A doubly annelated triple calix[4]arene in the cone/1,2-alternate/cone conformation†

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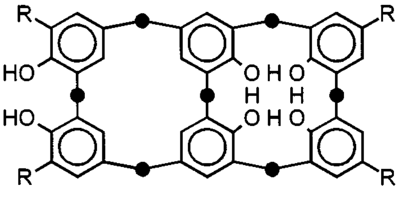
Received (in Cambridge) 11th November 1997, Accepted 14th July 1998

The doubly annelated triple calix[4]arene **2a**, substituted by four nitro groups was synthesised by fragment condensation of the known *exo*-calix[4]arene **3** and the bisbromomethylated dimer of *p*-nitrophenol **4**. Single crystals of its calcium salt $[(\{[\mathrm{Ca}\cdot(\mathrm{DMSO})_4\cdot(\mathrm{H_2O})_2]^{2+}(4\mathrm{DMSO})\}(\mathbf{2a} - 2\mathrm{H})^{2-})\ 2\mathrm{DMSO}]$ were obtained from DMSO–water containing $Ca(HCO_3)_2$. Their X-ray analysis, the first crystallographic proof of the constitution of an annelated calixarene, shows both monoprotonated *endo*-calix[4]arene structures in the expected cone conformation, while the *exo*-calix[4]arene in the middle of the molecule is fixed in the 1,2-alternate conformation. The Ca^{2+} ion is completely solvated by four DMSO and two water molecules in a slightly distorted octahedral fashion. Each water binds two further DMSO molecules, one of which is included in the cavity of the *endo*-calix[4]arene parts, leading in this way to infinite chains of anions and cations. No direct contact between the Ca^{2+}-ion and the phenolate oxygens or the aromatic π-electron systems of **2a** is present. The pK_a-values for the first deprotonation step of each *endo*-calix[4]arene part of **2a** are similar to an analogous calix[4]arene **5** with two adjacent *p*-nitrophenol units, while in contrast to **5** no further deprotonation can be observed.

Introduction

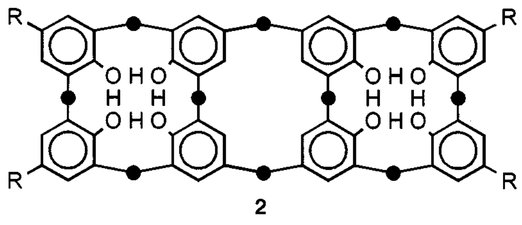
Calixarenes with special substituents may be obtained from *tert*-butylcalixarenes by (selective) derivatisation[1] or by cyclocondensation of suitably functionalized fragments.[2] The latter method has also been used to synthesize more sophisticated structures like bridged calix[4]arenes,[3] head-to-head or head-to-tail linked double calixarenes[4] or annelated double (**1**) and triple calixarenes (**2**), in which two adjacent phenolic units belong simultaneously to two $[1_4]$metacyclophane systems.[5]

Macrobi- and -tricyclic molecules of this type have interesting conformational properties. Molecular dynamics simulations show, in agreement with ^{1}H NMR spectroscopic studies, that the two calix[4]arene systems in **1** can only interconvert between cone, partial cone and 1,2-alternate conformations, while a complete conformational inversion (topomerization) is not possible. For triple calixarenes, such as **2**, two stereoisomers (conformers) are therefore expected, in which the calix[4]arene in the middle is fixed in the cone or 1,2-alternate conformation, respectively.



1

● = CH_2



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Calixarenes are able to form complexes (salts) with a variety of metal cations in solution as well as in the crystalline state. Various examples with alkali,[6,7] calcium[8] or aluminium,[9] with lanthanides[10,11,12] or actinides,[13,14,15] and with several transition metals[16,17] have been characterised by single crystal X-ray analysis.[18] Although examples of second[19] and even third sphere[20] coordination have been reported for such metal complexes of calixarenes, the interaction with the metal cations usually occurs either *via* the phenolate oxygen, *via* the π-electron system of the aryl rings or *via* the -SO_3^- functions in the case of sulfonated calixarenes.

We report here the synthesis of a new doubly annelated triple calixarene and the single crystal X-ray structure of its calcium salt. Not only is this the first X-ray structure of an annelated calix[4]arene, it also shows some peculiar differences to the metal complexes known so far for calixarenes.

