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R. Ostaszewski[ab]; Z. Urbanczyk-lipkowska[ab]; J. Jurczak[ab]; G. D. Andreetti[ab]; G. Calestani[ab]
[a] Institute of Organic Chemistry, Polish Academy of Sciences, Warszawa, Poland [b] Centro di Studio per la Strutturistica Diffractometrica del CNR, Parma, Italy

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Synthesis and structure of chiral diazacoronands derived from L-tartaric acid[1]

R. OSTASZEWSKI, Z. URBANCZYK-LIPKOWSKA, J. JURCZAK*, G.D. ANDREETTI and G. CALESTANI

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland, Centro di Studio per la Strutturistica Diffractometrica del CNR, 43100 Parma, Italy

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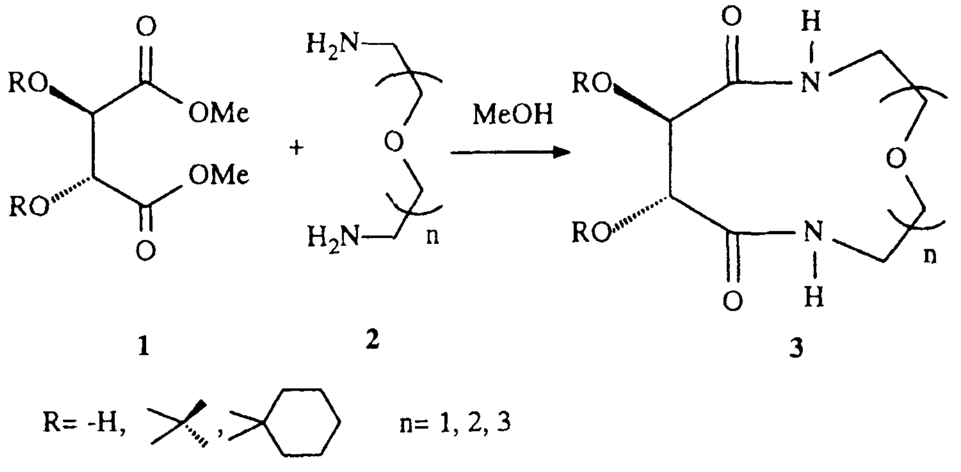
Six chiral di-N-p-toluenesulphonyl diazacoronands derived from L-tartaric acid were synthesized by the modified Richman Atkins procedure. The deprotection of isopropylidene acetal led to the formation of compounds 7 possessing an 1,2-diol subunit. ^{1}H and ^{13}C NMR, UV and MS techniques were used for structure assignment. The determination of the X-ray structure of compounds 6a and 7b pointed to a variety of ring conformations. The shape of the molecules is to a great extent determined by a system of intra- and intermolecular hydrogen bonds of a O• • •O and C• • •O nature. Compound 7b was found to form a supramolecular assembly (H-bonded dimers) both in solution and in solid state. Complexation studies of this group of compounds suggest that this process is mediated by the hydroxyl and sulfonyl group oxygen atoms.

INTRODUCTION

The design of molecular receptors focuses on the three-dimensional arrangement of the structural elements responsible for desirable intermolecular interactions[1]. Close conformational analysis of the free host as well as of the complex may lead to a better understanding of the stability and selectivity of the host-guest associates[2]. ^{1}H and ^{13}C NMR spectroscopy[3], as well as X-ray diffraction studies, along with molecular mechanics[4], have been used in these studies, giving better insight into the mechanism of interactions between the host and guests molecules.

L-Tartaric acid, commonly used as a chiral building block in organic synthesis[5], has been applied also for the preparation of macrocyclic ligands[6,7]. Several chiral crown ethers for enantioselective phase-transfer catalysis have been prepared by E.V. Dehmlov's group[8,9].

Recently we have published very convenient reaction between dimethyl esters and, α ω-diamines, successfully used for efficient synthesis of various macrocycles possessing several nitrogen and oxygen heteroatoms under normal and high-pressure conditions[10].



Scheme 1

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*To whom correspondence should be addressed.

However, in the high-pressure reaction between commercially available tartaric acid dimethyl ester (**1**) and amine **2** (Scheme 1) the desired products **3** failed to be formed. Application of high-pressure conditions gave rise to decomposition of diester **1**. Cyclization reactions on protected tartaric acid derivatives (hydroxy groups were protected as isopropylidene or cyclohexylidene acetals) gave the same results.

For our purpose the disulfonamide derivatives of diazacrown ethers, as compared with secondary amide groups might be of interest, since at room temperature they display a lower barrier of rotation between the nitrogen atom and the sulfonyl group[12]. They have been prepared in high yield by the Richman-Atkins method[13]. Previously we have shown that this reaction can be carried out in presence of phase-transfer catalyst (Bu_4NBr), giving the respective crown ethers in high yield[13].

In this paper we present the macrocyclization reaction based on substrate **4** yielding chiral azacoronands possessing an 1,2-diol subunit which modifies their complexation properties. In order to understand the specifity of interactions between these ligands, conformational studies of compounds **6** and **7** and of their nonhydroxyl counterparts were undertaken. ^1H and ^{13}C NMR, UV in solution and X-ray analysis in solid state were used. Complexing properties were investigated employing L-SIMS and biphasis picrate extraction.

RESULTS AND DISCUSSION

Syntheses

The cyclization reaction between compounds **4** and **5** was performed in a hot (100°C) dimethylformamide solution containing potassium bicarbonate and tetrabutylammonium bromide (Scheme 2). In all cases the small amounts of the respective tetramers present in the crude reaction mixture found by NMR were lost in work-up. The desired coronands were obtained in good yields (18 – 31% Table 1). Elemental analysis showed that coronand **6c** form crystals containing a half of water molecule. The deprotection of isopropylidene acetals of crowns **6** was very difficult. No reaction occured with p-toluenesulfonic acid in a THF/H_2O mixture even under reflux for 12 hours. The reactivity of several other acid catalyst was either too low, or—as in the case of H_2SO_4—the desired reaction was followed by decomposition, and coronands **7** were obtained in poor yield. Only 3% hydrochloric acid in a hot THF/H_2O mixture deprotects isopropylidene acetal in good yield (Table 1). Pure crown ethers **7** were obtained after flash chromatography.

