46)**

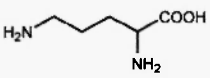
- The reaction of resorcinarenes 37 (a) and (47) with formaldehyde and sodium sulphate affords water soluble compounds 48 (a,b) /49/.



	R
37 (a)	Me
47	C_9H_{19}

		R
(48)	a	Me
	b	C_9H_{19}

It was observed that 48 (a) forms host-guest complexes with α-amino acids (49-53) and a stable 1:1 complex with diglycidylmethyl phosphonate (54) /50/.



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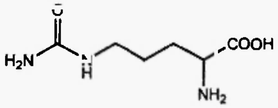

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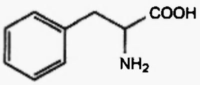

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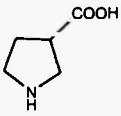
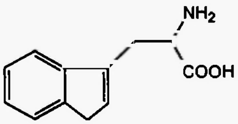


(52)



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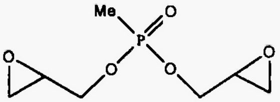
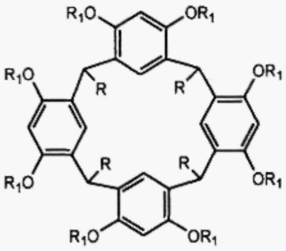


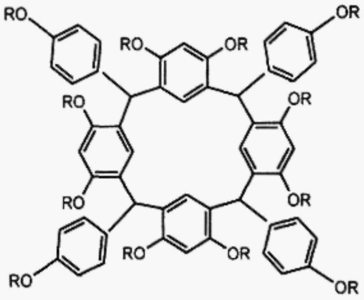
(54)

* Investigating functionalization of hydroxyl groups of resorcinarenes, it was shown that resorcinarene 55(a) may be converted into 55 (b,c) /51/ and resorcinarene 56 (a) into 56 (b-e) derivatives /52/.



R = Me, Et

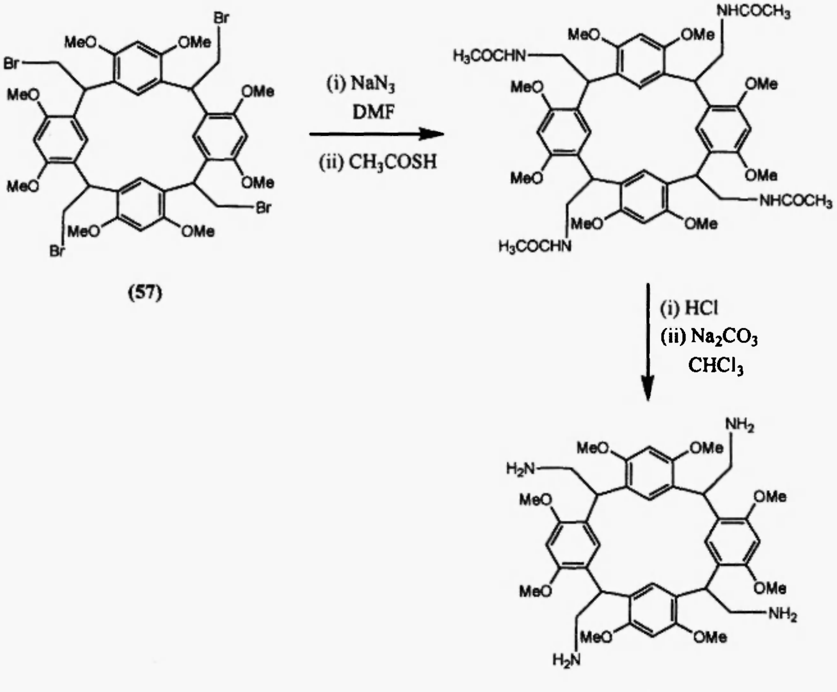
		R_1
55	a	H
	b	Me
	c	$COCH_3$



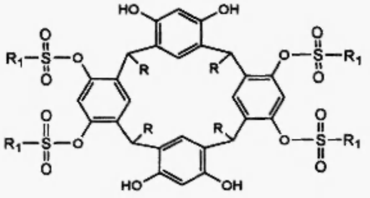
		R
56	a	H
	b	Me
	c	$COCH_3$
	d	$COCH_2CH_2CH_3$
	e	CH_2Ph

* In the study of aminomethylation of resorcinarenes /53,54/ following reactions of tetra(bromomethyl) resorcinarene (57) leading to tetra(aminomethyl) resorcinarene (58) have been made.

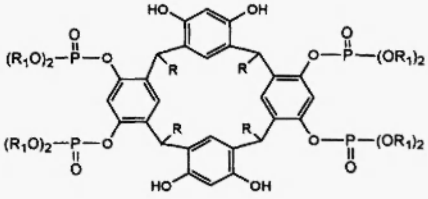
* Resorcinarene of C_{2v} symmetry tetrasulphonates 59 (a-e) and tetra phosphates 60 (a-c) are useful as molecular platforms for the design of cation receptors, containing different binding units in the molecules /55/.



(58)

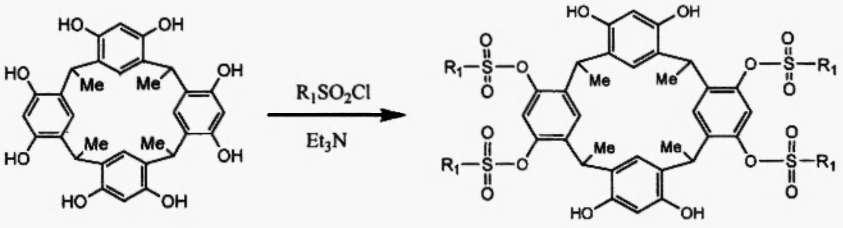


		R	R$_1$
59	a	Me	p-Tol
	b	Me	p-ClC$_6$H$_4$
	c	Me	Mes
	d	Pr	p-Tol
	e	C$_5$H$_{11}$	p-Tol



		R	R$_1$
60	a	Me	i-Pr
	b	Me	Bu
	c	C$_5$H$_{11}$	Et

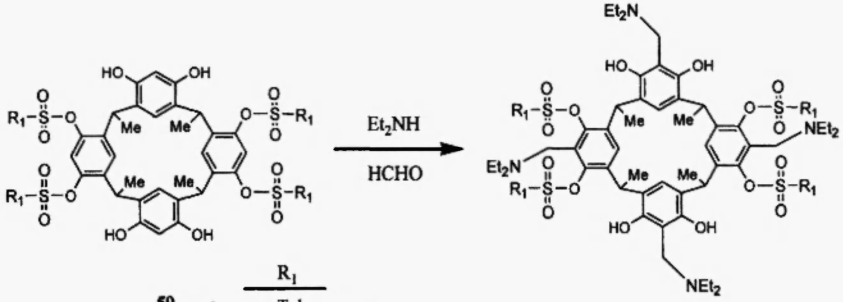
In order to obtain 59 (a-c), the resorcinarene 37 (a) was treated with arylsulphonylchlorides. The intramolecular hydrogen bonds S=O----H-O enable asymmetric arrangement of four arylsulphonyl groups and molecular chirality of 59 (a-c). It was observed that 59 (c) forms in the solid state and in CDCl$_3$ the cross-shaped dimmer linked by four intermolecular OH----OH hydrogen bonds /55/.



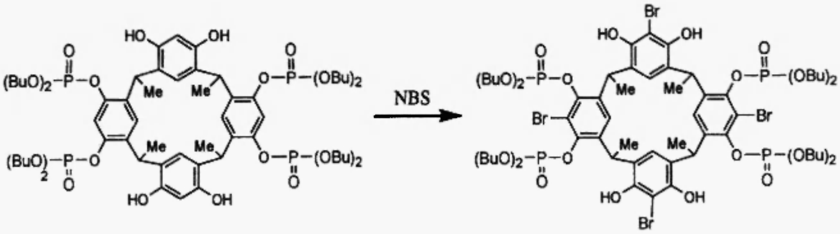
37 (a)

		R$_1$
59	a	p-Tol
	b	p-ClC$_6$H$_4$
	c	Mes

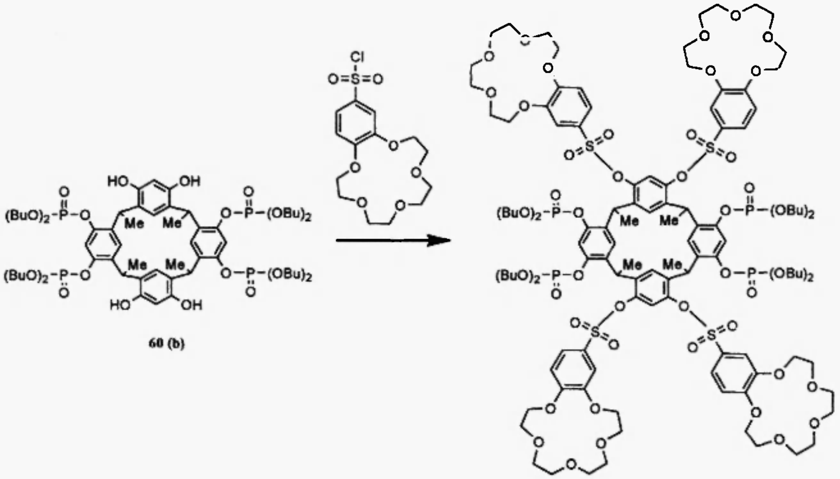
The following reactions of tetrasulphonates and tetraphosphates have been made /51/.



		R$_1$
59	a	p-Tol
	b	p-ClC$_6$H$_4$
	c	Mes

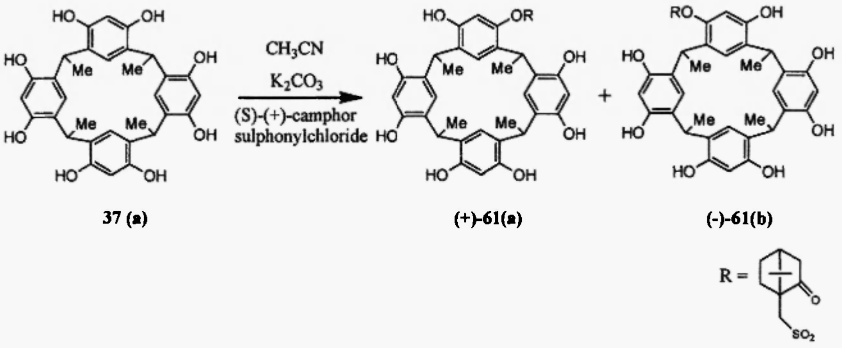


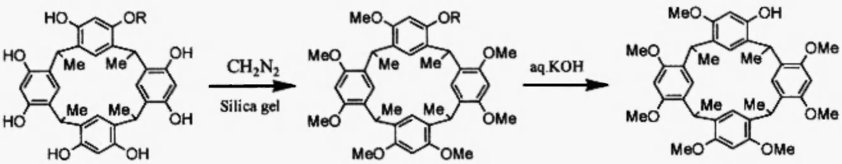
60 (b)



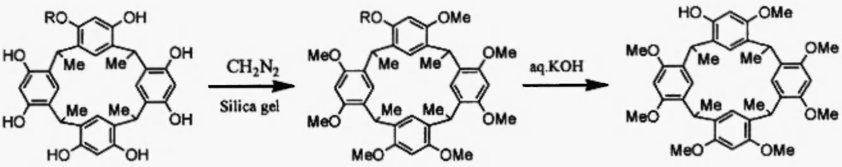
* Chiral, enantiomerically pure resorcinarene (+)-63 and (-)-63 have been synthesized from resorcinarene 37 (a), which was mono O-functionalized with (S)-(+)-10-camphorsulphonyl chloride. They were serving as a chiral auxiliary to give diastereomers (+)-61(a) and (-)-61(b), which were separated by H.P.L.C. /56/.

The treatment of (+)-61(a) and (-)-61(b) with ethereal diazomethane solution in the presence of silicagel as a lewis acid gave permethylated resorcinarene (+)-62(a) and (-)-62(b) without epimerization. The chiral auxiliary was removed by treatment of (+)-62(a) and (-)-62(b) with potassium hydroxide solution to give enantiomeric (+)-63 and (-)-63, stable towards moderate acid and basic conditions /56/.



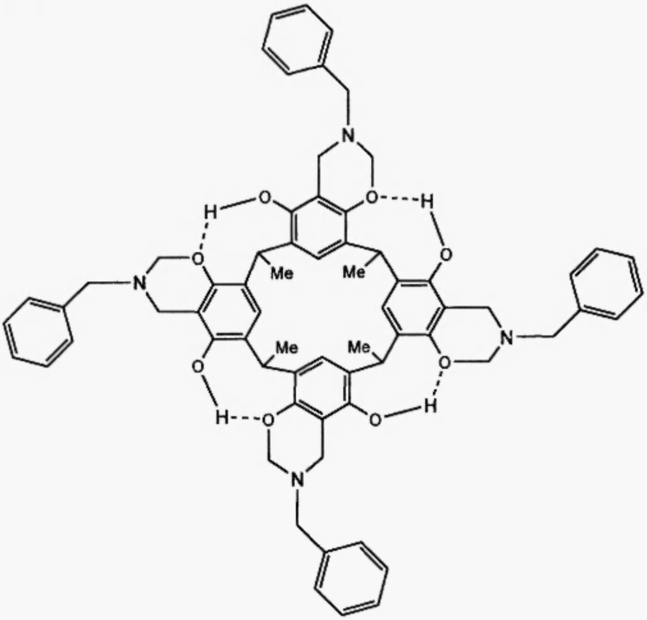


(+)-61(a) **(+)-62(a)** **(+)-63**



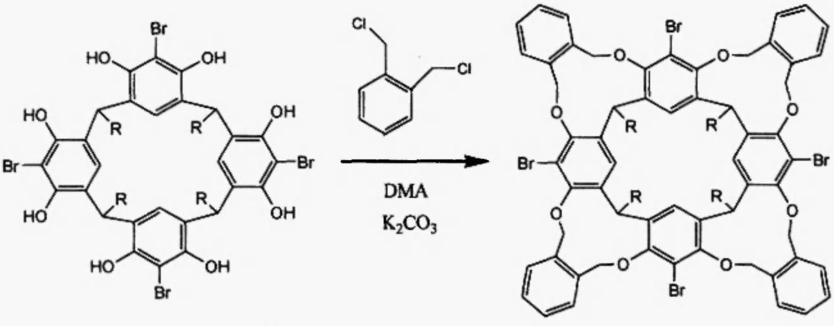
(-)-61(b) **(-)-62(b)** **(-)-63**

* For chiral tetrabenzoxazine resorcinarene (64), the enantionmerization barrier has been determined by computer simulation of the dynamic HPLC experiment /57/.



(64)

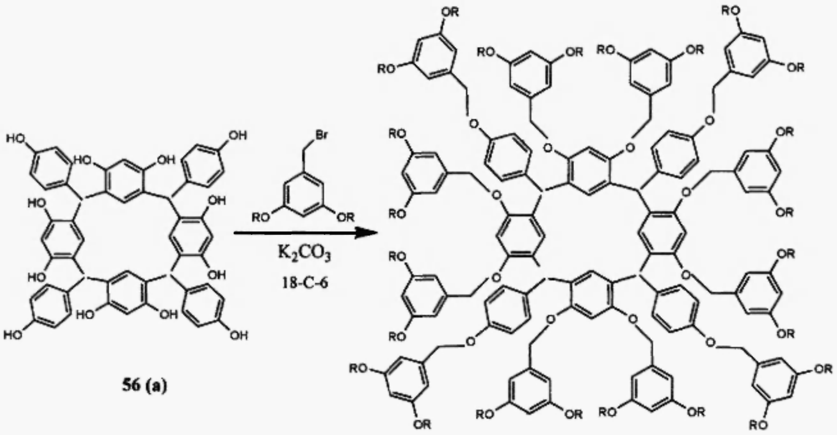
- The reaction of 65 (a,b) leads to bromo-o-xylyl cavitands 66 (a,b) /58/.