Results and discussion

Synthesis

The condensation of the *exo*-calix[4]arene **3** with the bisbromomethylated dimer **4** was carried out in analogy to known procedures (dioxane, $TiCl_4$, reflux, 7 days) (Scheme 1). After the usual work up (Experimental section) a single product could be isolated finally by simple recrystallization (7% yield, not optimised) for which the mass spectrum agreed with the expected annelated triple calixarene **2a**.

The ^{1}H NMR spectrum (DMSO-d_6) showed four signals of equal intensity for the four types of aromatic protons. The

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† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see ‘Instructions for Authors’, *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/144.

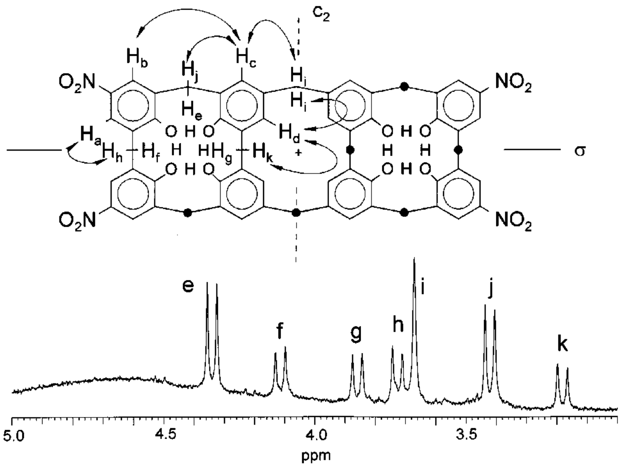
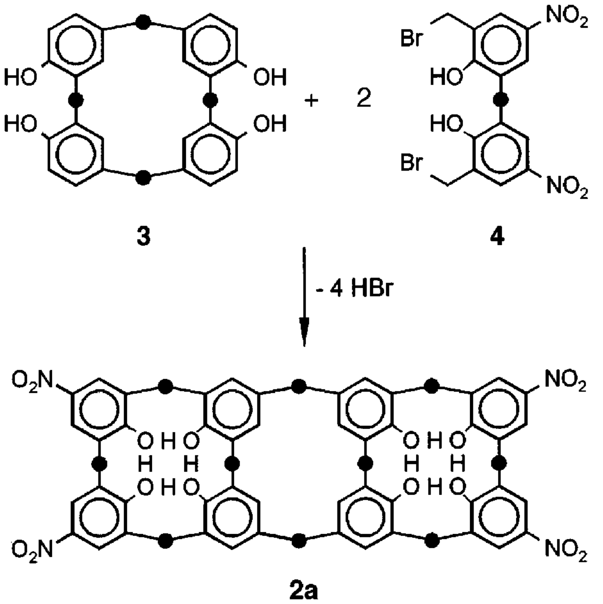


Fig. 1 Section of the ^1H NMR spectrum (400 MHz, DMSO-d_6) of **2a**. The attribution of the signals is based on 2D-COSY (cross peaks for a/b, c/d, e/j, g/k, f/h) and 2D-NOESY (cross peaks indicated by arrows). The broad bump around 4.6 ppm is due to the OH protons exchanging with water.



Scheme 1

expected *m*-coupling was not resolved. Fig. 1 shows the section corresponding to the methylene protons and their attribution based on 2D-COSY and 2D-NOESY spectra. Three pairs of doublets (ratio 2 : 1 : 1) are in agreement with a cone conformation of both *endo*-calix[4]arene systems at the end of the molecule. The singlet found for the methylene protons H_i strongly suggests a cone/1,2-alternate/cone conformation (C_{2h}-symmetry) since in the cone/cone/cone isomer (C_{2v}-symmetry) the diastereotopic methylene protons would probably not be isochronous and thus would appear as a pair of doublets (AB-system)with geminal coupling.

Single crystal X-ray analysis

All attempts to obtain single crystals of the rather insoluble **2a**, using DMSO or mixtures of DMSO with various solvents were initially unsuccessful. By chance, however, tap water was added once to such a DMSO solution which resulted, after three days at room temperature, in the formation of transparent yellow crystals which, although extremely unstable without the mother liquor, were of excellent quality for X-ray diffraction.