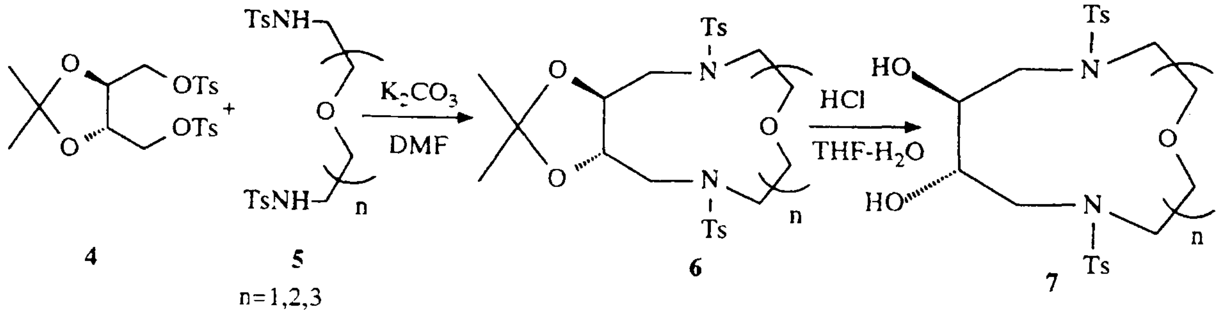
Simple diazacoronands derivatives **8** were prepared according to the known procedure[13].

The data of the prepared compounds are shown in Table 1 and 2.

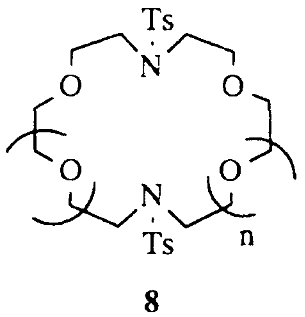
Solid state structure

Atomic coordinates of compounds **6a** and **7b** are collected in Table 3. Figures 1 and 2 show, respectively, the conformation of a molecule of compound **6a** and of two independent molecules of compound **7b**, along with the numbering scheme adopted in structure determination.

Molecules of both compounds are chiral. Compound **6a** has a 9-membered ring and compound **7b** a 14-membered one with two ring nitrogens substituted by the bulkly toluenesulfonic group. Table 4 shows lengths and bond angles of both compounds.



Scheme 2



n= 0,1

8

Table 1 Yields, physical properties and analytical data of diazacoronands **6**, **7**[a]

Compound No.	*Yield (%)*	*M.p. (°C)*	*[α]d (in CH_2C_2)*	*Formula*	*Calcd.(%)/Found(%)*		
					C	*H*	*N*
6a	31	146- 147	+36.8 c = 1.6	$C_{25}H_{34}O_7S_2N_2$	55.74 55.42	6.36 6.41	5.20 4.86
6b	18	oil	-4.8 c = 1.09	$C_{27}H_{38}O_8S_2N_2$	55.65 55.82	6.57 6.73	4.81 4.58
6c	25	oil	-37.36 c = 1.136	$C_{29}H_{42}O_9S_2N_2$ $+0.5H_2O$	54.78 54.84	6.82 6.73	4.41 4.18
7a	77	198– 200	3.0 c = 1.02	$C_{22}H_{30}O_7S_2N_2$ $+0.5H_2O$	52.05 51.85	6.16 6.15	5.52 5.52
7b	82	135– 137.5	81.5 c = 1.00	$C_{24}H_{34}O_8S_2N_2$	53.12 52.78	6.31 6.30	4.48 4.75
7c	68	150– 151.5	-28.4 c=1.15	$C_{26}H_{38}O_9S_2N_2$	53.22 53.24	6.53 6.62	4.77 4.41

[a] The structures of compounds **6** and **7** were also confirmed by high-resolution EI-MS data presented in Table 2.

Table 2 ^{13}C NMR characterization spectra of compounds **6a-c**, **7a-c**.

	CH_3C-CH-CH_3	*$ArCH_3$*	*N-CH_2*	*O-CH_2*	*O-CH*	*CH_3-CH-CH_3*	*C_6H_4*
6a	27.4	21.5	50.5; 54.4	70.9	78.3	109.1	127.5; 129.7; 135.4; 143.6
6b	27.5	21.5	48.3; 51.9	69.8; 71.3	76.8	110.1	127.7; 129.5; 136.0; 143.3
6c	26.9	21.4	48.2; 51.2	70.1; 70.2 70.3	70.2	110.3	127.4; 129.4; 136.7; 142.9
7a	–	21.6	50.7; 51.9	70.3	66.7	–	127.0; 129.9; 135.7; 143.8
7b	–	21.5	51.7; 54.8	71.0; 70.1	70.8	–	127.4; 129.8; 134.9; 143.7
7c	–	21.5	50.4; 53.4	70.4; 70.7 71.6	70.6	–	127.3; 129.7; 135.5; 143.4

The overall shape of the molecules of both compounds is of the cage type, with two toluenesulfonic groups located at the broader side of the cage. The size of the internal cavity of compound **6a** remains within the range of the sum of the appropriate Van der Waals radii, the distance between the terminal methyl groups is only 6.98Å. Two independent molecules of the compound **7b** have an elongated shape of the chelate ring, with the potentially binding area stabilized by two different systems of quite strong (14) intramolecular hydrogen bonds of the C-H• • •O type, formed between the hydrogen atoms activated by the hydroxyl groups and the ring oxygen atoms (see Fig. 3).

The molecules of compound **7b** possesing two free hydroxyl groups form dimers owing to the intermolecular hydrogen bonding between them (Fig. 2 and Table 5). One of the ring oxygen atoms is disordered, this suggesting that in solution at least three stable conformations of the ring may exist simultaneously.

Figures 4 and 5 show in stereo the molecular arrangement in the unit cell. In both cases the molecules are packed with their longest axis down the longest unit cell dimension. The essential molecules-coupling forces include hydrogen bonding and rather weak intermolecular Van der Waals interactions.

In the crystal lattice of compound **6a** the only short intermolecular nonbonding distance is that between the oxygen and carbon atoms of the terminal methyl group of the molecules related by the 1-x,y-1/2,z-1/2 symmetry. In the case of compound **7b** the same groups are closely related by x-1,y,z-1 symmetry.

UV spectra

Properties of the compounds **6**, **7**, **8** in solution were investigated using UV spectroscopy. It is known from the X-ray data that compound **7b** occurs in crystaline state a hydrogen-bonded dimer. In order to determine whether this molecular aggregation occurs also in solution, a series of UV spectra of this compound was taken from acetonitrile solutions of different concentrations. It is clear from Fig. 6, that compound **7b** forms dimers in solutions of higher concentrations.

It was attempted to obtain the association constants of all compounds using the UV titration method. Absorbance changes upon addition of an inorganic salt into a crown ether solution were too small to allow for calculation of the exact values.