		R
65	a	Me
	b	CH_2CH_2Ph

		R
66	a	Me
	b	CH_2CH_2Ph

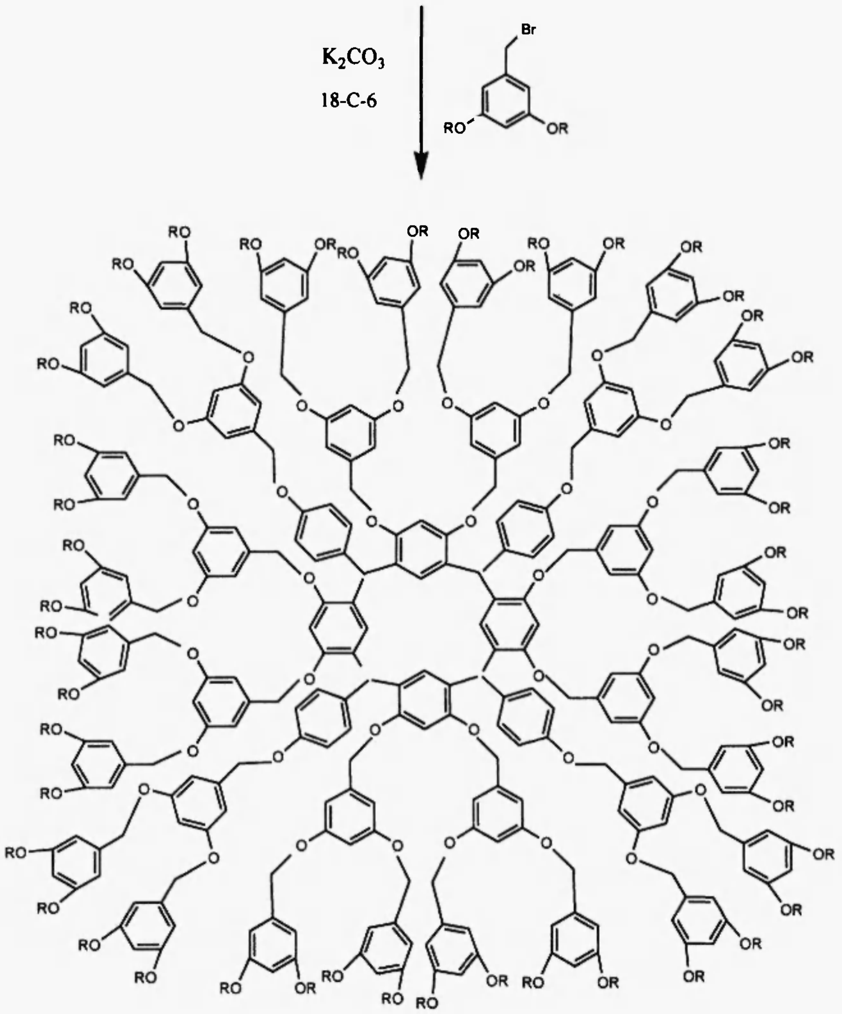
- A rapid, three step synthesis of dendrimers by divergent method, using resorcinarene as core molecule, was made. Highly functionalized resorcinarene 56 (a) and 67 having 12 and 16 hydroxyl groups, respectively, served for this purpose /59/.



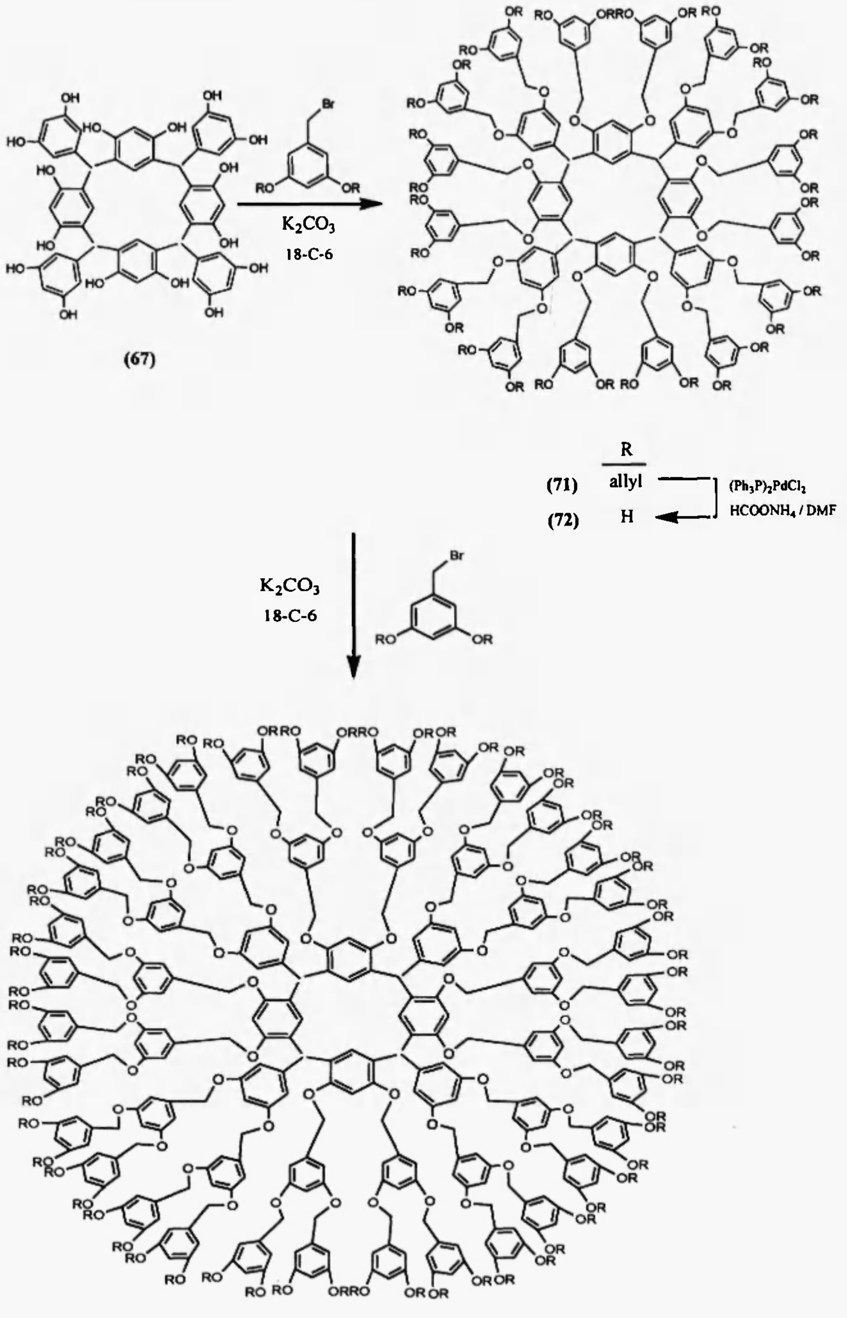
56 (a)

	R
(68)	allyl
(69)	H

$(Ph_3P)_2PdCl_2$
$HCOONH_4$ / DMF



(70) R = allyl



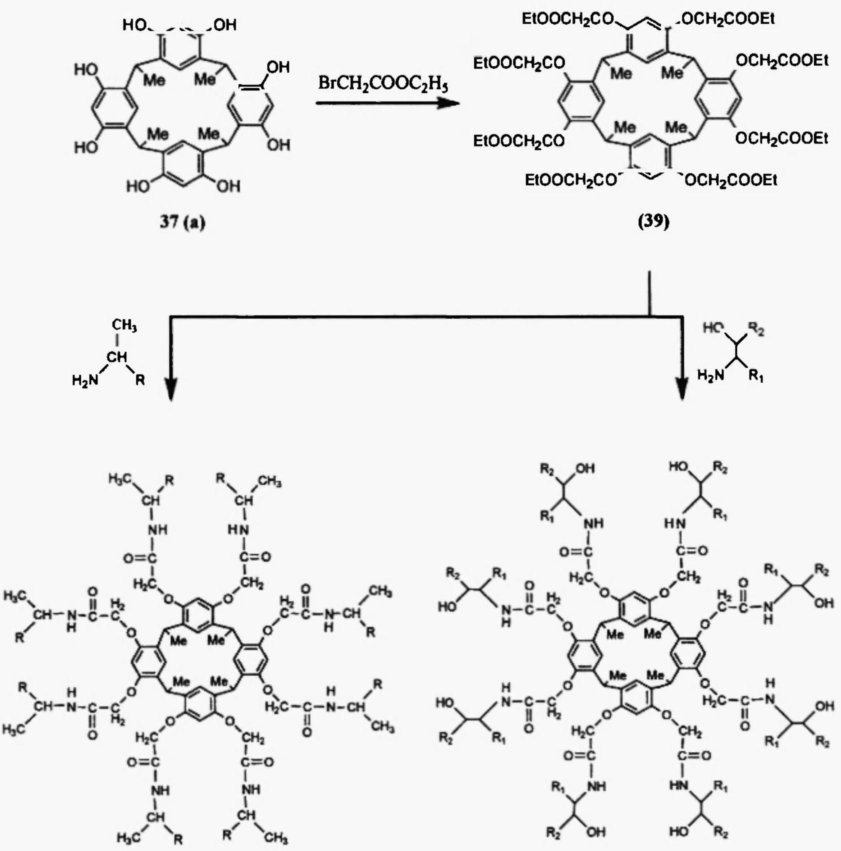
(67)

(71) R = allyl

(72) R = H

(73) R = allyl

* The formation of chiral, enantiomers of (74) and (75) is controlled by the chiral amines and amino-alcohols used for the reaction with 37 (a) /60/.



37 (a)

(39)

(74)

	R
a	Ph
b	C_6H_{11}

(75)

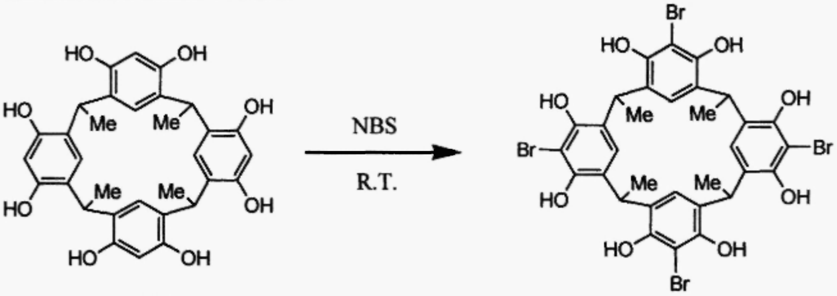
	R_1	R_2
a	C_2H_5	H
b	CH_3	Ph

Formation of dimers of this compound in solution was observed using the LSI-MS and ESI-MS methods.

6. FUNCTIONALIZATION OF RESORCINARENE

The presence of two electron-releasing hydroxyl groups on the aromatic ring of resorcinol units in resorcinarenes makes them highly activated for electrophillic aromatic substitution reactions. Several examples of substitution reaction at the four positions in between the hydroxyl groups have been reported.

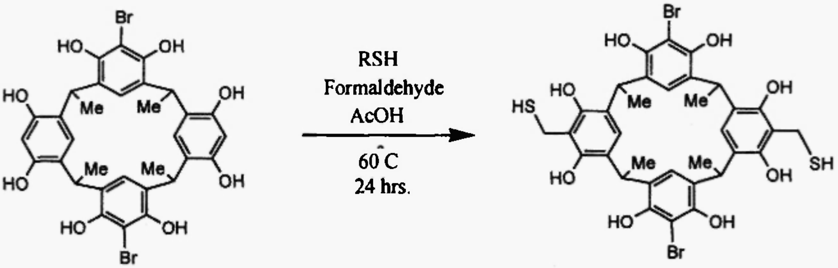
* Bromination /4,61/ of resorcinarene 37 (a) with N-bromosuccinamide at room temperature gives tetrabromide derivative (76) in 80% yield. The reaction takes place only at the four positions in between the hydroxyl groups without affecting other positions in the molecule, even when excess N-bromosuccinamide is used.



37 (a)

(76)

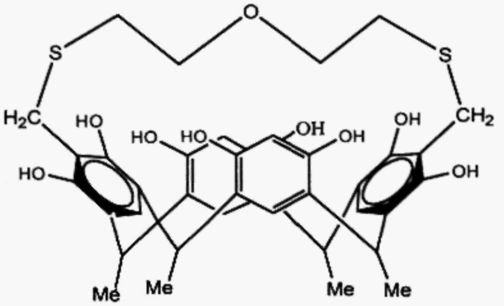
* Partial bromination of resorcinarene 37 (a) gave distal-dibrominated resorcinarene (77) /62/, which on thiomethylation /63/ yields thiomethylated resorcinarene (78). In this type of resorcinarenes, thiomethyl and bromo groups are at the extraannular position.



(77)

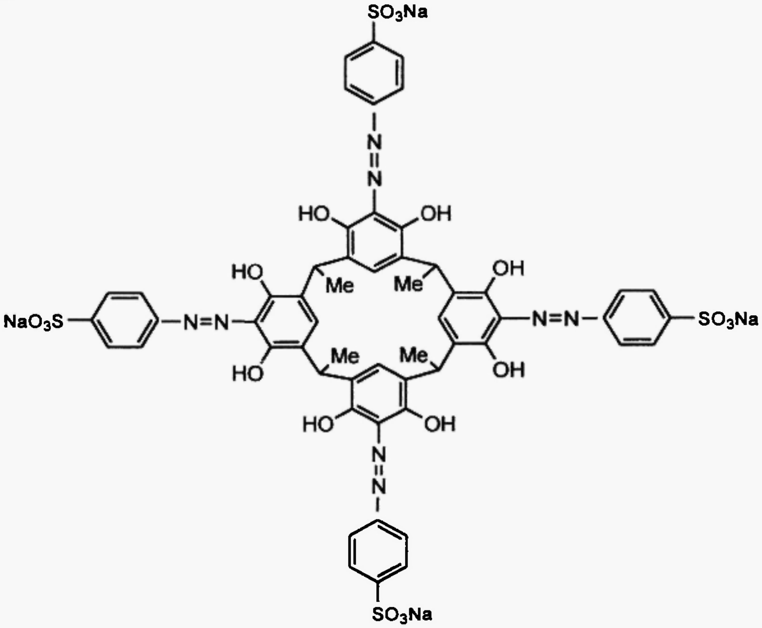
(78)

This thiomethylation with the appropriate α,ω-dithiols leads to the intramolecularly bridged derivative (79), the thiacrown resorcinarene /63/.



(79)

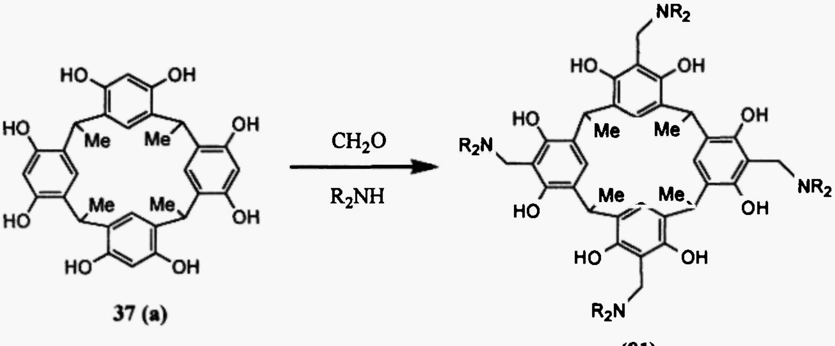
* Diazo coupling of resorcinarene 37 (a) with four equivalents of p-sulfonatebenzene diazonium affords tetradiazonium salt (80) in 29% yield /64/.



(80)

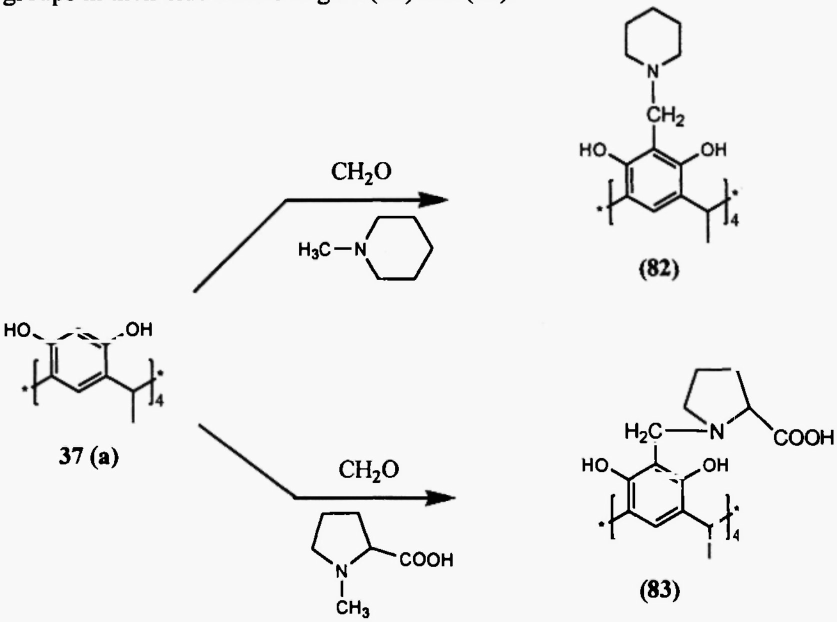
The product is water soluble and has a large extended cavity able to complex hydrophobic molecules like pyrene and coronene /60/.

* Several aminomethylated resorcinarene have been synthesized in high yields (59-83%) by a Mannich reaction of 37 9a) with formaldehyde and a secondary amine /28,65,66/.