Surprisingly the crystal structure revealed not only the molecular skeleton of **2a** but also an ion with octahedral coordination. X-Ray fluorescence spectroscopy unambiguously proved the presence of calcium in the crystals while it could be shown in the same way that the sample used for crystallisation was free of calcium.[21] In fact the crystals proved to be a calcium salt of **2a**, in which the calcium ions stemmed from the tap water. All attempts to obtain single crystals by addition of demineralized water or in the presence of Ca-salts such as $CaCl_2$ or $CaSO_4$ failed. Using water containing small amounts of $Ca(HCO_3)_2$ single crystals were obtained immediately and reproducibly.

Table 1 Selected dihedral and interplanar angles of the dianion $(\mathbf{2a} - 2H)^{2-}$. Reference planes P_{endo} (C07,C14,C21,C28) and P_{exo} (C21, C29,C21A,C29A) are defined by the methylene carbons as indicated

Torsion angles/°			
C20–C15–C14–C02	82.8	C15–C14–C02–C03	−90.6
C03–C04–C07–C08	87.8	C04–C07–C08–C09	−82.4
C09–C10–C28–C26	84.8	C10–C28–C26–C27	−100.1
C27–C22–C21–C19	95.3	C22–C21–C19–C20	−77.6
C23–C22–C21–C19	−83.4	C22–C21–C19–C18	102.2
C18–C17–C29A–C24A	−53.1	C17–C29A–C22A–C23A	−26.8
Interplanar angles/°			
(C01–C06)–P_{endo}	124.7	(C15–C20)–(C01–C06)	113.2
(C08–C13)–P_{endo}	131.9	(C01–C06)–(C08–C13)	113.1
(C22–C26)–P_{endo}	115.4	(C08–C13)–(C22–C26)	105.4
(C15–C20)–P_{endo}	135.1	(C22–C26)–(C15–C20)	108.5
(C22–C26)–P_{exo}	134.0	P_{endo}–P_{exo}	89.1
(C08–C13)–P_{exo}	60.2		

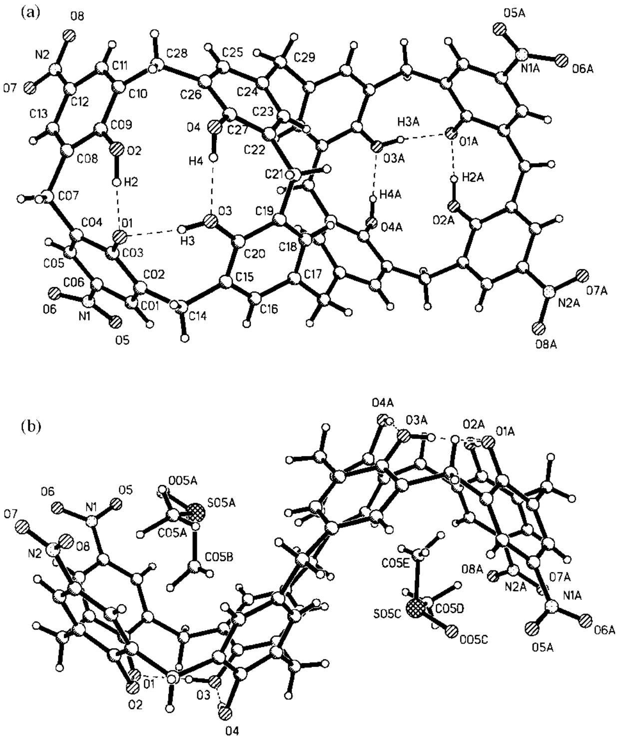


Fig. 2 Molecular structure and numbering scheme of the dianion $(\mathbf{2a} - 2H)^{2-}$ seen from two directions. The intramolecular hydrogen bonding is indicated by dashed lines. The inclusion of one DMSO (third sphere coordination) is shown in part (b).

This calcium salt of the doubly annelated triple calix[4]arene **2a** shows several remarkable features in comparison to the known structures of calixarene salts. Fig. 2 shows the dianion $(\mathbf{2a} - 2H)^{2-}$ which lies on a crystallographic centre of symmetry. As expected, the two *endo*-calix[4]arene units at the end assume the cone conformation, while the *exo*-calix[4]arene in the middle is found in the 1,2-alternate conformation. Table 1 contains the torsion angles around Ar–CH_2 bonds which may be used for an unambiguous description of the conformation.