Complexation studies

Cation complexation properties of the above diazacoronands were studied using extraction of the latter from water to the dichloromethane phase and by liquid-SIMS methods. Extraction experiments informed about cation complexation mediated by the picric anion,[15] while in

Table 3 Fractional Atomic Coordinates (10^4) with E.S.D.'s in parentheses.

Atom	x/a	y/b	z/c	B_{eq}*
		Compound 6a		
S1	41132(3)	69623(5)	0973(2)	4.3(1)
S2	63828(3)	79732(5)	4210(2)	4.4(1)
O11	3929(1)	7715(2)	1890(6)	3.8(5)
O12	4250(1)	6300(2)	2495(5)	5.3(7)
O21	6269(1)	7455(2)	6163(5)	6.1(7)
O22	6559(1)	8803(2)	4577(6)	6.6(9)
O1	5044(1)	8760(2)	0315(6)	6.1(7)
O2	5993(1)	6179(1)	1205(5)	4.8(5)
O3	5433(1)	5482(1)	-0826(5)	5.0(5)
N1	4578(1)	7217(2)	-0539(5)	4.0(5)
N2	5913(1)	8075(1)	2695(5)	3.8(5)
C1	4539(1)	7954(2)	-2039(8)	5(1)
C2	4980(2)	8471(2)	-1998(8)	5(1)
C3	5458(1)	9197(2)	0760(11)	6(1)
C4	5898(1)	8703(2)	0798(9)	5(1)
C5	5572(1)	7371(2)	2605(6)	3.6(7)
C6	5634(1)	6773(2)	0609(6)	3.5(5)
C7	5896(1)	5416(2)	0055(6)	3.9(7)
C71	6217(2)	5308(3)	-1961(9)	7(1)
C72	5919(2)	4732(3)	1797(10)	6(1)
C8	5215(1)	6199(2)	0254(6)	3.7(5)
C9	4850(1)	6508(2)	-1434(6)	4.1(7)
C11	3708(1)	6548(2)	-1023(6)	4.0(7)
C12	3655(1)	5706(2)	-1221(7)	4.4(7)
C13	3355(1)	5390(2)	-2908(7)	4.6(9)
C14	3101(1)	5916(2)	-4302(7)	4.5(9)
C15	3159(1)	6772(2)	-3983(9)	5(1)
C16	3450(1)	7095(2)	-2361(10)	6(1)
C17	2779(2)	5576(3)	-6101(9)	6(1)
C21	6811(1)	7437(2)	2601(6)	3.7(7)
C22	6995(2)	7783(3)	0649(9)	6(1)
C23	7320(1)	7359(3)	-0598(9)	6(1)
C24	7495(1)	6596(2)	0129(8)	5(1)
C25	7312(2)	6266(2)	2078(11)	6(1)
C26	6966(1)	6663(2)	3332(9)	6(1)
C27	7864(2)	6143(3)	-1251(13)	8(2)
		Compound 7b		
		Molecule 1		
O1	4393(6)	764(2)	2915(7)	5.3(2)
O1′	439(2)	642(5)	381(1)	2.8(3)
C2	5819(6)	930(2)	3931(7)	5.0(2)
C3	5742(6)	1370(2)	3647(6)	5.1(1)
O4	4356(4)	1538(1)	4042(4)	4.73(9)
C5	4314(7)	1965(2)	4043(6)	4.8(1)
C6	2558(7)	2102(2)	4101(5)	4.6(1)
N7	1297(5)	2041(1)	2774(4)	3.90(9)
C8	186(7)	1686(2)	2596(6)	4.7(1)
C9	844(6)	1329(2)	1941(5)	4.0(1)
C10	-451(6)	996(2)	1610(6)	4.5(1)
C11	198(7)	607(2)	1078(5)	4.4(1)
N12	1173(5)	349(1)	2202(4)	3.73(8)
C13	2830(6)	187(2)	2051(6)	4.5(1)
C14	4269(8)	386(3)	2851(9)	6.5(3)
S15	753(2)	2432(0)	1804(1)	4.24(3)
O16	-342(6)	2296(1)	532(4)	5.7(1)
O17	2269(5)	2648(1)	1777(4)	5.6(1)
C18	-445(6)	2749(1)	2618(5)	3.7(1)
C19	328(6)	3077(1)	3382(5)	4.1(1)
C20	-663(8)	3325(2)	3978(6)	4.9(1)
C21	-2339(8)	3253(2)	3867(6)	5.2(2)
C22	-3074(7)	2921(2)	3127(7)	5.1(1)
C23	-2148(6)	2666(2)	2524(6)	4.5(1)
O24	1349(7)	1454(1)	726(5)	6.3(2)
O25	-1884(6)	1135(1)	597(7)	7.8(2)
S26	103(1)	55(0)	2976(1)	3.86(3)
O27	1256(5)	-99(1)	4181(4)	5.08(9)
O28	-1349(4)	277(1)	3101(4)	5.0(1)
C29	-645(6)	-362(1)	1899(5)	3.7(1)
C30	-1988(6)	-304(2)	742(6)	4.4(1)
C31	-2553(8)	-635(2)	-118(6)	5.2(1)
C32	-1871(8)	-1012(2)	160(6)	4.9(2)
C33	-557(8)	-1058(2)	1316(7)	5.3(2)
C34	72(7)	-740(2)	2182(6)	4.5(1)
C35	-338(1)	3533(2)	4520(9)	7.4(3)
C36	-250(1)	-1367(2)	-759(8)	7.3(2)
		Molecule 2		
O1A	-9400(4)	2153(1)	-2695(4)	4.79(9)
C2A	-10929(6)	1963(2)	-3425(7)	4.8(1)
C3A	-10724(6)	1520(2)	-3227(6)	4.5(1)
O4A	-9454(4)	1387(1)	-3865(4)	4.54(9)
C5A	-9136(7)	964(1)	-3772(6)	4.5(1)
C6A	-7293(7)	898(1)	-3768(5)	3.9(1)
N7A	-6114(5)	905(1)	-2360(4)	3.55(9)
C8A	-6287(6)	1242(1)	-1438(5)	3.6(1)
C9A	-5607(5)	1639(1)	-1813(5)	3.5(1)
C10A	-5837(7)	1953(2)	-774(5)	4.3(1)
C11A	-5133(7)	2371(2)	-986(5)	4.6(1)
N12A	-6222(5)	2589(1)	-2160(4)	3.84(9)
C13A	-7831(7)	2746(2)	-1951(6)	4.5(1)
C14A	-9392(6)	2577(2)	-2972(7)	4.6(1)
S15A	-5781(2)	463(0)	-1628(1)	3.90(3)
O16A	-7336(5)	257(1)	-1670(4)	5.3(1)
O17A	-4638(5)	519(1)	-294(4)	5.2(1)
C18A	-4703(6)	183(1)	-2658(5)	3.5(1)
C19A	-5475(7)	-146(2)	-3369(5)	4.4(1)
C20A	-4537(7)	-388(2)	-4051(6)	4.9(1)
C21A	-2864(8)	-313(2)	-3958(6)	5.1(1)
C22A	-2155(7)	28(2)	-3264(7)	5.2(1)
C23A	-3032(7)	276(2)	-2584(6)	4.6(1)
O24A	-3858(5)	1608(1)	-1810(5)	6.1(1)
O25A	-5049(8)	1832(1)	592(4)	6.9(1)
S26A	-5248(1)	2885(0)	-3010(1)	3.67(2)
O27A	-3861(4)	2662(1)	-3283(4)	4.9(1)
O28A	-6522(4)	3051(1)	-4130(3)	4.91(9)
C29A	-4395(6)	3290(1)	-1905(5)	3.6(1)
C30A	-3051(6)	3228(1)	-783(6)	4.3(1)
C31A	-2470(7)	3540(2)	112(6)	4.8(1)
C32A	-3112(8)	3928(2)	-146(6)	4.9(1)
C33A	-4402(7)	3990(2)	-1301(7)	4.9(1)
C34A	-5065(6)	3673(2)	-2160(6)	4.5(1)
C35A	-190(1)	-596(2)	-4608(9)	7.1(2)
C36A	-237(1)	4265(2)	817(8)	6.6(2)