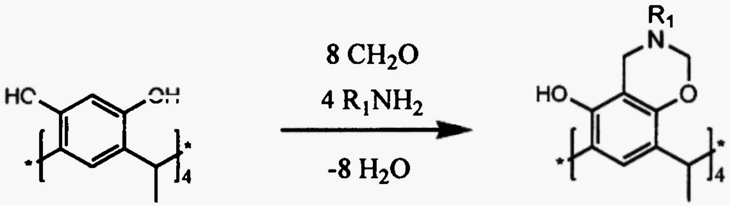
(81)

This reaction can also be performed with amines carrying functional groups in their side chains to give (81) and (83).



In the case of (83), the product is chiral and water soluble. This type of compounds, which are optically active, can be used as an alternative for lanthanide chiral NMR shift reagents /67/.

When the reaction takes place with primary amines, the resulting secondary amine reacts intramolecularly with one of the hydroxyl groups at the ortho- positions, and a second equivalent of formaldehyde gives rise to the formation of 1,3-oxazine rings, as in (84) /68/.



37 (a) (84)

7. COMPLEXATION OF CATIONS WITH RESORCINARENE

* A solvent extraction separation of uranium, in the presence of thorium, cerium and lanthanides with a new calix[4]resorcinarene bearing eight hydroxamic acid groups (C_4RAHA) is described /69/.

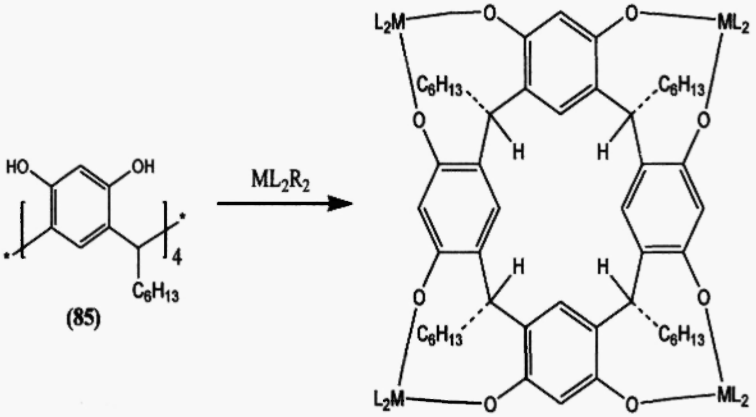
Quantitative extraction of uranium is possible in ethyl acetate solution of C4RAHA at pH 8.0. The λ_{max} and molar absorptivity (ε) for uranium is 356 nm and 8352 L mol^{-1} cm^{-1}. The binding ratio of uranium with C4RAHA as evaluated by Job's method is 4:1. The system obeys Beer's law over the range 0.075–6.0 μg ml^{-1} of uranium with Sandell sensitivity 0.0284 μg cm^{-2}. A preconcentration factor of 142 was achieved by directly aspirating the extract for GF-AAS measurements. The two-phase stability constant evaluated at 25 °C for uranium is 15.91. The complexation is characterized by favorable enthalpy and entropy changes. A liquid membrane transport study of uranium was carried out from source to the receiving phase under controlled conditions and a mechanism of transport is proposed. Uranium has been determined in standard and environmental samples.

* Novel ionophore, C-thiophenecalix[4]resorcinarene has been synthesized and characterized by IR, NMR and C, H, N analysis. Poly(vinyl chloride) (PVC) based membranes of ionophore using dibutylphthalate (DBP), dioctylphthalate (DOP), 1-chloronapthalene (CN), tris(2-ethylhexyl) phosphate (TEHP) and bis(2-ethylhexyl)sebacate (DOS) as plasticizing solvent mediators were prepared and used as CrO_4^{-2}selective sensors /70/.

Of the various sensors prepared, the one with membrane composition 2:66:120 mg (I: PVC: DBP) exhibited the best performance. This sensor works well over a wide concentration range 5.6×10^{-6}–1.0×10^{-1} M (detection limit ~0.30 ppm) with Nernstian compliance (29.0 mV per decade) between pH 6.5–10.0 with a fast response time of ~13 s. The selectivity coefficient values as determined by fixed interference method

(FIM) indicate excellent selectivity for CrO_4^{-2}ions over a large number of anions. The sensor exhibits adequate shelf-life (~5 months) with good reproducibility (S.D. ± 0.2 mV). The sensor has been used in the potentiometrie titration of chromate with Pb(II). Determination of chromium in electroplating waste using the sensor was successfully achieved.

* Complexation of all eight hydroxy groups of calix[4]resorcinarene (85) was achieved using $[Zr\text{-}(\eta^5\text{-}C_5H_5)_2Me_2]$ and $[Fe(Phen)(mes)_2]$ /71/.



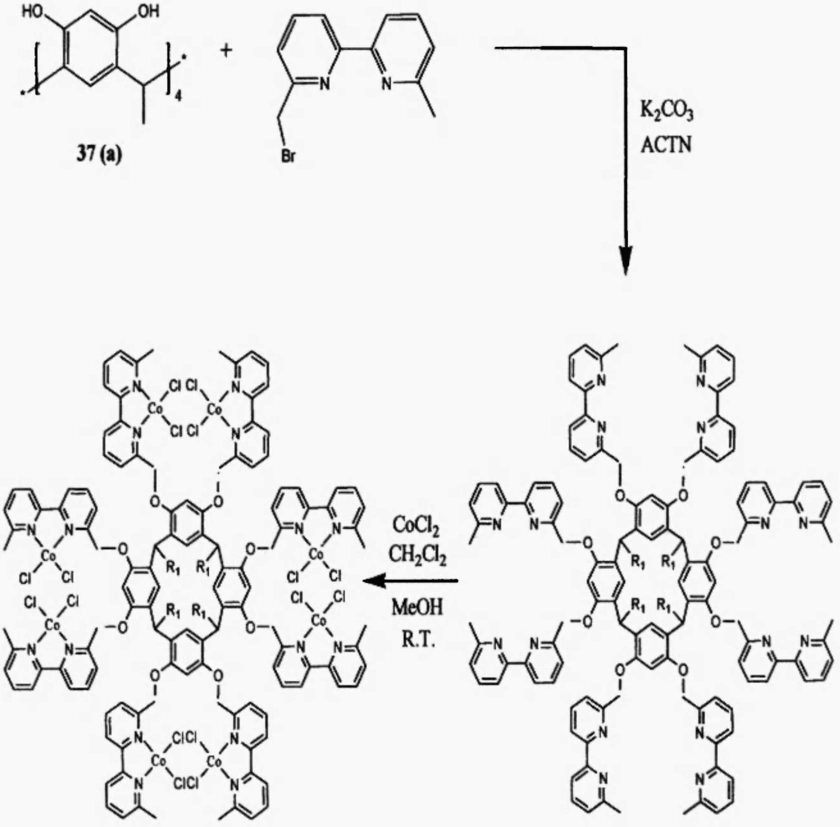
(85)

(86) M = Zr, L = C_5H_5, R = Me

(87) M = Fe, L_2 = Phenanthorline,
R = Mesityl

The result of the x-ray analysis of (86) reveals that the ligand (85) adopts the expected cone conformation and the symmetry of the bowl-shape is close to C_4. The four zirconium ions of (86) define an almost square framework with an average Zr---Zr distance of 7.763(3) A°. Complex (87) is paramagnetic, but no magnetic interaction within the tetrametallic unit could be observed. The magnetic moment per Fe atom is essentially constant down to about 80 K, with a value of 5.1 μg, typical of Fe(II) complexes.

* The octapodal, resorcinarene-based bipyridyl ligand (88) was shown to allow the formation of the octanuclear cobalt complex (89) /72/.

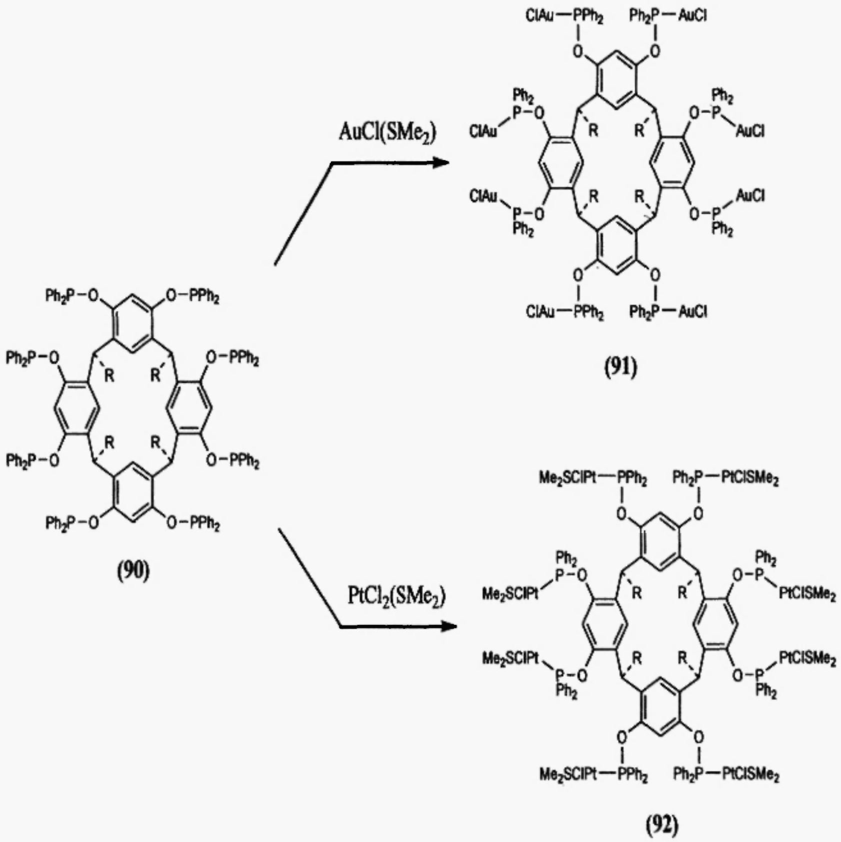


(89)

(88)

* The chlorophosphine-base strategy has also been applied to the formation of resorcarene-derived phosphates (90) /73/. This compound represents the calixarenes with the highest number of phosohinito units reported. Its 31P NMR spectrum shows two singlets of equal intensity. Based on molecular mechanics calculations, showing that the PPh2 groups force the bowl to become flattened, it has been suggested that the structure consists of alternating PPh2 groups directed inwards and outwards with respect to the flattened bowl.

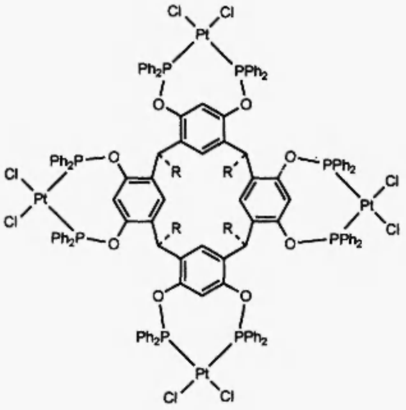
Treatment of this ligand with $[AuCl(SMe)_2]$ gives the octopus molecule (91). In (91), only one ^{31}P resonance was observed, indicating a molecule more symmetrical than the parent free ligand. Probably in (91), all eight AuCl groups are directed towards the centre of the bowl.



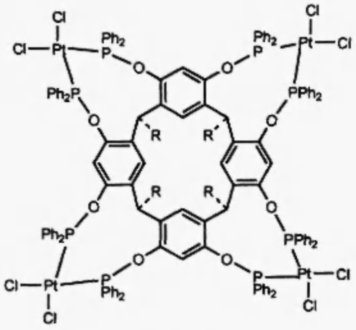
* Reaction of (90) with [$PtCl_2(SMe)_2$] gives a tetraannular complex in which each platinum atom is bound to two P sites arranged in a cis fashion /73/.

Molecular mechanics calculations suggest that the resulting complex adopts structure (93) rather than (94).

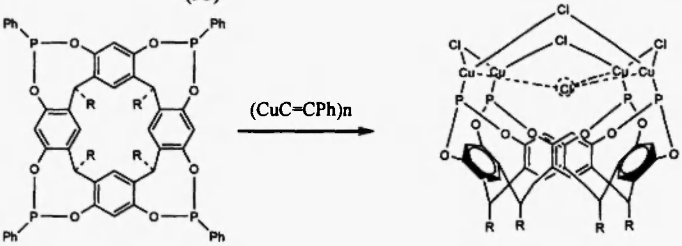
* Treatment of ligand (95) with [(CuC==CPh)n] in the presence of pyridinium chloride yielded the unique complex (96), in which a $Cu_4(\mu\text{-}Cl)_4$ moiety bridges the bowl /74/.



(93)



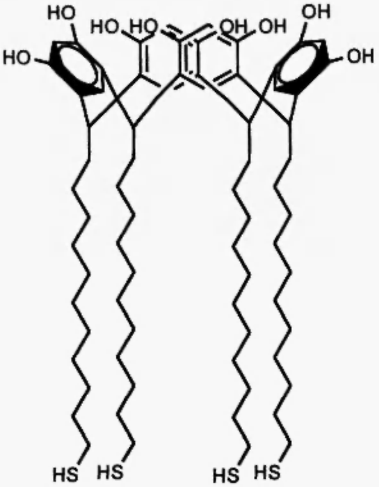
(94)



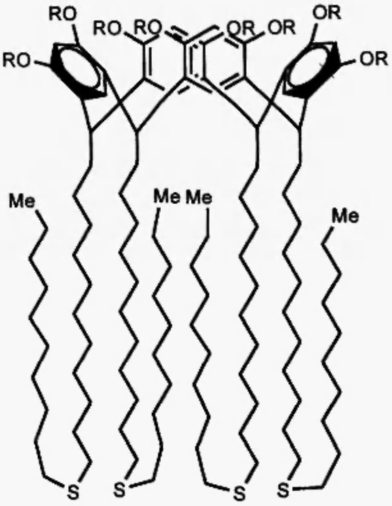
(95)

(96) Where, $R = CH_2CH_2C_6H_5$

* The resorcinarenes (97-99), bearing long chain thioalkyl chains, have been developed for anchoring to a gold surface so as to produce self-assembled monolayers /75,76/.



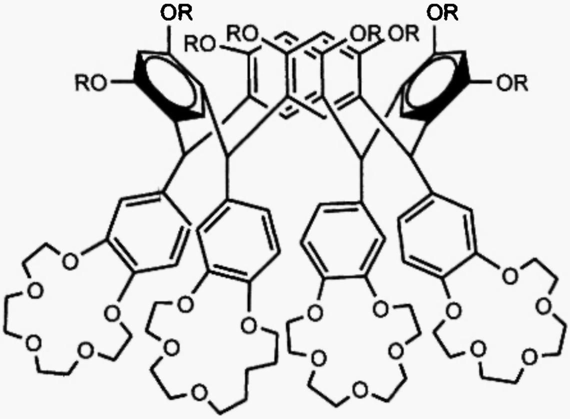
(97)



(98) $R = CH_3$
(99) $R = C(O)CH_3$

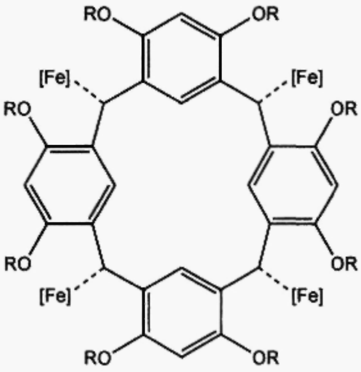
Potential applications of such systems include receptors and sensors. Thus, the layer obtained from (97) displays strong selectivity for some adsorbates, like Vitamin C, from dilute solutions. With the tetrasulphides (97) and (99), monolayers obtained at room temperature are kinetically disordered, but on heating at 60°C, a highly ordered structure with few defects can be obtained. It is probable that the monolayer recognizes after reversible Au-S bond breaking to an energetically more favorable structure having all alkyl chains held parallel. This leads to compacted monolayers of high stability which are currently being investigated for possible use as sensors.

* With metallocene substituted by one chlorocarbonyl group, multi-redox active molecule such as (100) was isolated. The presence in (100) /77/ of lewis acid binding sites of the crown-ether type should be noted. Their presence may be helpful for combining lewis acid catalytic activation with ferrocenyl-mediated redox reactions on small guest substrates, like CO_2, CO etc.



(100) $R = -C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$

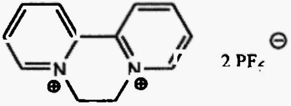
Resorcinarene-derived molecule bearing multi-redox active sites have also been described recently. The multi-ferrocenyl resorcinarene complexes (101-103) were obtained in high yield /77,78/.



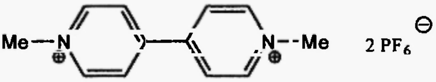
Where [Fe] = $(\eta^5\text{–}C_5H_5)Fe(\eta^5\text{–}C_5H_4)$

	R
(101)	H
(102)	COC_6H_5
(103)	$-CO(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$

The elemental properties of (100) and (103) were examined carefully by cyclic voltametry and differential pulse voltametry. For complex (100), containing eight ferrocenyl units, a single, reversible, one-electron oxidation wave was observed, indicating independent one-electron transfers occurring at the same potential. For complex (103), two reversible oxidation waves were observed at + 0.58 V and + 0.67 V (vs. SCE) in CH_2Cl_2, representing two reversible two-electron transfers. As shown by ^1H NMR studies using Nuclear Overhauser Effect (NOE) difference spectroscopy, complex 100 forms solution complex with diquat (104). Similar complexation in the lower box-like cavity of 100 was found for paraquat (105).