Table 2 Hydrogen-bonding parameters

Atoms involved	Distance/Å		Angle/°	
	O···O	O–H	H···O	O–H···O
O2–H···O1	2.515	0.944	1.571	176.4
O3–H···O1	2.597	0.848	1.757	170.6
O4–H···O3	2.716	0.847	1.880	168.8
O01–H[1]···O05A	2.715	0.839	1.884	170.2
O01–H[1]···O05B	2.734	0.839	1.995	146.5
O01–H[2]···O05B	2.753	0.856	1.995	173.5

Additionally the dihedral angles of the single phenolic units (best planes through the six carbon atoms) with their reference planes are indicated for a more pictorial description. These reference planes are defined as usual by the four bridging methylene carbons C07, C14, C21, C28 for the *endo*-calixarenes (rms = 0.062 Å) and C21, C29, C21A, C29A for the *exo*-calixarene. The two planes of the *endo*-calixarenes are parallel (due to the symmetry centre) and perpendicular (89.1°) to the plane of the *exo*-calixarene. Both nitro groups are more or less in plane with their adjacent phenyl rings with dihedral angles of 16.3° (N1) and 1.6° (N2).

All hydrogen atoms could be determined experimentally with high significance. One nitrophenol unit is deprotonated in each of the opposite *endo*-calix[4]arene parts and both adjacent hydroxy groups form intramolecular hydrogen bonds to this phenolate oxygen (O1, O1A). An additional hydrogen bond from O4 to O3, which is more basic than O2, completes the stabilisation of the anion. These different bondings are clearly reflected in the O–O-distances (see Table 2). From O2H···O1 *via* O3H···O1 to O4H···O3 the decreasing strength of the hydrogen bonds due to the different acidity of the donor (*p*-nitrophenol *vs*. *p*-alkylphenol) and the different basicity of the acceptor (phenolate > *p*-alkylphenol > *p*-nitrophenol) is reflected by an increased O–O-distance, which is highest for the non-connected oxygens O4 and O2 (2.919 Å).

The structure of the dianion thus confirms indirectly the high acidity of calix[4]arene systems with adjacent *p*-nitrophenol units,[22] and in addition it shows for the first time the monoanion of such a calix[4]arene structure with all stabilising hydrogen bonds. One might have expected an equal statistical distribution of the negative charge over the two phenolic oxygens O1 and O2 which *a priori* are equivalent, but the localisation of the two phenolate oxygens at the diagonally opposite end units is most probably caused by electrostatic repulsion and connected with the slightly distorted conformation of the dianion in the crystalline state.

Fig. 3 shows the solvated Ca^{2+}-cation which is situated on a crystallographic twofold axis. It is surrounded by four DMSO and two water molecules in a distorted octahedral fashion (for details see Table 3).

Two DMSO molecules are coordinated *via* hydrogen bonds (O–O-distances 2.753 and 2.715 Å) to (each of) the two axially oriented water molecules in a second coordination sphere, and one of these DMSO molecules (S05) is embedded into the cavity of a terminal *endo*-calix[4]arene system (third sphere coordination). This inclusion (shortest distances C05A–C25 = 3.825 Å, C05B–C20 = 3.576 Å) is shown in Fig. 2(b).[23] The inclusion of the more deeply embedded methyl group (C05B) can be further characterized by the distances to the centers of the aryl rings (3.712 Å C1–C6; 4.113 Å C8–C13; 3.739 Å C15–C20; 3.670 Å C22–C27). Two further DMSO molecules are not involved in the complexation/solvation and obviously just fill gaps in the crystal lattice. As in other structures containing DMSO, two positions of the sulfur atom are found for each DMSO molecule above and below the triangle formed by the two carbons and the oxygen. (For DMSO with S05 the disorder includes two positions for the oxygen.) Occupancies for these two sulfur positions are S021 0.866, S031 0.860, S041 0.545, S051 0.397 and S061 0.516.