*Calculated from anisotropic thermal parameters as $B_{eq} = 8\pi^2 \cdot D_u$ where D_u is the determinant of the U_{ij} matrix in orthogonal space

the second method neutral complexes were observed directly.[16]

According to Table 6, binding properties depend rather on the spatial construction of the molecules than on their ring size. Generally, molecules with free hydroxyl groups (**7a** – **c** series) bind 4 – 15 times more effectively then their isopropylidene derivatives with the same ring size. The fact that the compound **7a** (11-membered ring), displays the best complexing properties and that compounds of the **8** series do not bind at all suggests that

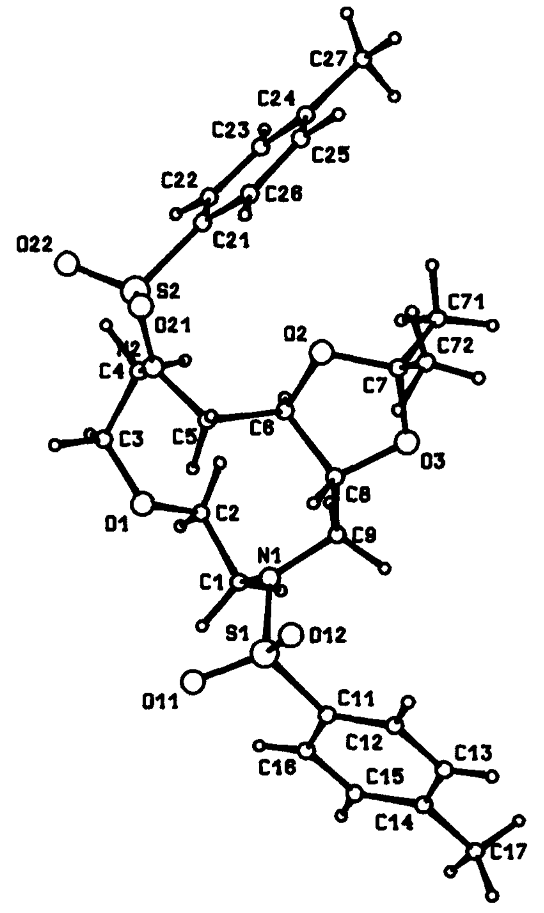


Figure 1 Conformation and numbering scheme adopted during structure determination of compound **6a**.

cation coordination proceeds via the hydroxyl and/or toluenesulfonyl oxygen atoms, and is not very selective.

Table 7 presents the data on selectivity of complexation of the Na^+ cation by derivatives differing in ring size, as determined by the liquid-SIMS method. These data show that the Na^+ complexes are stronger in the case of host possessing larger rings. The presence of an isopropylidene group in crown ether lowers the complexation properties of our compounds. The best selectivity was found for compound **7c** with a 17-membered ring.

CONCLUSIONS

It was shown that chiral diazacoronands can be synthesized using L-tartaric acid as substrate. By this procedure a chiral diol subunit was introduced into the cyclic molecule. Molecules with ring size ranging from 11 to 17 atoms show perceptible complexation of alkali metal ions. If the hydroxyl group is eliminated (compounds **8a-b**) or transformed to isopropylidene acetals (**6a-c**), the complexing properties are lowered or almost negligible. The interesting supramolecular assembling of molecules prior to complexation (hydrogen bonded dimers), observed both in solution and in solid state, may also explain the complexation behaviour of **7b**. The fact that alkali metal ions are bonded with the above molecules via hydroxyl and probably sulfonic oxygen atoms could be used in the further design of macromolecules which may form complexes either via ring heteroatoms or in cooperation with external groups containing oxygen atoms. Additional evidence for the external character of complexation is afforded by the fact that the internal cavity of all investigated compound can be stabilized by three different patterns of the C-H• • •O hydrogen bonds formation, as found in the solid state.

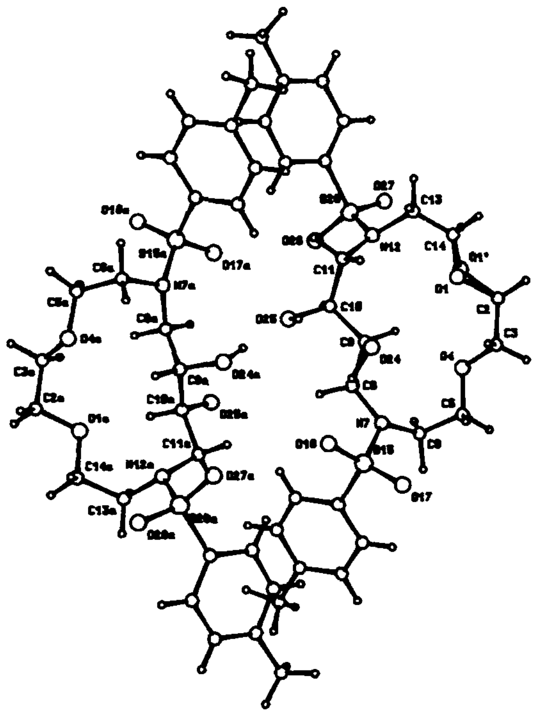


Figure 2 Conformation and numbering scheme adopted during structure determination of the two independent molecules of **7b**.