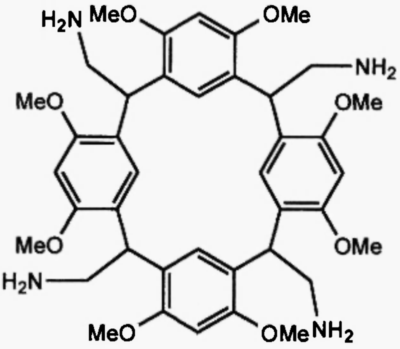
(104)



(105)

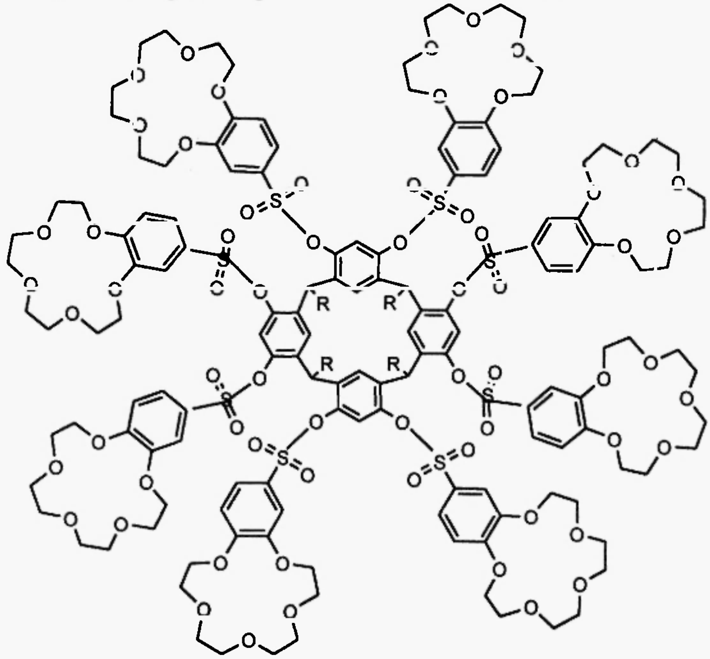
In view of the longer distance separating the ferrocenium centers and the bipyridinium recognition sites it is not surprising that the diquat complexation could not be detected electrochemically. Introduction of metallocenes into cavity-shaped molecules remains a potentially powerful method for the detection of host-guest complexes.

* Aminomethylated calix[4]resorcinarene (106) forms the 2 : 1 complex with Cu^{+2} ions /79/.



(106)

* Resoricnarenes of C_2V symmetry tetrasulfonates 107 (a-c) are useful as molecular platforms of the design of cation receptor for alkali metals and NH_4^+ ions, containing binding units in the molecules /80/.

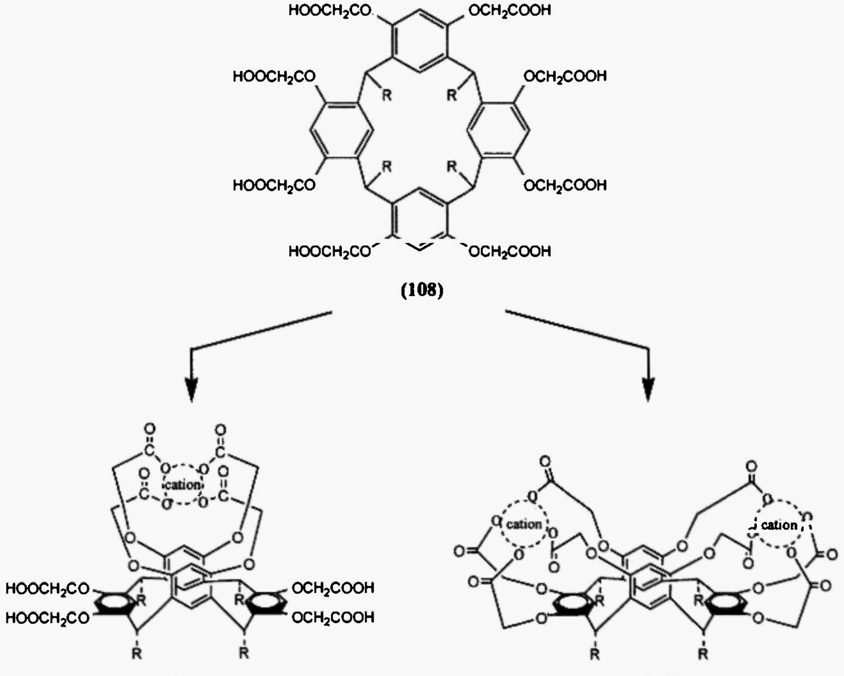


(107)

	R
a	Me
b	Me
c	C_5H_{11}

* Complex formation of 3,5,10,12,17,19,24,26-octa(carboxymethoxy)-1,8,15,22-tetraundecyal calix[4]arene (108) with Li^+, Na^+, K^+ and NH_4^+ ions was studied by ^1H NMR spectroscopy and p^H-metry in water-DMSO solutions /81/.

Binding of one cation occurs during the stepped deprotonation of four carboxymethyl groups in (108). The K^+ ion was found to be bound more efficiently than Li^+ and Na^+. The further deprotonation to the penta- and hexa- anion leads to the coordination with two cations. The most stable binuclear complex is formed with the Li^+ ion.

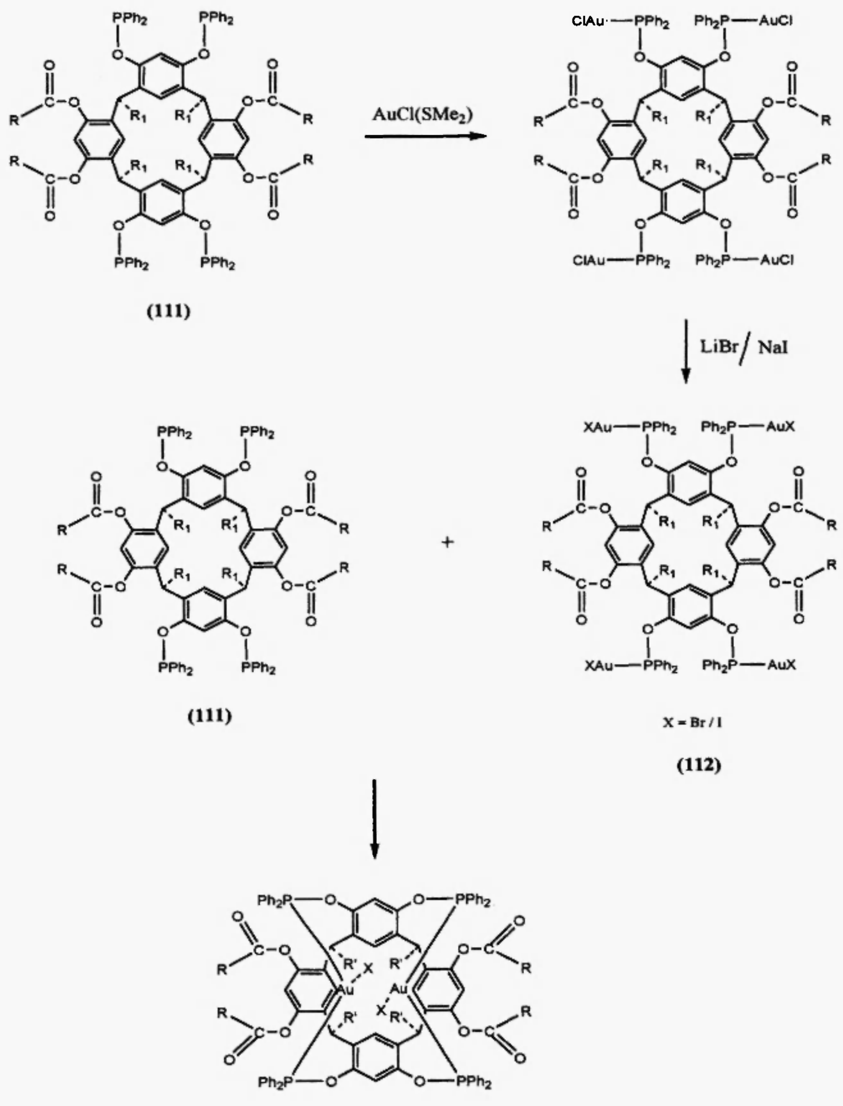


(108)

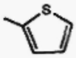
(109)

(110)

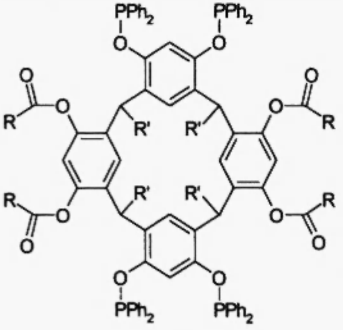
* Gold(I) halide derivatives of several tetrakis(diphenyl phosphinito)tetraester resorcinarene compounds 113(a-e) have been prepared /82/. These complexes are shown to exist in boat conformations, and two different boat conformers were characterized by x-ray structure determinations. The structural characterization of both boat conformers of the same parent resorcinarene is unprecedented.



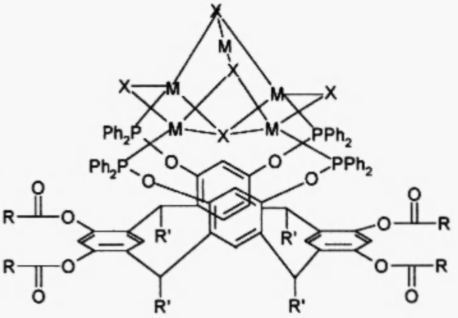
Where, X = Br / I
R' = CH_2CH_2Ph

113	R
a	-$OCH_2C'CH$
b	-OCH_2Ph
c	-C_6H_4
d	-$CH_3C_6H_5$
e	

* The reaction of Hg (II) halides with the Cu (II) and Ag (I) halides complexes of tetraphosphonito resorcinarenes has been studied /83/.



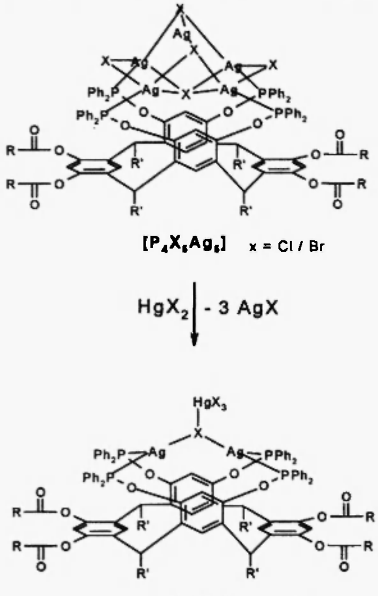
(110)



$[P_4X_5M_5]$

When M = Cu / Ag
X = Cl, Br or I
R' = CH_2CH_2Ph
R = $OCH_2C{\equiv}CH$
OCH_2Ph
C_6H_{11}
C_4H_3S
p-Me.C_6H_4

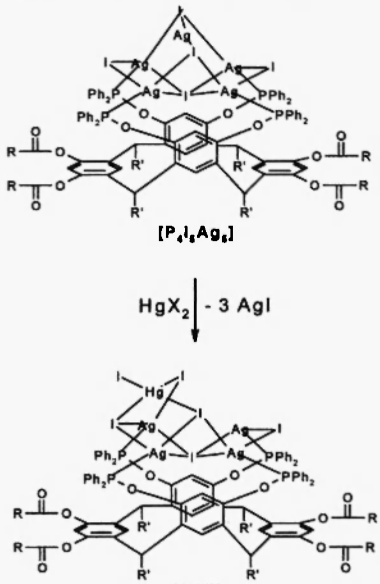
The reaction of $P_4M_5X_5$ with HgX_2, when M = Ag & X = Cl or Br, occurs with elimination of Ag (I) halide and formation of $[P_4Ag_2X(HgX_3)]$ (114) but when M = Ag & X = I, the complexes $[P_4Ag_4I_5(HgI)]$ (115) are formed.



$[P_4X_5Ag_5]$ x = Cl / Br

HgX_2 ↓ - 3 AgX

(114) x = Cl / Br

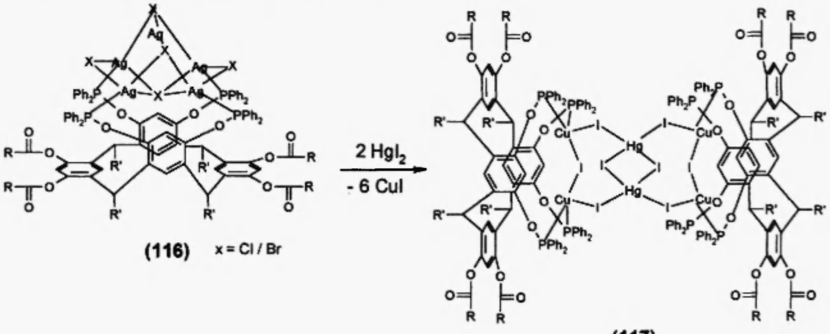


$[P_4I_5Ag_5]$

HgX_2 ↓ - 3 AgI

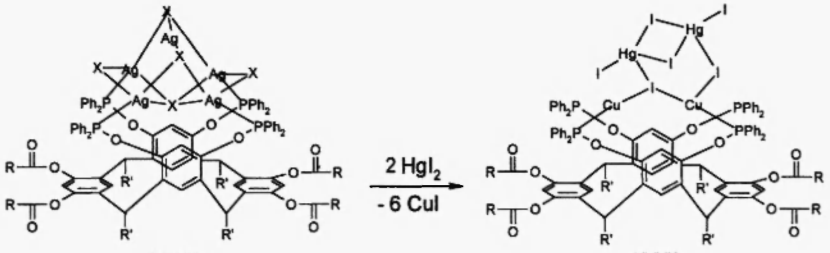
(115)

* When M = Cu & X = I, the products were the remarkable capsule complexes $[(P_4Cu_2I)_2(Hg_2X_6)]$ (117).



(116) **(117)**

When M = Ag & X = I, the reaction with CuI & HgI_2 gave the complexes $[P_4Cu_2I(Hg_2I_5)]$ (118).

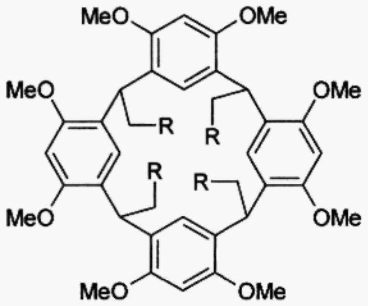


(116) **(118)**

Many of these complexes are structurally characterized as containing mercurate anions weakly bonded to cationic tetraphosphonito resorcinarene complexes of Cu(I) or Ag(I) in an unusual form of host-guest interaction. In contrast the complex $[P_4Ag_4I_5(HgI)]$ is considered to be derived from an anionic silver cluster with an iodo mercury (II) cation.

Fluxionality of the complexes in solution is interpreted in terms of easy, reversible making and breaking of secondary bonds between the Cu(I) or Ag(I) cations and the mercurate anions.

* Resorcinarene 119 (a-d) interact with $FeCl_3$ in chloroform. Resorcinarene octamethyl ethers, bearing carboalkoxy groups in the side chains, have been shown to interact with Fe(II) in organic media /84/.

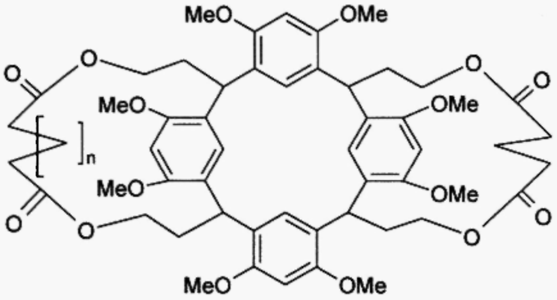


(119)

	R
a	CH_3
b	COO.iPr
c	CH_2OH
d	CH_2Br

^1H NMR studies, carried out using Ga^{II} instead of Fe^{III} suggest that these systems have two active sites of interactions: the first located at the aromatic moiety and the other in the vicinity of the carbonyl groups. As a confirmation of this, resorcinarenes without carbonyl groups in the side chains have been found to exhibit only one active site.

* Rigid resorcinarene 120 (a, b & c) give 2 :1 complexes with $GaCl_3$ /82/.



(120)

	n
a	1
b	2
c	3

* New ytterbium complexes with resorcinarene (121-127) containing methoxycarbonyl, methyldiethyl amino groups and bromine as the substituents in the resorcinol ring and methyl or phenyl substituents in the macroring were synthesized /85,86/.