Table 3 Selected bond distances (Å) and bond angles (°) around the Ca^{2+}-ion

Ca–O01	2.329	Ca–O03	2.223	Ca–O06	2.272
{Ca–S032	2.877	Ca–S062	3.467}		
O01–Ca–O03	91.1			O01–Ca–O03A	82.8
O01–Ca–O06	84.3			O01–Ca–O06A	101.5
O01–Ca–O01A	172.0			O03–Ca–O03A	82.0
O03–Ca–O06	95.8			O03–Ca–O06A	166.9
O06–Ca–O06A	89.2				
{S032–Ca–S06B	143.5			S032–Ca–S03B	123.2}

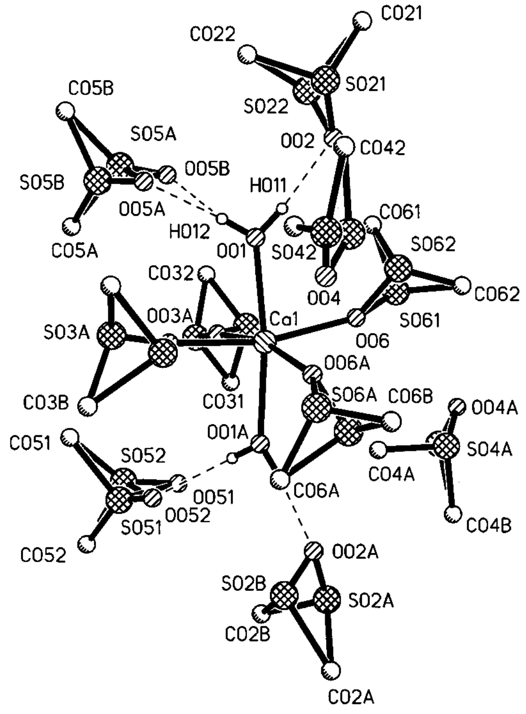
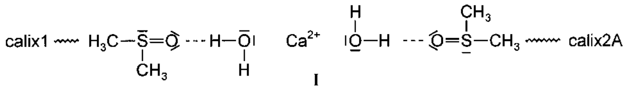


Fig. 3 Coordination around the Ca^{2+}-ion with the numbering used. For each sulfur atom the two different positions are shown. For distances and angles see Table 3, for hydrogen bonding details see Table 2.

The structure of the calcium salt shows some remarkable and, in comparison with other salts derived from calixarenes, quite unusual features. There is neither a direct interaction of the cation with the phenolate oxygen nor with the π-electron systems of the annelated calixarene over which the negative charge may be spread.[24] The shortest distance between Ca and O1 is 10.60 Å. On the other hand there is no strong solvation of the calixarene *e.g. via* hydrogen bonds. Obviously the anion is rather apolar, due to the two arrays of intramolecular hydrogen bonds.

Each calcium cation connects two cavities of two different triple calixarenes to which it is bound in the third sphere.[20] Therefore infinite "chains" of the type **I** are running through the crystal along the *c*-axis (Fig. 4) where adjacent Ca^{2+}-ions are found in a distance of 16.32 Å including Ca–Ca–Ca angles of 118.2°. The main planes of the two cavities (see above) connected in this way are perpendicular to each other (interplanar angle 90.6°). The distance between the two DMSO methyl groups bound into these cavities is C052–C05B = 10.096 Å, while the distance of two DMSO methyl groups bound into the



$$\text{calix1} \sim H_3C-\underset{CH_3}{\overline{S}}=O\cdots H-\underset{H}{\overline{O}}\quad Ca^{2+}\quad \overset{H}{O}-H\cdots O=\overset{CH_3}{S}-CH_3 \sim \text{calix2A}$$