EXPERIMENTAL

Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, or DMSO-d_6 with Me_4Si as an internal reference standard with a Varian 200 MHz spectrometer. An unambiguous assignment of all individual signals in ^1H NMR spectra was not possible in all cases. The macrocyclization reactions were carried out in a dry nitrogen atmosphere. Flash chromatography was performed on silica gel 60, E. Merck, particle size 0.040 – 0.063 mm, 70 – 230 mesh.

Extraction experiments informing about cation complexation mediated by the picric anion were performed according to already know procedure (15) and mean val-

Table 4 Bond Distances (Å) And Angles (°) With E.S.D.'s In Parentheses.

Compound 6a

Bond distances

S1-O11	1.420(3)	C24-C27	1.514(7)
S1-O12	1.434(3)	C25-C26	1.386(7)
S1-C11	1.771(3)	O1-C2	1.430(6)
S1-N1	1.649(3)	O1-C3	1.404(4)
S2-O21	1.441(3)	O2-C6	1.445(4)
S2-O22	1.438(3)	O2-C7	1.419(4)
S2-C21	1.767(3)	O3-C7	1.429(4)
S2-N2	1.619(3)	O3-C8	1.450(4)
C11-C12	1.362(5)	N1-C1	1.470(5)
C11-C16	1.385(5)	N1-C9	1.473(4)
C12-C13	1.398(5)	N2-C4	1.491(5)
C13-C14	1.377(5)	N2-C5	1.495(4)
C14-C15	1.393(5)	C1-C2	1.514(6)
C14-C17	1.497(6)	C3-C4	1.492(4)
C15-C16	1.360(6)	C5-C6	1.512(5)
C21-C22	1.366(6)	C6-C8	1.529(4)
C21-C26	1.383(5)	C7-C71	1.499(6)
C22-C23	1.362(7)	C7-C72	1.491(6)
C23-C24	1.387(6)	C8-C9	1.518(5)
C24-C25	1.354(7)		

Bond angles

C11-S1-N1	106.2(1)	C24-C25-C26	122.5(3)
O12-S1-N1	106.7(1)	C21-C26-C25	118.8(3)
O12-S1-C11	107.8(1)	C2-O1-C3	116.3(3)
O11-S1-N1	106.9(1)	C6-O2-C7	108.3(2)
O11-S1-C11	108.5(1)	C7-O3-C8	107.9(2)
O11-S1-O12	120.0(1)	S1-N1-C9	115.3(2)
C21-S2-N2	110.1(1)	S1-N1-C1	116.8(2)
O22-S2-N2	106.3(1)	C1-N1-C9	116.8(2)
O22-S2-C21	106.4(1)	S2-N2-C5	119.3(1)
O21-S2-N2	107.1(1)	S2-N2-C4	119.5(2)
O21-S2-C21	107.0(1)	C4-N2-C5	117.7(2)
O21-S2-O22	119.7(2)	N1-C1-C2	111.5(3)
S1-C11-C16	118.8(2)	O1-C2-C1	107.4(3)
S1-C11-C12	120.0(2)	O1-C3-C4	117.2(2)
C12-C11-C16	121.3(3)	N2-C4-C3	113.2(3)
C11-C12-C13	119.1(3)	N2-C5-C6	115.3(2)
C12-C13-C14	121.1(3)	O2-C6-C5	108.5(2)
C13-C14-C17	120.9(3)	C5-C6-C8	113.0(2)
C13-C14-C15	117.4(3)	O2-C6-C8	101.5(2)
C15-C14-C17	121.6(3)	O2-C7-O3	106.7(2)
C14-C15-C16	122.6(3)	O3-C7-C72	109.7(2)
C11-C16-C15	118.4(3)	O3-C7-C71	107.7(3)
S2-C21-C26	119.9(2)	O2-C7-C72	107.8(3)
S2-C21-C22	120.6(2)	O2-C7-C71	110.2(3)
C22-C21-C26	119.5(3)	C71-C7-C72	114.6(3)
C21-C22-C23	120.2(4)	O3-C8-C6	101.2(2)
C22-C23-C24	121.8(3)	C6-C8-C9	115.8(2)
C23-C24-C27	121.1(3)	O3-C8-C9	106.2(2)
C23-C24-C25	117.2(3)	N1-C9-C8	113.0(2)
C25-C24-C27	121.8(3)		

Compound 7b

Bond lengths

Atoms	*Mol. 1*	*Mol. 2*	*Atoms*	*Mol. 1*	*Mol. 2*
C2-O1	1.450(8)	1.425(6)	O16-S15	1.435(4)	1.431(4)
C14-O1	1.25(1)	1.429(7)	O17-S15	1.434(4)	1.440(4)
C2-O1′	1.48(2)	–	C18-S15	1.766(5)	1.776(5)
C14-O1′	1.27(2)	–	C19-C18	1.386(5)	1.365(7)
C3-C2	1.480(9)	1.482(9)	C23-C18	1.396(7)	1.382(8)
O4-C3	1.403(7)	1.417(7)	C20-C19	1.388(8)	1.399(9)
C5-O4	1.412(7)	1.421(5)	C21-C20	1.365(9)	1.368(9)
C6-C5	1.518(8)	1.519(8)	C22-C21	1.376(9)	1.374(9)
N7-C6	1.479(6)	1.498(6)	C35-C21	1.51(1)	1.48(1)
C8-N7	1.466(7)	1.477(6)	C23-C22	1.370(9)	1.38(1)
S15-N7	1.612(3)	1.627(3)	O27-S26	1.428(4)	1.433(4)
C9-C8	1.513(9)	1.509(5)	O28-S26	1.426(4)	1.436(3)
C10-C9	1.504(8)	1.516(7)	C29-S26	1.764(4)	1.767(4)
O24-C9	1.442(8)	1.430(6)	C30-C29	1.396(6)	1.377(6)
C11-C10	1.536(9)	1.532(9)	C34-C29	1.379(7)	1.377(7)
O25-C10	1.421(7)	1.419(6)	C31-C30	1.399(9)	1.372(7)
N12-C11	1.478(6)	1.474(6)	C32-C31	1.365(9)	1.385(9)
C13-N12	1.497(7)	1.475(7)	C33-C32	1.377(8)	1.373(8)
S26-N12	1.628(4)	1.630(4)	C36-C32	1.501(9)	1.500(9)
C14-C13	1.409(9)	1.527(7)	C34-C33	1.379(9)	1.379(9)