The absorption, excitation, phosphorescence and luminescence spectra of these complexes were studied. The positions of triplet levels of the ligands were measured and the values of relative quantum yields for the complexes were calculated.

The ytterbium ion in complexes with studied calix[4]resorcinarenes exhibits metal-centered 4f luminescence upon ligand excitation. Ligand 121 & 122 are the most favorable for ligand-lanthanide ion energy transfer for ytterbium ion.

* The boat conformation of C-methyl calyx[4]resorcinarene (128) is present as tetraphenolate (129) in NaOD solutions /87,88/.

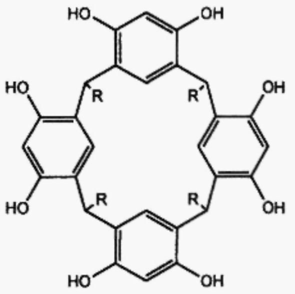
Tetraphenolate (129) binds methyl trialkyl ammonium cations with high binding constants (K = 3×10^4 cm^{-1} in 0.5 N NaOD) exceeding the correxponding constants in biological systems /89,90/.

The strength of binding is only affected by changing the ionic strength /85/ or solvent polarity /91/, but decreases strongly when the length of the alkyl groups increases. This indicates that the interaction is based electrostatic attraction between the positively charged $R_3N^+.Me$ and negatively charged tetraphenolate (129).

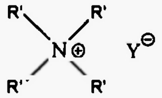
The affinity of tetraphenolate (129) for methyl ammonium cation is interestingly in the case of the acetylcholine (131). In the presence of (129), the rate of the hydrolysis of acetylcholine is deceased. This effect can be attributed to the strong affinity of (129) for the positively charged ammonium substituent.

* Pyrene-modified N-alkyl pyridinium cations are also complexes by tetraphenolate (129) with association constant similar to that of acetylcholine (131) [K = 50000 M^{-1}]. Inouye and his co-workers found that such non-fluorescence complexes could be used as optical sensors for the detection of acetylcholine, since fluorescence was regenerated after addition of acetylcholine to a solution of the non-fluorescence complex.

* NMR diffusion measurements were used to probe the differences in the characteristics of the hexameric capsule of [c]-undecane resorc[4]arene (134) in a $CDCl_3$ solution in the absence and presence of tetrahexyl ammonium bromide (135).



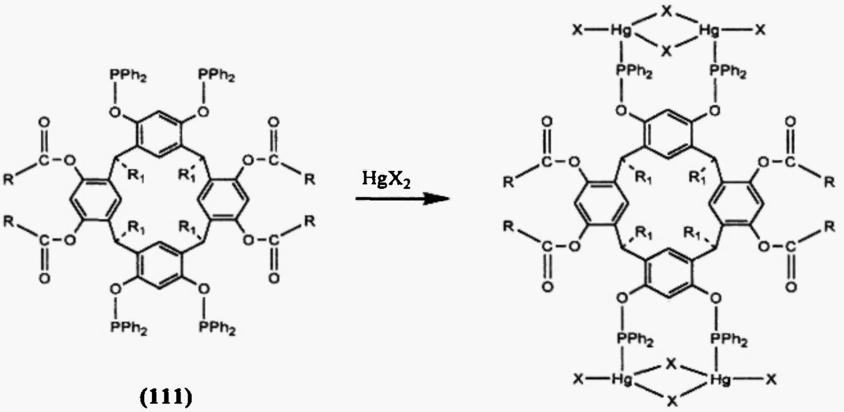
(134) R = $C_{11}H_{23}$



(135) R' = hexyl
Y = Br

It was found that the non-encapsulated THABr forms a 1 : 1 complex with (134), which is in fast exchange with its constituents. Water molecules seem not to participate in the construction of the THABr hexameric capsule of (134) in a $CDCl_3$ solution. In the absence of THABr the major species in $CDCl_3$ solution seems to be $[(134)_6(H_2O)_8]$.

* Treatment of tetrakis(diphenyl phosphinite)tetraester resorcinarene (111) with $HgCl_2$ (X = CI, Br, I) yielded mercury (II) halide derivatives of resorcinarene ligands (135), and complexes were characterized in both the solid and solution states /92/. This is a new structural form for the much-studied mercury (II) halides complexes with phosphine ligands and it arises since the resorcinarene-derived ligands act as if they contain two separate diphosphinite bidentate ligands, each having a long bite distance that can span the $Hg_2(\mu\text{-}X)_2$ unit. These complexes were characterized by ^{1}H NMR and ^{31}P NMR spectroscopy by elemental analysis and in several cases by x-ray structure determinations.

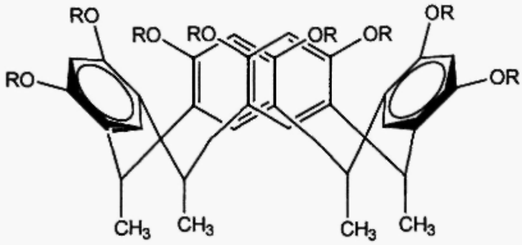


(111)

(135)

This is the first structural characterization of mercury (II) halide diphosphine complexes with 1 : 1 of Hg : P stoichiometry, and the first examples of complexes $[Hg_2X_2(\mu\text{-}X)_2L_2]$ with the 'syn' arrangement of the phosphorous donor ligand.

* The impregnation of octacarboxymethyl C-methyl calix[4]resorcinarenes (136) into a polymeric matrix, Amberlite XAD-4, is reported and was characterized by IR spectroscopy /93/.

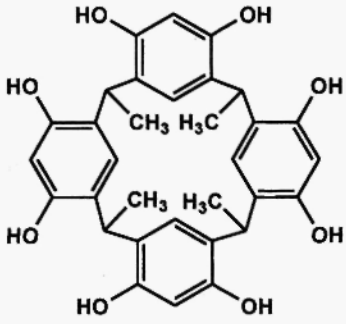


(136)

The sorption capacity of the impregnated resin is $0.34X10^{-3}$ mol g^{-1}. The resin was used for the sorption of the Th(IV) and U(VI) from aqueous solution. The properties of capacity, p^H effect and breakthrough curves of the impregnated resin were investigated. The capacity of the resin of Th(IV) and U(VI) was found to be $0.29X10^{-3}$ mol g^{1} and 0.27 X 10^{-3} mol g^{-1} respectively. The metal ions were eluted with 0.4-2 M HCl or HNO_3. Chromatographic separation of Th(IV) ad U(VI) was accomplished by adjustment of p^H to 3 and 6, respectively. The impregnated resin exhibits a high chemical stability, reusability and fast equilibrium. Separation of Th(IV) and U(VI) from other metal cations in synthetic solutions was achieved.

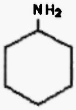
8. HOST-GUEST RELATIONSHIP

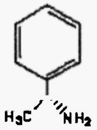
* The solid complexes of calix[4]resorcinarenes with various amines, amino alcohols & pyridine were obtained. Their composition was determined by ^1H NMR and spectro-photometric methods /94/..

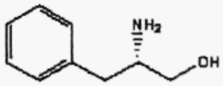


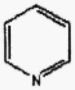
(8)

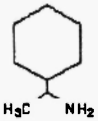
Primary Amines :-

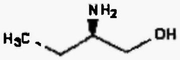


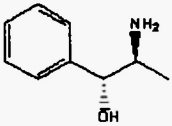




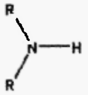




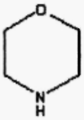


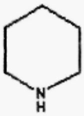


Secondary Amines :-

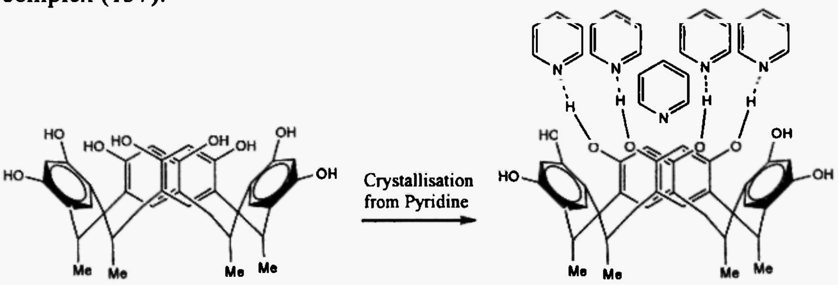


R = $-CH_3$,
$-CH_2CH_3$,
$-CH(CH_3)_2$





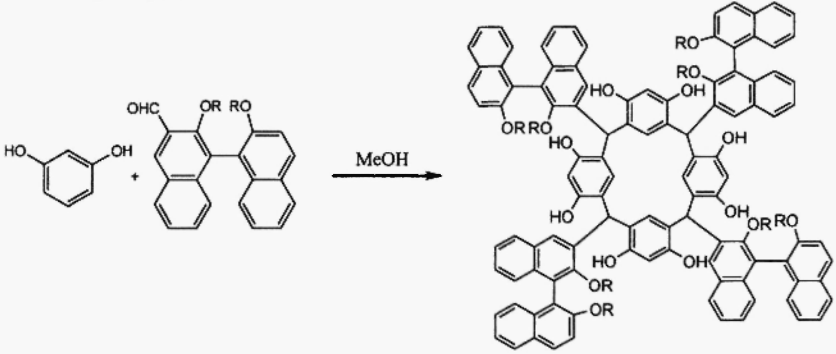
* The crystallization of (8) from pyridine leads to the formation of the complex (137).



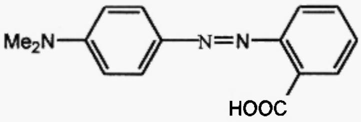
(8) **(137)**

In complex (137), four pyridine molecules are situated over resorcinarene (8) molecule. They form hydrogen bonds with four hydroxyl groups of two opposite resorcinol units. The fifth pyridine molecule is situated loosely over the resorcinarene cavity.

* The analysis of saccharides is of importance, due to their therapeutic properties /95,96/, as well as in diabetes treatment and in industrial fermentation processes. Binaphthyl resorcinarenes (138) have been used for this study /97,98/.



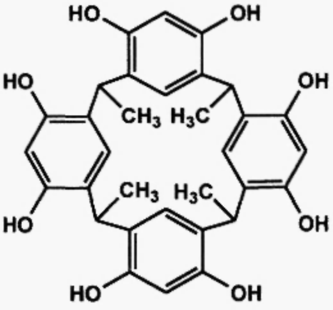
138 (a) : R = -H
(b) : R = -CH_3



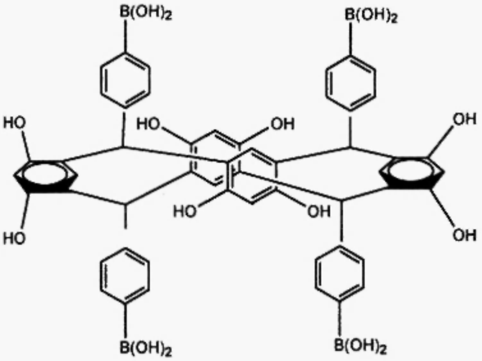
(139)

Resorcinarenes 138(a) & (b) from water soluble complexes with methyl red (139) bind saccharides. Methyl red, serving as a chromophore, is weakly, non-covalently bound to the resorcinarene molecule. Complex 138(a)/139 & 138(b)/139 show intensive absorption at visible spectral range. Resorcinarene 138(a) & 138(b) form 1:1 complexes with saccharides by a competition with color label (139). This process can be monitored visually, in this way allowing the chemical sensing for saccharides. It was shown that 138(a) & 138(b) are selective receptors. They bind oligosaccharides [D(+)-maltose, maltotriose, maltotetraose, α-D-lactose β-D-lactose] more strongly than monosaccharides [α-D-glucose, D(+)-galactose, D(-)-fructose] & the two saccharides like species : L-sorbitol & L-gulconic acid γ–lactone /99/.

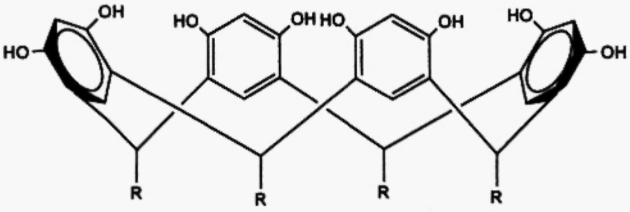
* Another analysis of saccharides is based on the observation that colorless solutions of (8), (140) & (141) upon heating undergo significant color appearance /97,100/.



(8)



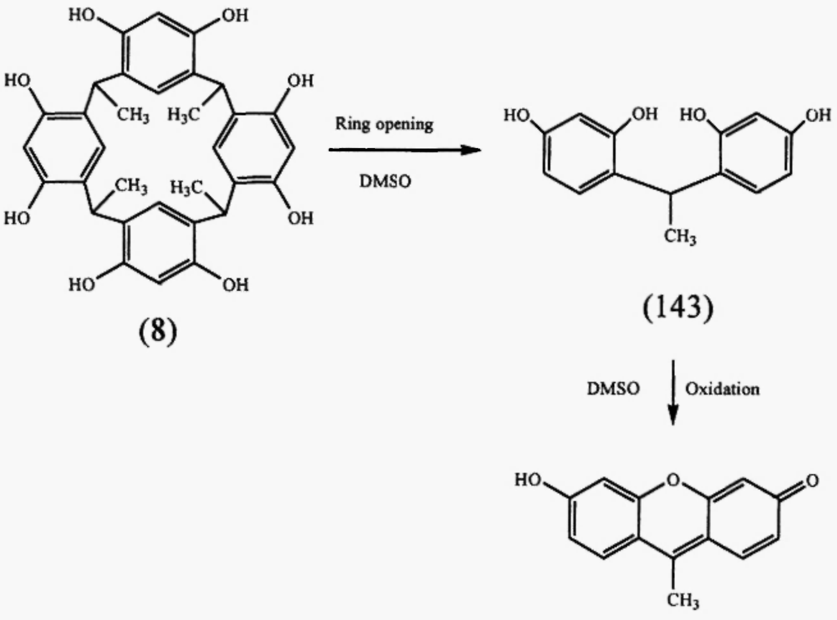
(140)



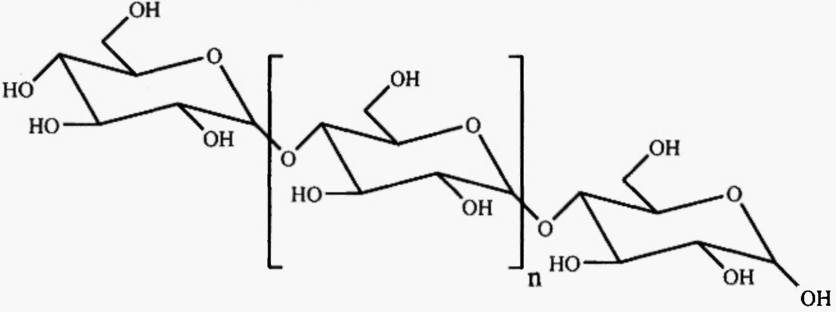
141 (a) : R = $-CH_3$
(b) : R = $-PhB(OH)_2$

This behavior results from the formation of xanthenes (142), which are strongly absorbing species. The complexation of xanthenes, serving as chromophores with mono or oligosaccharides, enables their visual detection /95/.

The formation of xanthenes begins with the ring opening of the macrocycle leading to acyclic resorcinol oligomers, an example is conversion of (8) into the compound (143).



This process is catalyzed by strong acids, which form in situ by O_2-induced radical decomposition of DMSO. The subsequent oxidation of (143) gives xanthenes (142). The heating of solutions of Malto-dextrin (144) in anso / H_2O (9:1) in the presence of resorcinarene (141) enables their visual detection due to color changes /97/.



(144)

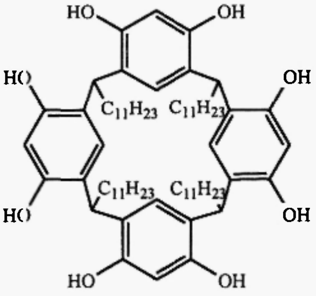
* Slow evaporation of solution of resorcinarene (8) in acetone with no precautions taken to exclude adventitious water leads to formation of an ice like cyclic $(H_2O)_8$ cluster in the solid state structure of an organic supramolecular complexes /100/. The crystal structure consists of two-

dimensional bilayer of (8) in corporating water & acetone molecules. The water octamer is stabilized by its environment in the supramolecular lattice, the network is hydrogen bond.