I

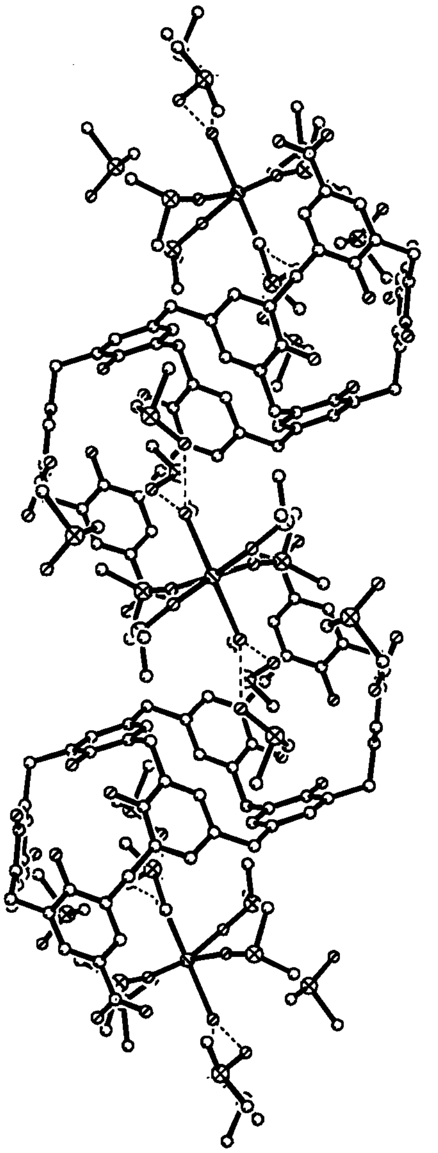


Fig. 4 Arrangement of cations and anions in infinite chains running in *c*-direction. Hydrogen bonds are indicated by dashed lines. Only the most populated of the sulfur atoms is shown.

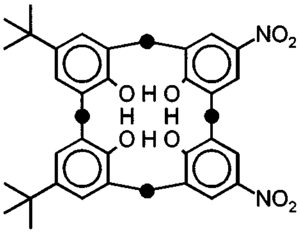
cavities of the same triple calixarene is C05B–C05E = 7.074 Å. The longest extension of the solvated Ca^{2+}-system is C021–C02A = 14.141 Å.

Fig. 5 illustrates the packing of the cation/anion chains, seen along the *b*- and *c*-axes. The shortest distances between Ca^{2+}-ions belonging to adjacent chains are 11.80 Å and 14.00 Å. Thus, completely solvated Ca^{2+}-ions are *entirely separated* from each other by shells formed with calixarene dianions $(\mathbf{2a} - 2H)^{2-}$.

Acidity of triple calixarene 2a

The unexpected crystallization of the calcium salt of **2a** suggests that its dianion is easily formed in the presence of weak bases like HCO_3^-. We therefore determined its pK_a values under conditions recently described for various calix[4]arenes containing one or two *p*-nitrophenol units.[22]

Fig. 6(a) shows the UV–VIS spectra of **2a** in the pH-range of 0.9 to 12.0. All spectra are compatible with a simple equilibrium, involving two colored species (*e.g.* an "apparently" single deprotonation step). The isosbestic points at 276 and 334 nm are more or less identical with those found for **5** (278 and 333 nm) which may be considered as a model for the two *endo* calixarene parts in **2a**. The apparent pK_a value of 2.09 ± 0.05 derived for **2a** is slightly higher than the $pK_{a1} = 1.98 \pm 0.05$ determined for **5**. In contrast to **5** [Fig. 6(b)], however, no further spectral changes occur above pH = 5 until at about pH = 12 precipitation starts. In particular the strong absorption band at 412 nm, ascribed to the dianion of **5** is not observed.



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The most reasonable explanation for these observations is, that the deprotonation of the two *endo*-calixarene parts of **2a** occurs (more or less) independently, with respect to the spectroscopic properties as well as to the mutual electrostatic influence. The apparent pK_a of 2.09 ± 0.05 would represent then the average between pK_{a1} ($pK_a - \lg 2 = 1.79$) and pK_{a2} ($pK_a + \lg 2 = 2.39$) and the dianion thus formed (and found in the crystal structure) cannot be further deprotonated under the experimental conditions.

This raises the question, why the calix[4]arene **5** can form a dianion ($pK_{a2} = 13.2 \pm 0.2$) while both *endo*-calix[4]arene parts of **2a** can be deprotonated only once. A reasonable explanation can be given by the rigidity of **2a**. Calix[4]arenes and their monoanions assume a cone conformation, stabilized by intramolecular hydrogen bonds. However, the most likely conformation for the dianion of **5** is a 1,2-alternate conformation which enables a stabilization of each nitrophenolate by an intramolecular hydrogen bond and maximum separation of the two negative charges. Such 1,2-alternate conformation with an anti-arrangement of the two adjacent nitrophenol units is not possible for **2a**, where the conformational "mobility" of the *endo*-calixarene part is restricted to cone, partial cone (anti-arrangement of the *p*-nitrophenol units) and 1,2-alternate with a *syn*-arrangement of the *p*-nitrophenol units. Thus, either a charge separation (partial cone) or a stabilization by two intramolecular hydrogen bonds (cone) is possible.