Bond angles

Atoms	*Mol. 1*	*Mol. 2*	*Atoms*	*Mol. 1*	*Mol. 2*
O1-C2-C3	104.4(5)	108.2(4)	N12-S26-O28	106.9(2)	106.7(2)
C2-O1-C14	117.0(6)	112.2(4)	N12-S26-C29	108.6(2)	107.1(2)
O1-C14-C13	122.7(7)	105.8(4)	O16-S15-O17	119.2(3)	116.9(2)
O1′-C2-C3	128.3(7)	–	O16-S15-C18	107.7(3)	107.4(2)
C2-C1′-C14	114(1)	–	O17-S15-C18	107.0(2)	108.0(2)
O1′-C14-C13	130.0(9)	–	S15-C18-C19	119.5(3)	119.2(4)
C2-C3-O4	109.4(5)	108.5(5)	S15-C18-C23	120.6(4)	118.6(4)
C3-O4-C5	114.7(4)	114.7(4)	C18-C19-C20	117.8(5)	118.3(5)
O4-C5-C6	108.8(5)	107.8(4)	C19-C18-C23	119.9(5)	121.7(5)
C5-C6-N7	112.1(5)	113.7(5)	C18-C23-C22	119.9(5)	118.0(5)
C6-N7-C8	119.2(4)	117.6(3)	C19-C20-C21	122.8(6)	121.5(6)
C6-N7-S15	117.3(3)	114.0(2)	C20-C21-C22	118.4(6)	118.0(6)
N7-C8-C9	113.7(5)	113.6(4)	C20-C21-C35	121.2(6)	119.2(6)
C8-N7-S15	120.0(3)	115.2(3)	C21-C22-C23	121.0(6)	122.3(6)
N7-S15-O16	107.6(2)	111.5(2)	C22-C21-C35	120.4(6)	122.7(6)
N7-S15-O17	107.6(2)	107.5(2)	O27-S26-O28	119.7(2)	119.9(2)
N7-S15-C18	107.3(2)	104.8(2)	O27-S26-C29	107.1(2)	107.7(2)
C8-C9-C10	111.1(5)	107.9(4)	O28-S26-C29	106.8(2)	107.2(2)
C8-C9-O24	110.6(5)	111.5(3)	S26-C29-C30	118.8(3)	120.6(3)
C9-C10-C11	113.9(5)	114.0(5)	S26-C29-C34	121.2(3)	120.3(3)
C9-C10-O25	109.2(5)	111.6(5)	C29-C30-C31	118.4(5)	119.9(4)
C10-C9-O24	110.9(4)	110.0(4)	C30-C29-C34	120.0(4)	119.1(4)
C10-C11-N12	112.6(4)	112.3(4)	C29-C34-C33	119.3(5)	120.5(5)
C11-C10-O25	108.4(5)	107.1(4)	C30-C31-C32	122.2(5)	121.4(5)
C11-N12-C13	117.2(4)	116.0(4)	C31-C32-C33	117.7(6)	118.1(6)
C11-N12-S26	117.3(3)	115.9(3)	C31-C32-C36	121.9(5)	119.6(5)
N12-C13-C14	114.9(6)	113.5(5)	C32-C33-C34	122.4(6)	120.8(6)
C13-N12-S26	116.1(3)	115.5(3)	C33-C32-C36	120.4(6)	122.3(6)
N12-S26-O27	107.4(2)	107.6(2)			

ues from five independent runs for each experimental point are shown in Table 6.

General procedure for the preparation of diazacoronands 6

To a heated (80°C) suspension of potassium carbonate (13.8 g, 0.1 mol) in dimethylformamide (100 mL), containing tetrabutylammonium chloride (0.29 g, 0.001 mol), a solution of **4** (9.4 g, 0.02 mol) and **5** (8.2 g, 0.02 mol) in dimethylformamide (100 mL) was added dropwise. Heating was continued for additional 12 h, whereupon the reaction mixture was cooled and water (250 mL) was added. The mixture was extracted with chloroform (3 × 30 mL); the combined extracts were washed with water (2 × 25 mL) and dried ($MgSO_4$). After evaporation of solvents, the residue was crystallized from a

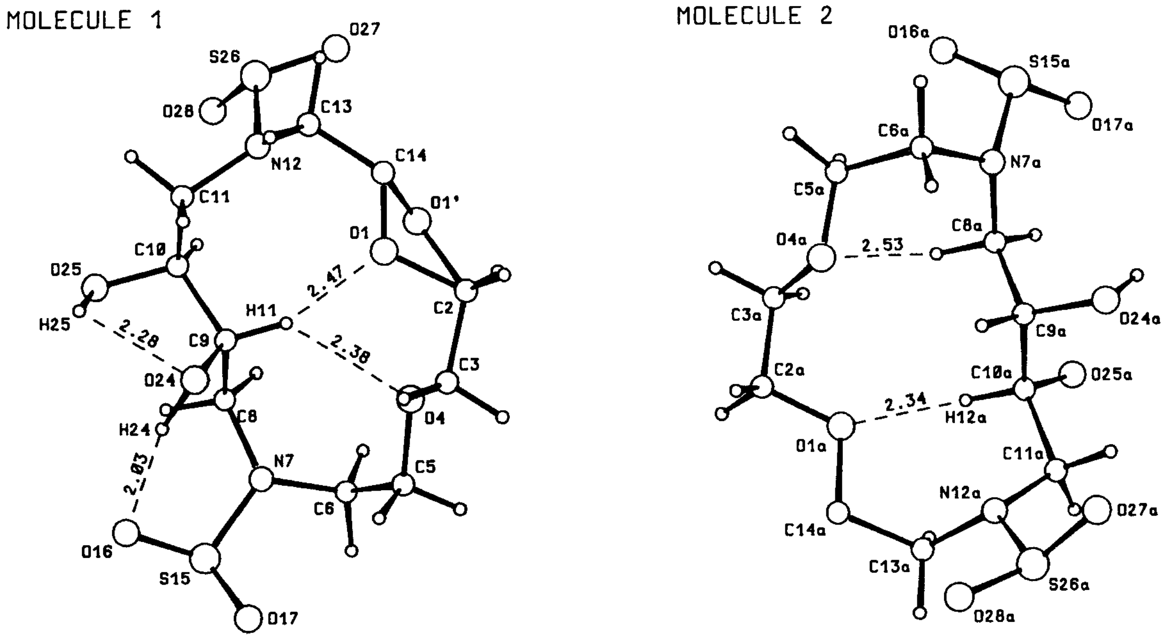


Figure 3 Intramolecular hydrogen bonding patterns in the two independent molecules of compound **7b**.