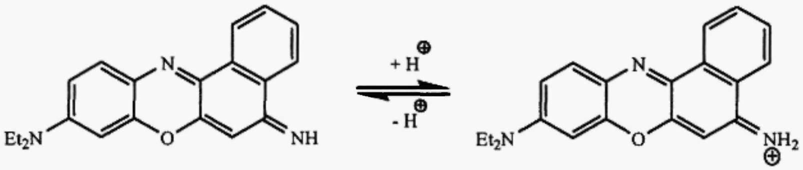
* Co-crystallization of resorcinarene (8) with 2, 2'-bipyridyl yields a doubly solvated 1:1 adduct resorcinarene: 2, 2'-bipyridyl: methanol : water (1:1:1:1:16) /99/. The resorcinarene, methanol & water molecules combine by means of multiple O-H----O hydrogen bonds to form paired, essentially – planar two-dimensional nets in which Centro symmetric pairs of resorcinarene bowls act as self-assembled carcerands to form large cavities in which pairs of 2, 2'-bipyridyl molecules are held by a combination of O-H----N & O-H----O hydrogen bonds.

In the case of resorcinarene (8) with 4,4'-trimethylene dipyridine from methanol yields a solvated 1:2 adduct resorcinarene : 4-4 -trimethylene dipyridine : Methanol (1:2:0:5) /101/. The resorcinarene acts as a quadruple donor and he dipyridines both acts as double accepters, in O-H----N hydrogen bonds. The supramolecular structure consists of linear and nearly planar ribbons with the bowls towards the – $(CH_2)_3$- spacer units of a neighboring ribbon, acting as guests.

* Resorcinarene (145) forms a host-guest complex with Nile-Blue (146^+) /102,103/. The Nile Blue exists in a basic and in an protonated for (146) & (146^+), respectively.



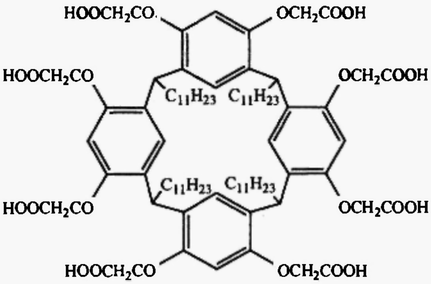
(145)



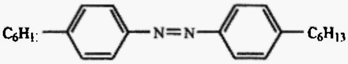
(146) **(146^+)**

The Nile Blue salts serve as indicator dyes in optical sensors /104/ and are used as photo sensitizers in photodynamic therapy /105/. This host-guest interaction has been investigated by dissolving resorcinarene (145) and Nile Blue (146) in two polar solvents, dichloromethane & toluene. In the first steps the weakly bound complex (145). (146) is formed. Simultaneously, the formation of the tightly bound ionic species (145^-). (146) takes place. The subsequent step affords supramolecular complex (145). (146^+). It was observed that the fluorescene lifetime of (146^+) significantly decreases upon complexation /103/.

* Resorcinarene (147) is a macro cyclic amphiphile able to form interfacial ultra thin liquid crystalline layers. By spreading a mixture of (147) with the mematic liquid crystalline azobenzene (148), the homogeneous host-guest mixed mono layers are formed in a water surface. They display bilayered structure by further compression /106/.

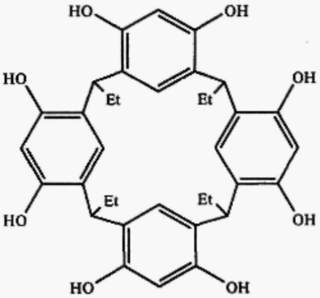


(147)



(148)

* The x-ray analysis of the complex of resorcinarene (149) with 3-phenyl propionic acid choline ester (as a chloride) (150) with composition of $2(149.150^+).2Cl^-.9H_2O$ formed through multiple action-л interaction between aromatic rings of (149) and quaternary ammonium group of (150) has been reported /107/.



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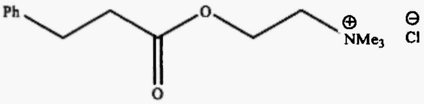
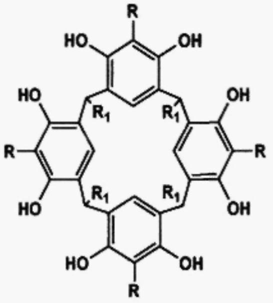
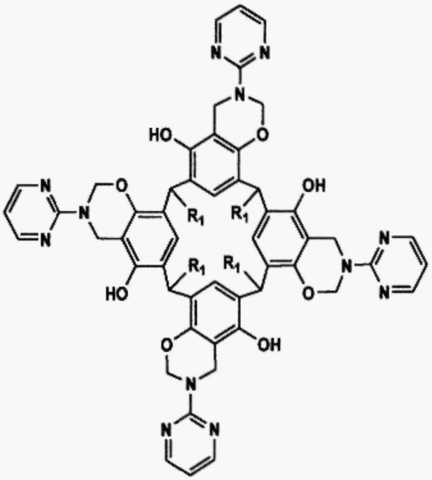


(150)

* Lipophillic compounds (145) & (151-155) have been investigated in view of their molecular recognition of pyrimidine & xanthene bases /108,109/.



$R_1 - C_{11}H_{23}$
(145) : R = H
(151) : R = OH
(152) : R = $CH_3CH_2N(Me)_2$
(153) : R = $C_5H_{10}NCH_2CH_3$
(154) : R = $CH_3CH_2NC_4H_8NCH_3$

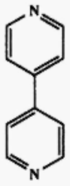


(155)

Extraction studies have shown the following sequence of extraction abilities in chloroform for (145): cytosine > Uracil > Thymine and for (151): Thymine > Uracil > cytosine.

Here, (152), (153), (154) & (155) are probably poorer extractants because of steric hydrance and they form weaker hydrogen binds with guest. The calix[4]pyrogallolarene (155) possesses 12 hydroxyl groups. Thus its own self-association is much stronger that that of (145). Therefore, its complexing abilities are inhibited. The calix[4]resorcinarene (145) is a stronger complexing agent than the (155) because of the self-aggregation properties. One should mention here that resorcinarene (145) forms 1 : 4 host-guest complex with dioxane /110/.

* The complex (157) consisting of resorcinarene (8) & 4,4'-bipyridine (156) may serve as a host for ferrocene, acetyl ferrocene & diacetyl ferrocene (158) /111/.



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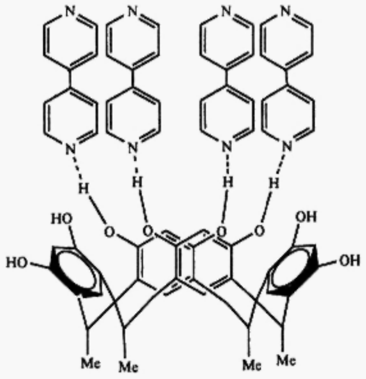

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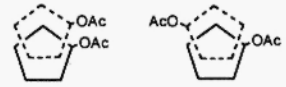


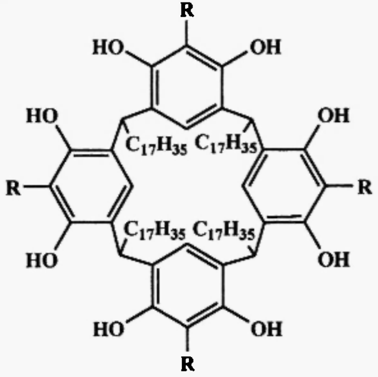
(a) 1,1'conformer

(b) 1,3'conformer

(158)

It was observed that (158), when serving as a guest, adopts 1,1'-conformation (158 a), although it usually exists as 1,3'-conformer (158 b).

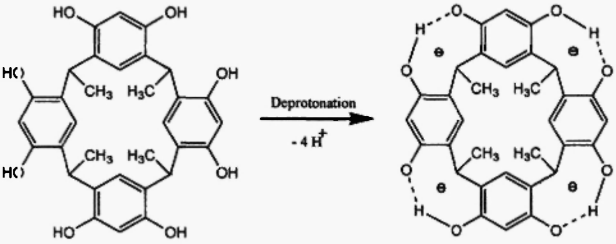
* Resorcinarene 159 (a,b) may self assemble selectively to form vesicles, stabilized by hydrogen bonds /112/.

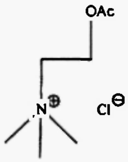


159 (a) : R = H
(b) : R = OH

Vesicles from 159(a) & 159(b) consist of unimolecular membranes in which the hydroxyl groups face the aqueous phase. It was shown that resorcinarene 159(a) plays the role of an artificial potassium ion-channel when embedded in planar bilayers of soyabean lecithin /112/.

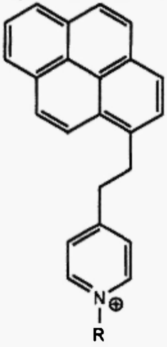
* In the study of synthetic sensors /113/, for the detection of acetylcholine chloride (160) the fluorophore displacement may be used. In NaOD solution, resorcinarene (8) seems like tetraphenolate (161).





(8) **(161)** **(160)**

When pyrene-modified N-alkyl pyridinium action (162) serving as fluorophore is bound in the cavity of (161), its fluorescence is quenched.



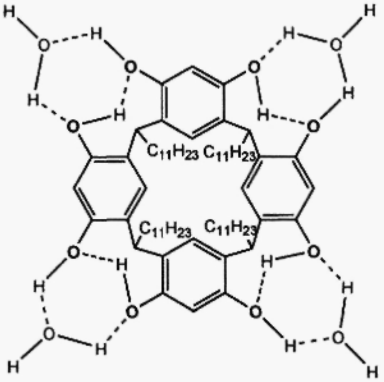
(162)

The addition of (160) results in the release of (162) and the regeneration of its fluorescence /113/. Here, strongly basic conditions necessary to deprotonate four hydroxyl groups of resorcinarene (8) may cause degradation of (160). In order to overcome this inconvenience, resorcinarene (8) may be replaced by calix[n] arene p-sulfonates (n=4 or 6).

* Complexation studies of resorcinarene (145) with several cyclohexane diols showed that, of all possible isomers, cis-1,4-cyclohexanediol is bound most tightly ($K \approx 10^3$ m^{-1} in $CDCl_3$ at 25°C), with a cis/trans selectivity /114/.

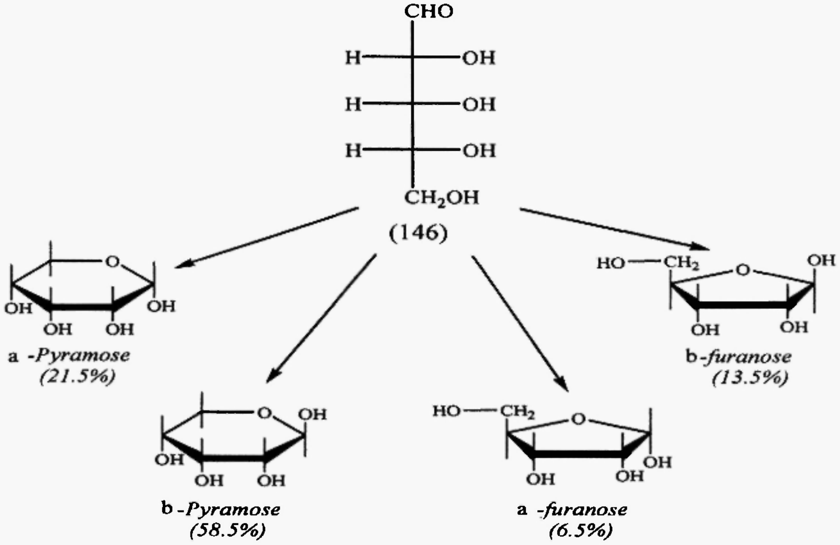
The associated free energy of complexation (ΔG compl. = -4.11 kcal mol^{-1}) is more that two times that of the corresponding mono-ol, cyclohexanol (2 X -1.42 = -2.84 kcal mol^{-1}). Open chain diols are also bound less strongly than cyclic diols.

* Resorcinarene (145) binds also with four water molecules & glycerols molecules. The 1:4 stoichiometries of both the glycerol and the water complex suggests that each pair of hydroxyl groups forms a binding site, and that four binding sites occupying a fixed position with respect to each other, and independently interact with small polar guests /115,116/.

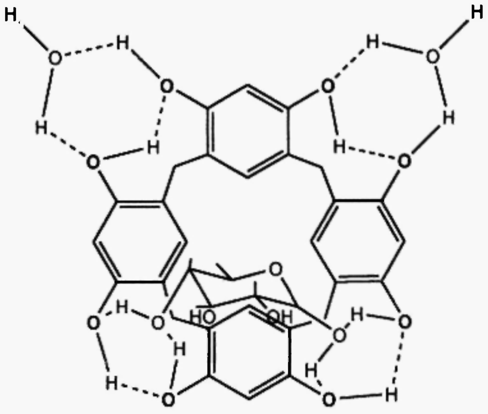


(145) . $4H_2O$

* D-ribose (146), a polyhydroxy pentaldehyde (aldopentose) exists in two cyclic pyranose (six membered) or two furanose (five membered) forms /115,116/.



D-ribose was extracted from concentrated aqueous solution (5.5 M) by a solution of host (145) in CCl_4. This indicates that host-ribose interactions compete favorably with ribose-H_2O & host-H_2O interactions.



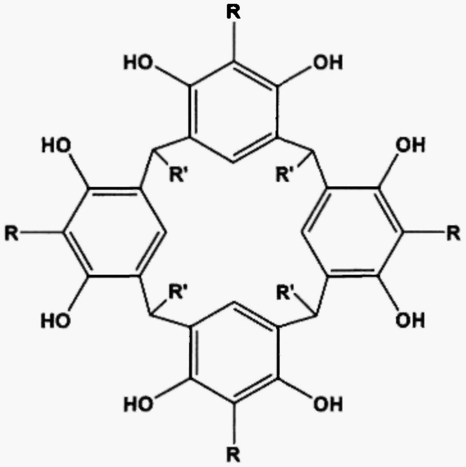
(145) Ribose.4H_2O

Extensive NMR investigation showed that ribose is complexed exclusively in the α-pyranose form. Extraction experiment with several other related sugars showed that fucose & 2-deoxy ribose are even more readily extracted than ribose itself & that xylose is not extracted at all.

It was also reported that the driving force for complexation is not only hydrogen bonding but also interaction between an aliphatic moiety in the guest & the electron-rich aromatic rings in the host /117/.

Guest molecules containing acetyl groups (e.g. borneol acetate) show complexation with host(10), although in this case, the carbonyl group might be involved in hydrogen bonding with (one of) the hydroxyl groups of the host.

* The complexation behavior of resorcinarene has also been studied in aqueous systems /118,119/. In the absence of hydrogen bonding, a driving force for complexation, the affinity of tetrasulfonate (147) for polar guests seems to be governed by hydrophobic interactions /118/. This results in a complete reversal of selectivity in the complexation of sugars. Here, CH-л interactions /117/ play an important role in the binding of hydrophobic molecules.



(147) (a) $R = (CH_2)_2SO_3Na$, $R' = H$

(b) $R = (CH_2)_2SO_3Na$, $R' = OH$

The enhanced affinity of the more hydrophilic resorcinarene (147 b) for almost all substrates investigated is most probably the result of the increased л-electron basicity of the host.

* Host (145) complexes methyl and n-octyl glycopyranosides via hydrogen bonding in a polar media. In the case of the methyl derivative in $CHCl_3$, a 2:1 (host-to-guest) sugar encapsulation complex with a remarkable β/α anomer selectivity was found. In the case of n-octyl glycoside, it is bound to host (145) to give a 1:4 (host to guest) complex with only a low anomer selectivity. The four guest molecules are bound at the four unit hydrogen bonding sites of the host with an exceptionally high cooperatively that arises from intracomplex guest – guest hydrogen bonding involving the five $-CH_2OH$ & two -OH groups of the adjacent glycoside molecules /120/.

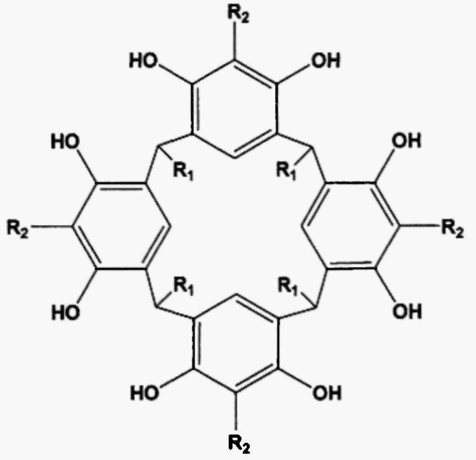
* Several detection systems consisting of monolayers of host (145) assembled at the air-water surface or supported on solid supports like SnO_2 /121/ or Au /122/, make use of the stereo selective complexation of sugars by host (145).

* The complexation of amino acids by resorcinarenes (147 a & b) has only been studied in water /119/. Amino acids with polar side chains exhibit no affinity for 147 (a & b). Only the more hydrophobic amino acids, carrying aliphatic or aromatic side chains, have been complexed with binding constants up to 70 M^{-1}.

* Dicarboxylic acids also form complexes with resorcinarene (145) in $CDCl_3$ via a two-point hydrogen bonding interaction /123/. The free energy of binding is strongly dependent on the length of the carbon spacer separating the two carboxylic end groups, once more emphasizing the rigid structure of the host glutaric acid is most strongly bound, exhibiting a high selectivity over pimelic acid.