Conclusions

Annelated triple calixarenes of type **2** possess two calix[4]arene substructures in the cone conformation stabilised by intramolecular hydrogen bonds between their *endo*-hydroxy groups. Due to the 1,2-alternate conformation of the *exo*-calix[4]arene structure in the middle these molecular cavities point into opposite directions,[25] while the whole molecular structure prevents these cavities from collapsing. This rigidity explains also that each *exo*-calix[4]arene part can only be monodeprotonated. Due to their two cavities these triple calixarenes represent interesting building blocks for supramolecular architectures, which in the special case could be further modified by reduction of the nitro groups and subsequent substitution of the resulting amino groups. We are presently studying the chemical modification of **2a** as well as its co-crystallisation with various metal cations and other potential guests such as bipyridines *etc.*

Experimental

Synthesis

The *exo*-calix[4]arene **3** has been described before.[5] The bisbromomethylated dimer **4** was obtained from 4,4′-dinitro-2,2′-methanediyldiphenol[26] with paraformaldehyde and HBr in acetic acid (33%) in the presence of $ZnCl_2$.

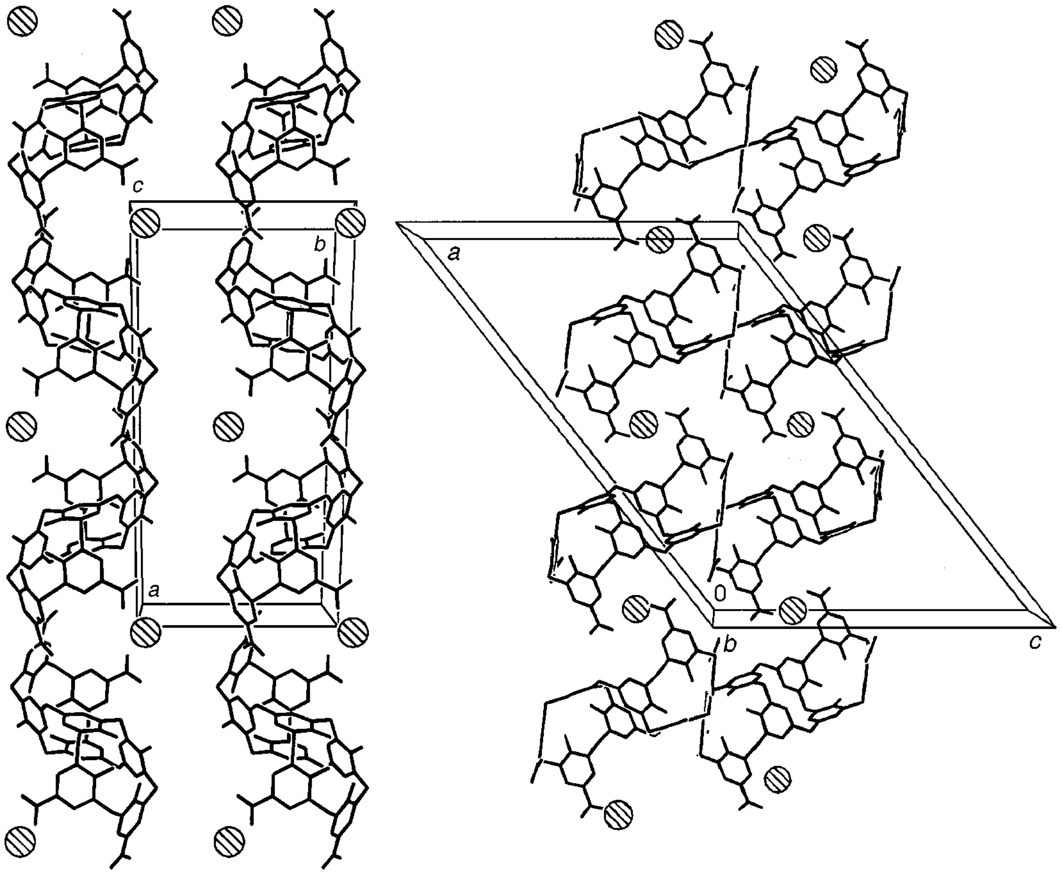

Fig. 5 Arrangement of the anion/cation chains in the crystal lattice, seen from the same direction as in Fig. 4 (right side) and perpendicular to this direction (left side). The Ca^{2+}-ions including their entire solvation shell (see Fig. 3) are symbolised by balls of arbitrary size. They are coplanar in the section shown at the left side.