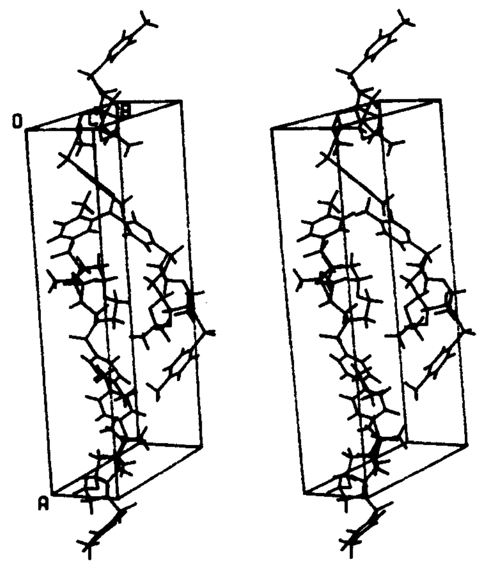


Figure 4 Stereo-diagram of the unit cell of compound **6a**.

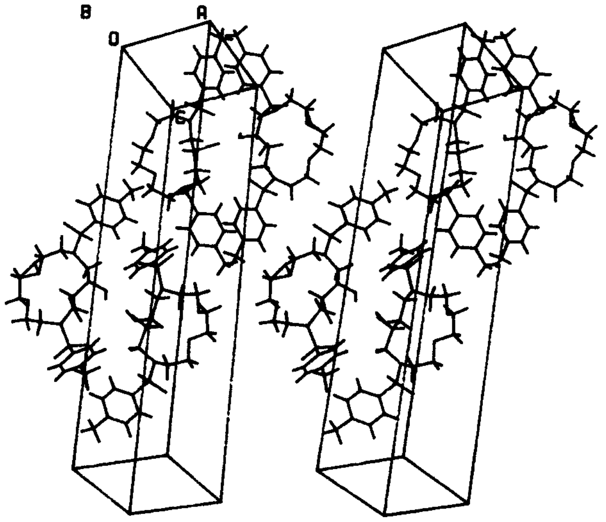


Figure 5 Stereo-diagram of the unit cell of compound **7b**.

mixture of ethyl acetate and hexane, to afford diazacoronands **6**. The yields, melting points, elemental analysies, characteristic mass spectra are presented in Table 1 and 7. ^{13}C NMR spectra are shown in Table 2.

6a ^{1}H NMR 1.35 (s, $C(C\underline{H}_3)_2$, 6H), 2.44 (s, $ArC\underline{H}_3$, 6H), 3.07 – 3.20 (m, $NC\underline{H}_2$, 4H), 3.48 (m, $NC\underline{H}_2$, 4H), 3.66 (m, $C\underline{H}_2O$, 4H), 4.31 (t, J=3.8 Hz, C$\underline{H}$O, 2H), 7.32, 7.72 (AB, J=8.2 Hz, Ar$\underline{H}$, 8H)

Table 5 Geometry Of The Possible Hydrogen Bonding In Compound **7b**.

	HYDROGEN BRIDGE	*D. . .A(Å)*	*D-H(Å)*	*H. . .A(Å)*	*D-H. . .A(°)*
1)	024-H24. . .N7	2.835	1.077	2.391	103.0
2)	024-H24. . .016	3.091	1.077	2.031	167.4
3)	025-H25. . .024	2.814	1.127	2.283	106.2
4)	024-H24'. . .025	2.988	0.947	2.045	173.7
5)	025A-H25'. . .024*	3.227	1.272	2.199	135.1

**symmetry: 1-x,y,z*

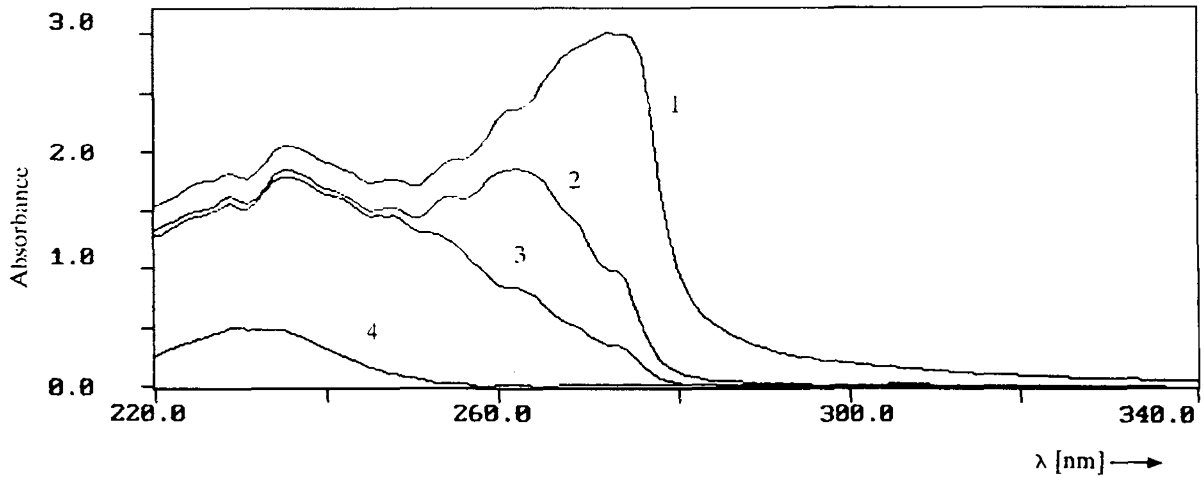


Figure 6 Changes in UV spectra of compound **7b** in MeCN upon dilution.
Curve 1: $c_L = 1.07\ 10^{-2}$ [mol dm^{-3}]
Curve 2: $c_L = 5.30\ 10^{-4}$ [mol dm^{-3}]
Curve 3: $c_L = 2.70\ 10^{-5}$ [mol dm^{-3}]
Curve 4: $c_L = 1.30\ 10^{-6}$ [mol dm^{-3}]

6b ^{1}H NMR 1.31 (s, $C(C\underline{H}_3)_2$, 6H), 2.41 (s, $ArC\underline{H}_3$, 6H), 3.27 – 3.40 (m, $C\underline{H}_2N$, 4H), 3.47 – 3.60 (m, $OC\underline{H}_2$, $NC\underline{H}_2$, 10H), 3.74 – 3.85 (m, $OC\underline{H}_2$, 2H), 7.28, 7.72 (AB, J=8.2 Hz, Ar$\underline{H}$, 8H)