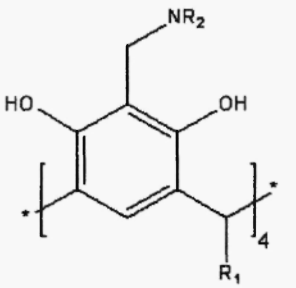
* The complex formation of (145) with triethyl amine and [2.2.2] cryptand was detected using conductomety /124/. The stoichiometry was established to be 1:3.

* Resorcinarene (8), (148), (149) & (150) form 1:1 complexes with caffeine in methanol containing 1% of water via hydrogen bond formation with the O(6) carbonyl oxygen of caffeine /125/.

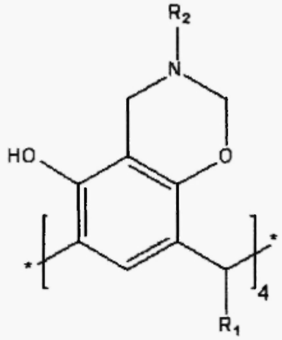


(8) $R_1 = CH_3$
(148) $R_1 = C_2H_5$
(149) $R_1 = n\text{-}C_3H_7$
(150) $R_1 = n\text{-}C_9H_{19}$
$R_2 = H$

* Sterically hindered tetra amino methylated resorcinarene (151) form inclusion complexes in $CDCl_3$ with acetanitrile & acetaldehyde which are kinetically stable on the NMR time scale at 233 K.



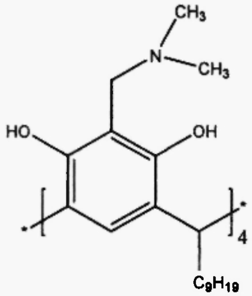
(151)
$R_1 = C_2H_5$
$R_2 = C_2H_5,$
i-Pr
$-(CH_2)_5-$



(152)
$R_1 = C_2H_5$
$R_2 = C_2H_5,$
i-Pr
$-(CH_2)_5-$

Resorcinarene tetrabenzoxazines (152), which also exist in crown conformation, do not form kinetically stable complexes with acetonitrile and acetaldehyde in $CDCl_3$ between 303 & 233 K.

* 5,11,17,23-tetrakis(N,N-dimethylaminomethyl)-2,8,14,20-tetranonyl calix[4]resorcinarene (153) was found to form, in solutions, host-guest complexes with tartaric acid, phthalic acid & succinic acid /126/.



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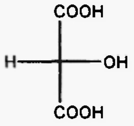

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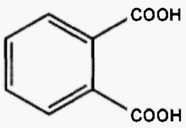

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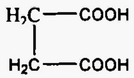
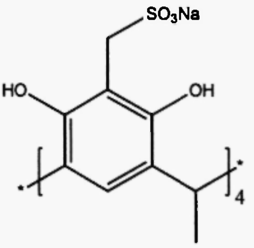


(156)

The stability of the complexes depends on the degree of protonation of the host in the complex and the structure of the guest.

* Supramolecular complexes of calix[4]resorcinarene tetramethylsulfonate (157) with certain organophosphorous compounds, such as dimethyl(1,1-dimethyl-3-oxobutyl)phosphonate, 1-O-[bis(N,N-dimethylamino)thiophosphonoyl]-2,4-O-methylenexylitol and 2-O-[bis(N,N-dimethylamino)thiophosphonoyl]-3,5-O-[(N,N-dimethylamino)thiopohosphonoyl]-1,4-anhydroxylitol, were prepared in aqueous and organic media /127/.



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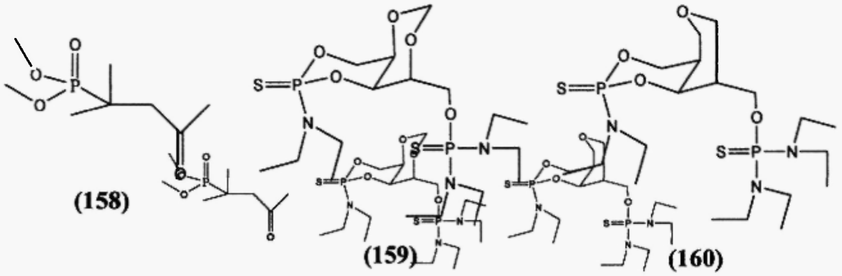
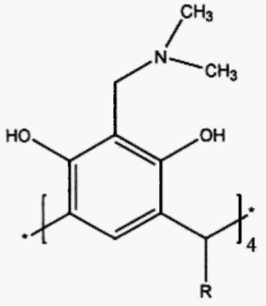


(158) **(159)** **(160)**

The complexes were isolated and characterized by elemenatal analysis, ^{1}H NMR & ^{13}C NMR spectroscopy.

* Electronic & ESR spectroscopy was used to show that the reactions of dimethylaminomethyl calix[4]resorcinarene (161) with Cu(II) salicylaldiminates (162) bearing alkyl substituents at the salicylaldiminate nitrogen atom give 1:1 adducts with the dimethylamino group co-ordinates axially to the Cu(II) complex /128/.



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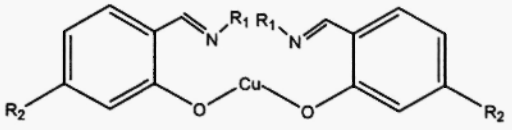
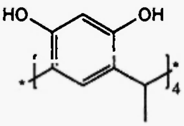


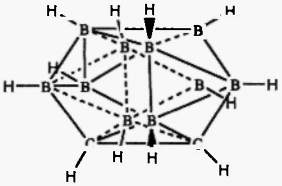
(162)

The spatially organized calix[4]resorcinarene structure and the stability of the adduct compared with the similar complex with 2-dimethylaminomethyl phenol. From alkyl to aryl substituents, salicylaldiminates are replaced by the amino derived from dimethylaminomethyl calix[4]resorcinarene. The same replacement takes place in the reaction with 2-dimethylaminomethyl phenol.

* Bowl-shaped C-methyl calix[4]resorcinarene (8) forms 1:1 complex with o-carborane /129/.



(8)



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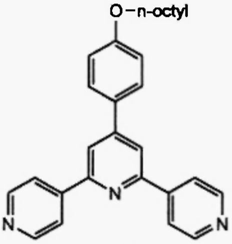
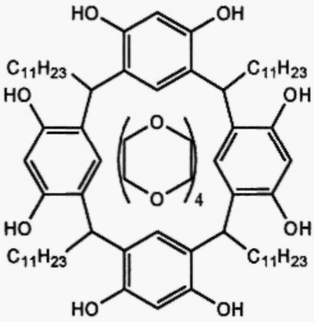


(164)

In this study, resorcinarene forms a 1:1 ball-and-socket nanostructure with O-carborane through two endo-cavity BC-H---Π hydrogen bonds. In the presence of 4,2':6,4''-terpyridine (164), two of these nanostructures are held together by four terpyridines through sixteen OH---N hydrogen bonds, completely shrouding two carboranes.

* The crystal structure of the molecular complex of C-undecyl calix[4]resorcinarene with dioxane has been determined by x-ray analysis /110/.



(165)

The asymmetric unit contains one host and four guest molecules. The calix[4]resorcinarene moiety adopts a bowl conformation with C_4v symmetry. Four undecyl chains are axially oriented.

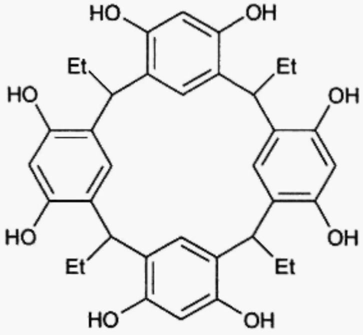
Calix molecules are packed in a bowl-to-bowl fashion with alternating hydrophilic and hydrophobic layers. One of the "hydrophilic" dioxane molecules is located at the rim of the calix moiety and is hydrogen bonded to the other one. There is no interaction to attract, or direct the dioxane molecule into the interior of the cavity. There is an exo complex formed. The dioxane molecules, located in the hydrophobic part, are highly disordered.

* The formation of strong molecular complexes of calix[4]resorcinarene with the poly functional phospho-organic compound diglycidyl methyl phosphonate was observed in organic media /130/.

Complex of different compositions were obtained with the isolated and initial reagents of 1:1 and 1:4. Three complexes were isolated and characterized by elemental analysis, ^{1}H NMR & ^{13}C NMR spectroscopy.

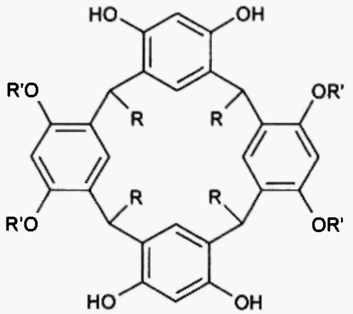
9. CAPSULES IN RESORCINARENES

* Formation of large capsules from resorcinarenes discussed by several groups /131,132/. The dimer of (22 a), which is linked by ten hydrogen bonding water molecules, encapsulates in the crystalline state the hydrogen-bonded complex Et_3N^+-H----OH_2. Bromide anions are situated outside the cavity /133/.

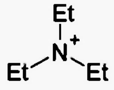


(22 a)

* The boat conformers of resorcinarenes (8) & (166) from hydrogen-bonded, solid-state capsules including two triethyl ammonium cation (167) simultaneously /134/.



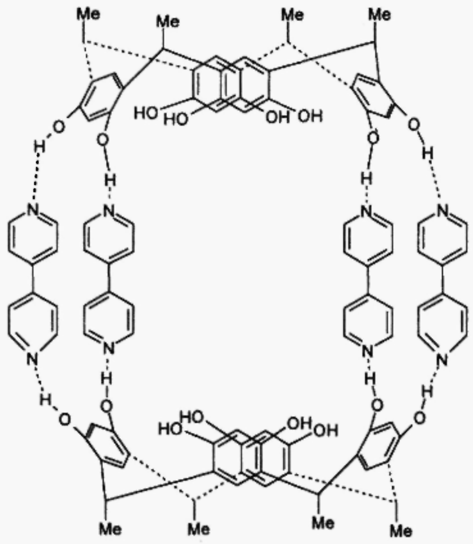
	R	R'
8	Me	H
166	Et	$-SO_2C_6H_5$



167

Two molecules of (8) or (166) in the boat conformation are linked via four hydrogen-bonded chloride anions from $Et_3N^+.HCl^-$ to form dimmers. The resulting large, negatively charged baskets(chambers) may encapsulate two (167) cations by strong electrostatic & hydrogen-bonding interactions.

* Co-crystallization of resorcinarene (8) with 4,4'-bipyridine in the presence of nitrobenzene (168) gives crystalline (8) : 3(168) assembly consisting of the large capsule. (169) held together by hydrogen bonds, which accommodates two nitrobenzene molecules /135/.



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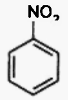
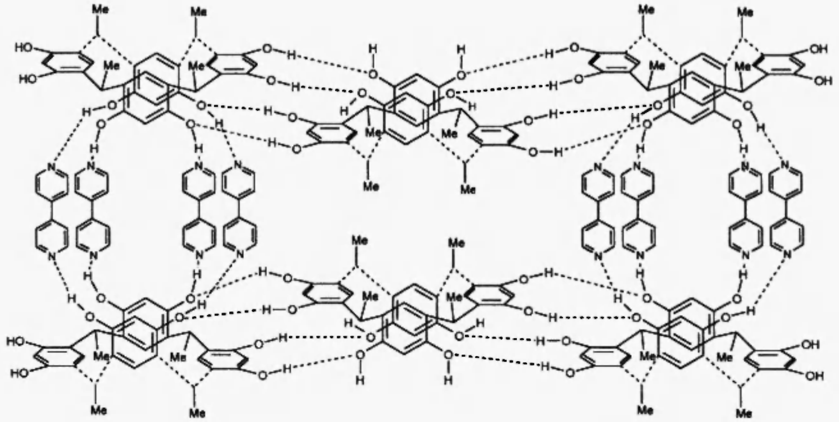


(170)

* Co-crystallization of resorcinarene (8) with 4,4'-bipyridine from ethanol in the presence of m-xylene yields a two-dimensional extended framework (170) /136/.

This process involves the structural reorganization of the wave-like, hydrogen bonded network (171) /137/ and capsule (169) /135/ affording in the presence of a suitable aromatic guest viz. m-xylene, the two-dimensional (170).



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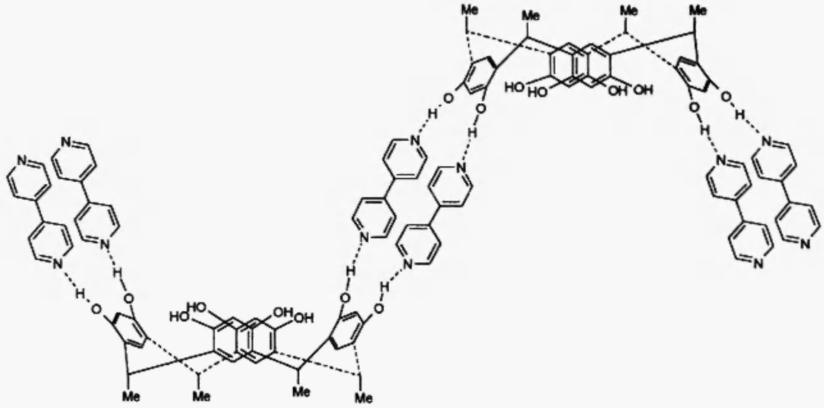


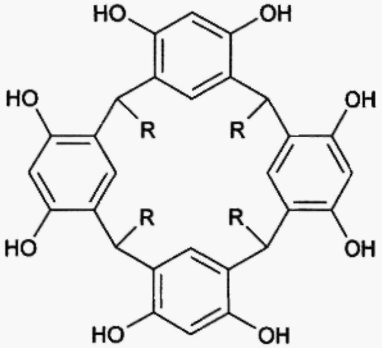
(171)

Resorcinarene (8) adopts in (171) a "T-shaped" conformation /136/. The above process is an example of the conformational isomerism, leading to supramolecular isomerism /135,137/.

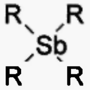
* Resorcinarene (8) & (22 d) form hexameric hydrogen-bonded capsules.

The hexamer of (8) has a shape of a cube with six resorcinarene as its sides and eight water molecules at corners. It was found that hexamer of (22 d) may encapsulate tetraalkyl ammonium & phosphonium salts /138/.

Covalent antimony (V) bromides may induce capsule formation, inside the capsule there is enough space to co-encapsulate aromatic guests, such as benzene, toluene or p-xylene /139/.



	R
8	Me
22 d	$C_{11}H_{23}$



		R
172	a	Bu
	b	Ph

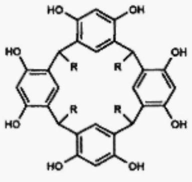
A capsule consisting of six (22 d) molecules, which incorporates Bu_4SbBr 172 (a), may encapsulate benzene, toluene, p-xylene and p-phenyltoluene. In the absence of 172 (a) no encapsulation of these aromatics takes place, since 172 (a), playing the role of a principal guest, determines the inner space of the capsule.

A capsule consisting of six (22 d) molecules, which incorporates Ph4SbBr 172 (b), may accommodate benzene, toluene and p-xylene; however, no encapsulation of p-phenyltoluene takes place. This fact results from a larger volume of 172 (b) than that of 172 (a), therefore, there is not enough space for encapsulation of p-phenyltoluene /139/.

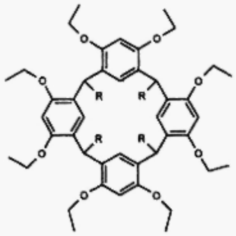
10. MONO- & MULTILAYERS OF RESORCINARENES

* Multipoint adsorptivity of 173, 174 & 175 crown conformers on polar surfaces of amorphous polar substrates, such as silica and poly(vinyl alcohol)

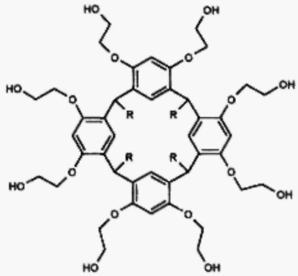
from solutions of less polar solvent viz. toluene, may serve for an easy formation of monomolecular layers /140/.



	R
173 a	C_5H_{11}
b	$C_{11}H_{23}$



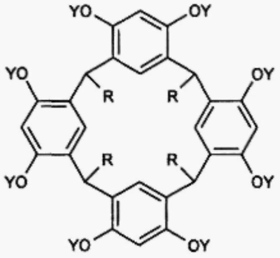
	R
174 a	C_5H_{11}
b	C_7H_{15}
c	$C_{11}H_{23}$



175 R = $C_{11}H_{23}$

The surface adsorption is achieved by simple immersion of substrate plates in a solution of less polar solvents and their desorption by immersion in polar solvents.

* Langmuir monolayers and multibilayered Langmuir-Blodgett (LB) films of resorcinarene 176 (a,b) deposited on hydrophobic substrates have been characterized using UV-vis and emission spectroscopies /141/.

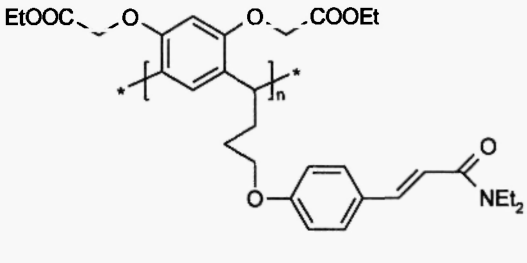


	Y	R
176 a	CH_2COOMe	$C_{11}H_{23}$
b	CH_2CONEt_2	$C_{11}H_{23}$

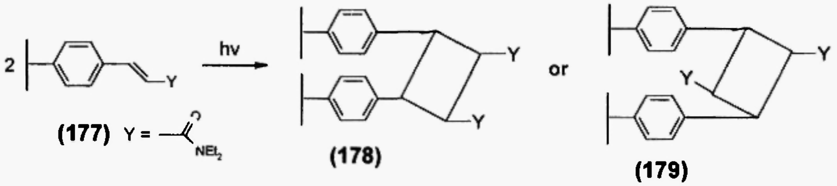
Luminescence spectra of multilayered LB films of 176 (a) / Tb^{+3} and 176 (b) / Tb^{+3} have been also discussed.

* Study of the adsorption of resorcinarenes (177) on polar substrate plates /142/ reveals that resorcinarenes and their O-carboxylated derivatives adsorb readily on silica surface to form self-assembled monolayers (SAMs) with

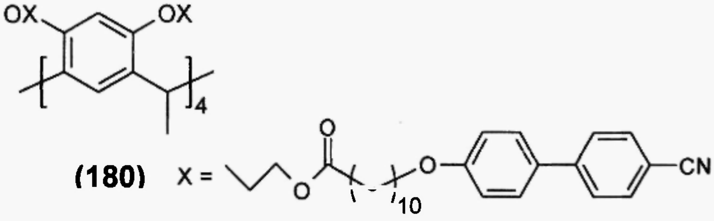
relatively dense packing. The crown conformer of (177) may be used for preparation of photofunctional monomolecular layers /143/. In order to enhance the desorption resistance, its photodimerization leading to (178) or (179) may be of use.



(177) n = 4



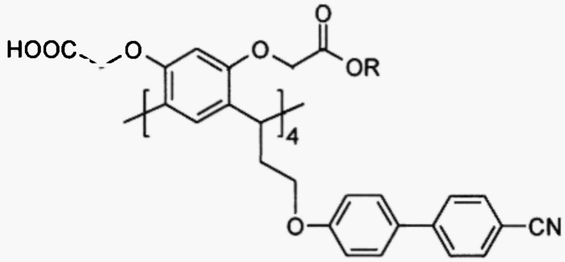
* Resorcinarene (180) shows liquid crystalline behavior. It possesses smectic A phase, which is transformed into nematic phase, in which a cornlike structure is formed /144/.



(180)

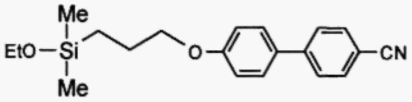
Resorcinarene (180) is promising to act as a high liquid crystal in its nematic phase.

Resorcinarene (181 a,b) were adsorbed on silica surface in order to investigate the fluorescence of cyanobiphenyl moieties and to compare it with fluorescence of (182), i.e. cyanobiphenyl modified by silylation /145/.



(181)

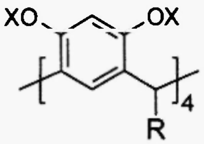
	R
a	H
b	Et



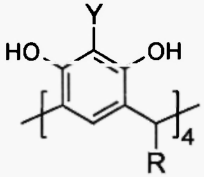
(182)

It was found that in the case of (181 a,b), the fluorescence intensity is significantly lower, this fact resulting from the high rigidity of resorcinarene structure.

* In the study of condensation of organic vapors within nanoporous thin films, resorcinarene (183) and (184) have been used for LB films /146/.

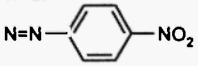


(183) $R = C_5H_{11}$
$X = P(O)(O\text{-}iPr)_2$



(184) $R = C_{11}H_{23}$

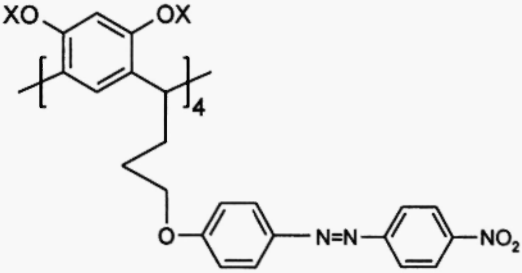
Y =



Adsorption of vapors of hexane, chloroform, benzene, toluene, p-xylene and aniline was investigated *in situ* using quartz-crystal microbalance (QCM), ellipsometry and surface plasmon resonance (SPR) techniques. The adsorption mechanism was proposed.

* Azobenzene units, incorporated into resorcinarenes 185 (a,b) existing in a crown conformation show efficient E / Z photoisomerization is densely packed monolayers on a water surface, in LB films and in surface-adsorbed monolayer /147/.

Resorcinarene 185 (c,d) may adsorb on a silica surface via hydrogen bonding affording densely packed SAMs, they may be used in the preparation of photofunctional monolayers containing azobenzene moieties /148/.



$X = CH_2COOH$

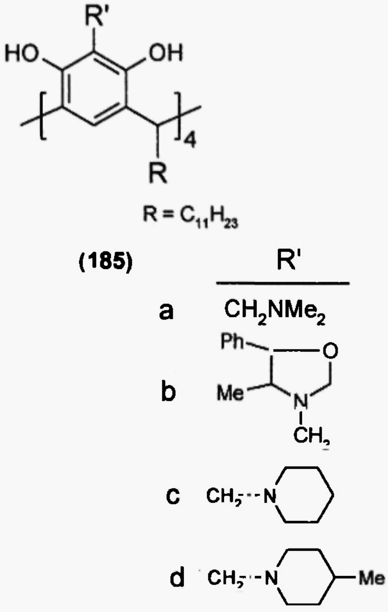
(185)

	R
a	H
b	cyclohexyl
c	C_8H_{17}
d	C_8F_{17}

Due to the presence of hydrogen bonds between the polar heads and silica surface, in the case of exposure to polar solvents, e.g. water, the partial desorption of macrocyclic amphiphiles, deteriorating the structure of SAMs occurs. In order to overcome this difficulty, self-assembled monolayers were constructed by the multi-point adsorption of 185 (c,d) as crown conformers on aminated silica substrates /148/. Resorcinarene 185 (c,d) form densely packed monolayers on the aminated plates. These monolayers show very good desorption resistance due to the COOH / NH_2 interactions. The monolayers show a high level of E / Z photoisomerization of incorporated azobenzene moieties. The level of E / Z conversion of 185 (d) is lower than in the case of 185 (c), due to steric hindrances in 185 (d) /148/.

A correlation was reported between the ability to control nematic liquid crystal alignment and wetting properties of mixed monolayers formed by co-adsorption of 185 (c) and (d) /149/. Mixed monolayers of 185 (c) and (d) have been prepared by the chemisorption via electrostatic interactions between aminated silica substrates and mixtures of 185 (c) and (d).

* Enantiomeric recognition of amino acids by resorcinarenes 186 (a-c) in Langmuir monolayers has been investigated /150/.

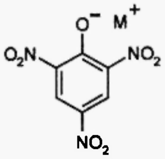


(185)

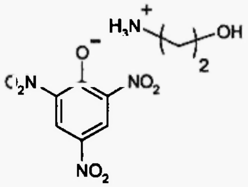
It was established that 186 (a-c) as opposed to nonderivatized 186 (d) show differences in parameters of their Langmuir monolayers, depending on the pH of the subphase. The protonation of the amine groups determines the properties of the monolayer /150/.

The transport of inorganic and organic cations across liquid membranes containing resorcinarene (173) and 186 (c,d) has been studied /151/.

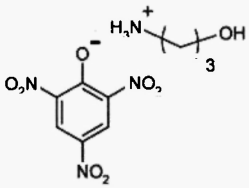
Alkali metal picrates (187) and primary ammonium picrates such as ethanolamine picrate (188) and n-butylamin picrate (189) have been used as inorganic and organic salts, respectively. It was observed that 186 (d) showed a high ionselectivity for lithium ion.



(187) M = alkali metal

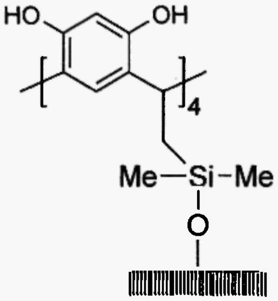


(188)

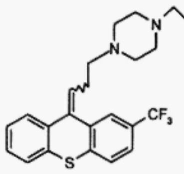


(189)

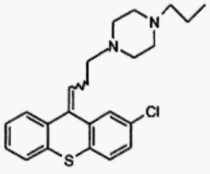
* The chromatographic behavior of the resorcinarene (190), HPLC stationary phase, has been characterized for the separation of cis- and trans-isomers of thioxanthene derivatives such as flupentixol, clopenthixol, chlorprothizene (191-193), respectively, and of benz [b,e] oxepin (194) /152/.



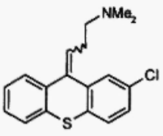
(190)



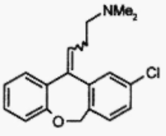
(191)



(192)

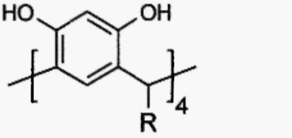


(193)



(194)

* The lipophilic resorcinarene 173 (b) and its octamethylether (195) may serve as dynamic coatings for modified stationary RP-18 phase for HPLC /153/.



$R = C_{11}H_{23}$

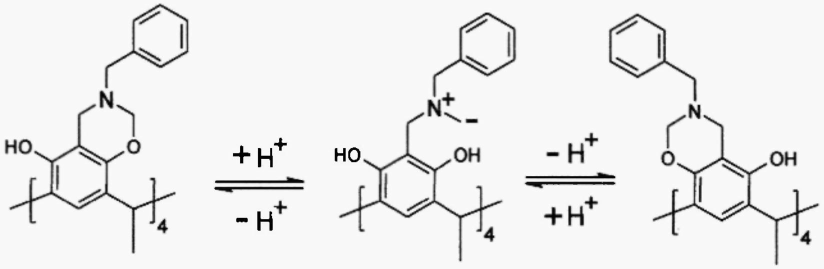
	X
(173)	H
(195)	Me

Resorcinarene (173) and (195) are strongly adsorbed on the modified silicagel RP-18 during HPLC of cresols, chlorophenols and nitrophenols. It was found that (173) coated RP-18 phases are useful beds for HPLC separation of pyrimidine bases, such as thymine, cytosine and uracil /154/.

* C-tetraundecyl resorcinarene (196), as colloidal suspensions, was used to prepare solid lipid nanoparticles (SLNs). Photon correlation spectroscopy studies revealed a particle hydrodynamic diameter of 150 nm /155/. Non-contact mode atomic force microscopy allows observation of the particles as

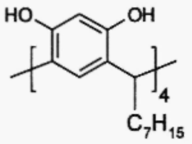
slightly flattened spherical objects of 236 (± 40) nm diameter and 145 (± 40) nm height. The study of the preparation parameters showed that shear force does not affect the hydrodynamic size of SLNs. In contrast, the viscosity and the pH of the aqueous phase, the amphiphile concentration in the organic phase and the volume of organic phase used, all lead to variation in the size of the particles.

* Chiral tetrabenzoxazine resorcinarene derivative (173) shows characteristic plateau formation during enantioselective HPLC separation on the shiral stationary phase ChiralPak AD /156/. By computer-assisted peak from analysis of the elution profiles obtained from temperature dependent dynamic HPLC (DHPLC) experiments, with ChromWin, the enantiomerization barrier $\Delta G^{\#}$ (298 K) = 92 ± 2 KJ mol^{-1}, the activation parameters $\Delta H^{\#} = 53.0 \pm 1.8$ KJ mol^{-1} and $\Delta S^{\#} = -131 \pm 14$ J (k mol^{-1}) wre determined.

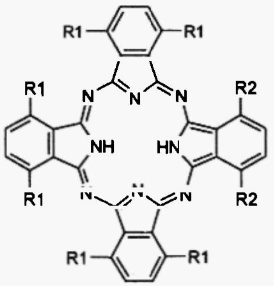


(173) **(173)**

* UV-vis adsorption spectra of floating layers of octa-substituted metal-free phthacyanines (AmPc) mixed with resorcinarene derivative (197), having C_7H_{15} alkyl chains, were studied during monolayer compression /157/.



(196)



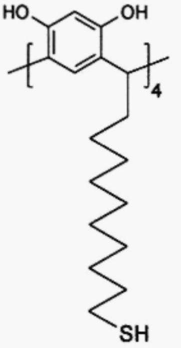
(197)

R1 = [iso C_5H_{11}-AmPc / $C_{10}H_{21}$-AmPc]

R2 = $(CH_2)_4OH$

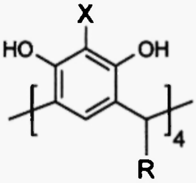
Most of the mixed floating layers, as well as those of the pure AmPc compounds, show characteristic spectra typically attributed to the AmPc condensed state, even at zero surface pressure. These results indicate the formation of aggregates of AmPc molecules on the water surface immediately after spreading. Mixed AmPc / resorcinarene floating layers with the molar ratio less than 1:2 show some spectral transformation at high values of surface pressure, which can be interpreted in terms of molecular rearrangement. Isolated AmPc molecules are thought to have formed due to their inclusion within the resorcinarene matrix.

* Selective molecular interactions at an interface formed by self-assembly of a macrocyclic synthetic host, resorcinarene (198) with four thiol groups (R_4SH), are investigated /158/. The recognition of guest adsorbates from aqueous solutions is monitored using surface plasmon resonance (SPR) and the orientation of the guest-molecule is probed using polarization modulation infrared adsorption spectroscopy (PM-IRRAS). The chemical selectivity of self-assembled monolayers (SAMs) of host-molecules such as resorcinarene extents to isomers of several different guest-molecules such as bipyridine and nitrophenol.



(198)

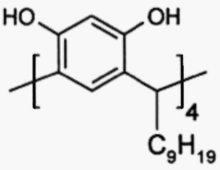
* Resorcinarene (173), (199), (200) form multilayers (7-40 layers) by self assembly from hydrophobic solvents such as hexane on various substrates /159/.



	R	X
(173)	$C_{11}H_{23}$	H
(199)	$C_{11}H_{23}$	OH
(200)	$(CH_2)_{10}SH$	H

These multilayers have been found to bind glutaric acid selectively.

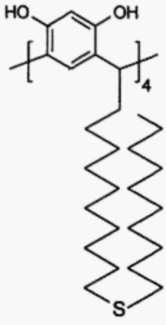
* The preferences of resorcinarene derivative (201) used as a neutral carrier for silver polymeric membrane electrode have been studied /160/. The sensor gave a good nerntion response of 58 ± 1 mV per decade for silver ion in the activity range 3.3 x 10^6 – 3.3 x 10^2 M Ag^+.



(201)

The limit of detection reached 2.1 x 10^6 M Ag^+ and exhibited high selectivity for silver ion against the alkaline, alkaline earths and transition metal ions.

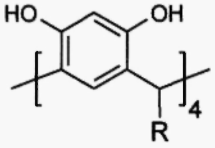
* Self-assembled monolayers of resorcinarene (202) receptor molecules on Au(III) were studied by UHV scanning tunneling microscopy and x-ray photoelectron spectroscopy /161/.



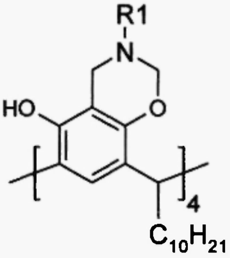
(202)

Highly ordered monolayer were observed with domains oriented at an angle of 60° relative to each other. Molecularly resolved images were investigated and lattice constants found which depended on the preparation solvent. The STM images of two samples, one prepared in 1 mM chloroform / ethanol adsorbate solution and one in 1 mM hexane adsorbate solution are consistent with having a $(21)^{1/2}$ X $2(3)^{1/2}$ and 4 X $2(3)^{1/2}$ lattice respectively.

* Stable monolayers of novel amphiphilic resorcinarene derivatives (201), (203) and (204) at the air-water interface were prepared /162/.



	R	X
(201)	C_9H_{19}	H
(203)	C_9H_{19}	CH_2NMe_2



(204)

Their interactions with Cu ion from the aqueous subphase were investigated by measuring surface pressure-area and surface potential-area isotherms, as well as by Brewster angle microscopy.

* Other examples of resorcinarenes are given in /163-173/.

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