6c ^{1}H NMR 1.28 (s, $C(C\underline{H}_3)_2$, 6H), 2.41 (s, $ArC\underline{H}_3$, 6H), 2.88 (s, $C\underline{H}O$, 1H), 2.96 (s, $C\underline{H}O$, 1H), 3.20 – 3.70 (m, $C\underline{H}_2N$, $C\underline{H}_2O$, 17H), 4.00 – 4.10 (m, $C\underline{H}_2O$, 2H), 7.29, 7.76 (AB, d J=8.1 Hz, Ar$\underline{H}$, 8H)

General procedure for the preparation of diazacoronands 7

To a stirred mixture of 3% hydrochloric acid (2 ml) and tetrahydrofuran (18 ml), 1 mM of the respective diazacoronand **3** was added. The reaction mixture was stirred under reflux for 8 hrs and cooled to room temperature whereupon sodium carbonate was added to pH 7. Solvents were evaporated and the residue was dissolved in CH_2Cl_2. The organic phase was washed with water (2 × 20 ml) and dried ($MgSO_4$); the solvent was evaporated. Purification by flash chromatography gave the respective diazacoronands **7**. The yields, melting points and characteristic mass spectra are presented in Table 1 and 7. ^{13}C NMR spectra are shown in Table 2.

Table 6 Extraction Of Metal Picrates From The Aqueous To The Organic Phase (%)^{A,B}.

Compound No.	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^+
6a	0.2	1.3	2.3	0.9	0.1	0.4
6b	0	1.7	2.4	1.8	0.3	1.9
6c	0	1.4	1.5	3.2	2.2	6.7
7a	0	3.3	9.7	7.2	6.5	6.2
7b	0	2.8	4.3	6.0	0.9	4.1
7c	0	1.3	5.2	1.7	1.4	3.3
9a	0	0	0	0	0	0
9b	0	0	0	0	0	0

a) Solvent: water and dichloromethane (1:1, v/v).
Picric acid = $7.1*10^{-5}$M diazacoronand = $0.7*10^{-3}$M
b) Range of error during experiment 0.008 – 0.013

7a ^{1}H NMR 2.41 (s, $ArC\underline{H}_3$, 6H), 2.75 – 4.10 (m, $C\underline{H}_2N$, $OC\underline{H}_2$, $OC\underline{H}$, -O$\underline{H}$, 15H), 4.45 – 4.50 (m, $C\underline{H}OH$, 1H), 7.32, 7.68 (AB, d J=8.1 Hz, Ar$\underline{H}$, 8H)

7b ^{1}H NMR 2.42 (s, $ArC\underline{H}_3$, 6H), 2.80 – 3.08 (m, $C\underline{H}_2N$, 4H), 3.36 – 3.78 (m, $NC\underline{H}_2$, $OC\underline{H}_2$, -O$\underline{H}$, 14H), 4.06 – 4.12 (m, $C\underline{H}OH$, 2H), 7.32, 7.70 (AB, J=8.0 Hz, Ar$\underline{H}$, 8H)

7c ^{1}H NMR 2.43 (s, $ArC\underline{H}_3$, 6H), 3.15 – 4.15 (m, $C\underline{H}_2N$, $OC\underline{H}_2$, $C\underline{H}O\underline{H}$, 24H), 7.32, 7.71 (AB, J=8.2 Hz, Ar$\underline{H}$, 8H)

Table 7 HR-MS and L-SIMS data for complexation of compounds **6**, **7**, **8**[a]

Compound No.	*Formula*	*L-SIMS* $[M+Na]^+$	*L-SIMS* $[M+H]^+$	*HR-MS* *Ratio*[b]	*HR-MS* *Calcd./Found*
6a	$C_{25}H_{34}O_7S_2N_2$	45	100	0.45	538.1807 538.1802
6b	$C_{27}H_{38}O_8S_2N_2$	100	85	1.17	582.2069 582.2072
6c	$C_{29}H_{42}O_9S_2N_2$	84	76	1.10	626.2325 626.2332
7a	$C_{22}H_{30}O_7S_2N_2$	95	100	0.95	498.1494 498.1488
7b	$C_{24}H_{34}O_8S_2N_2$	54	45	1.20	542.1757 542.1750
7c	$C_{26}H_{38}O_9S_2N_2$	77	53	1.45	543.1815[c] 543.1830[c]
8a	$C_{22}H_{34}O_7S_2N_2$	0	100	0	nd
8b	$C_{26}H_{38}O_8S_2N_2$	0	100	0	nd

[a] As a matrix solutions of 0.01 M NaBr and 0.0001 M diazacoronands in NBA were used.
[b] Numbers indicate the ratio of hights of $[M+Na]^+$ and $[M+H]^+$ peaks.
[c] For ion $[M-43]^+$, $C_{24}H_{35}O_8S_2N_2$.
nd not determined

X-Ray Structure Determination.

Details of the structure solution and refinement for compound **6a** ($C_{25}H_{34}N_2O_7S_2$): a=28.743(1), b=16.013(1), c=5.796(1) Å, V = 2667.7(5) A^3, Z = 4, orthorhombic space group $P2_12_12_1$, CuK_α, μ (CuK_α) = 21.5 cm^{-1}, R = 0.056, R_w = 0.061 for 3725 reflections have been given in ref. 1.

A prism-like crystal of **7b** ($C_{24}H_{32}N_2O_8S_2$), obtained by slow evaporation of the ethyl acetate/hexane solution, was used for intensity data collection on a four-circle CAD4 diffractometer. Unit cell parameters obtained by an automated centering procedure for 25 reflections (θ range 11 – 38°) are: a = 8.160(1), b = 33.057(4), c = 10.036(1) Å, β = 104.47(2)°, V = 2621(1) Å^3, Z = 4, d_{calc} = 1.302 g cm^{-3}; monoclinic space group $P2_1$.

5994 reflections were measured using CuK_α radiation and an $\omega/2\theta$ scanning mode (θ maximum 75°); from among them 5225 were observed. Three standard reflections were measured every 200 reflections. Intensities were corrected for fluctuation of the standard reflections (max 11%) and for the Lorentz-polarization factors.

The structure was solved by direct methods (SHELXS, 1986)[17] and refined by the full-matrix least-squares procedure (SHELX76, 1976)[18], to a conventional R-factor 0.047 (R_w=0.049 for statistical weights) using 5173 reflections with a 36 threshold. Atomic positions of all but hydroxyl hydrogen atoms were calculated after every six cycles of refinement, and were kept fixed along with the isotropic temperature factor U_{iso} of 0.07 Å^2. Positions of the hydroxyl H-atoms were found from the difference maps and were refined. Anisotropic thermal parameters were used for all non-hydrogen atoms.

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