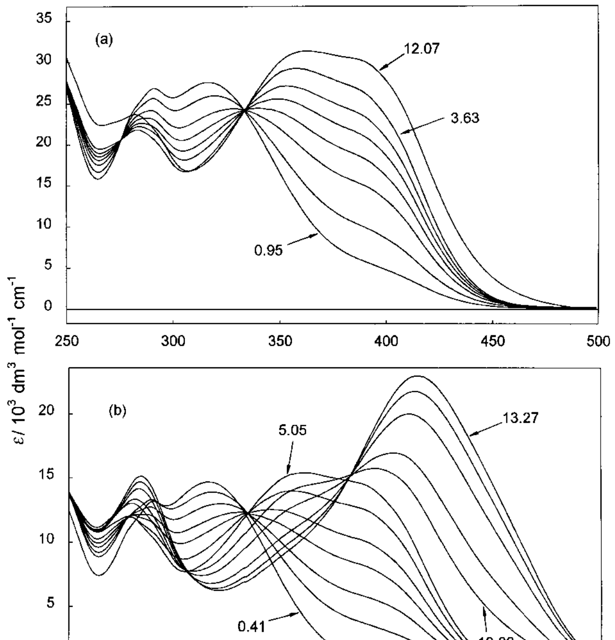

Fig. 6 UV–VIS spectra of **2a** (a) and **5** (b) as a function of pH (2-methoxyethanol–water (9:1); 0.95, 1.41, 1.89, 2.20, 2.52, 2.87, 3.63, 12.07). The spectrum of **2a** at pH = 12.07 is slightly disturbed by the beginning of formation of a precipitate. Up to pH = 5 the spectra of **5**[22] are analogous to **2a**, while at higher pH the formation of the dianion is indicated by the absorption band at 412 nm.

Synthesis of the doubly annelated triple calix[4]arene 2a (10,18,34,42,49,52,53,56-octahydroxy-5,23,29,47-tetranitro-(11,41)(17,35)-bismethanocalix[8]arene). 2.0 g (4.7 mmol) of the *exo*-calix[4]arene **3**, 7.14 g (15 mmol) of the bisbromomethylated dimer **4** and 4.0 g (21 mmol) $TiCl_4$ were dissolved in 250 mL of dry dioxane and refluxed for 7 days. The solvent was removed, the dark oily residue dissolved in ethyl acetate, 40 g of silica gel were added and the mixture evaporated again. The silica gel was extracted with ethyl acetate using a Soxhlet apparatus to give a brown oil. Trituration with acetone left a yellow precipitate which was filtered off and recrystallised from acetone to give 310 mg (6.3%) of a yellow product, mp >360 °C; MS-FD: *m*/*z* 1052.8 (M^+); ^1H NMR (DMSO, 400 MHz) δ 8.15 (s, 4H), 8.04 (s, 4H), 7.03 (br, 4H), 6.43 (b, 4H), 4.35 (d, *J* 12.58, 4H), 4.16 (d, *J* 13.01, 2H), 3.87 (d, *J* 12.76, 2H), 3.75 (d, *J* 12.90, 2H), 3.68 (s, 4H), 3.45 (d, *J* 12.61, 4H), 3.18 (d, *J* 12.74, 2H). ^{13}C NMR (DMSO, 100 MHz) δ 163.0, 149.0, 137.7, 131.8, 130.6, 129.8, 129.3, 129.0, 128.4, 127.6, 124.6, 124.4, 31.8, 30.9, 30.7, 30.5. Elemental analysis does not give satisfactory results for this compound. This may be due to incomplete combustion of the sample due to its high melting point. However, the spectral data and the X-ray analysis leave no doubt about the structure of **2a**.

Measurements

NMR and mass spectra were recorded with a Bruker DRX 400 and a Finigan MAT 230, respectively. The determination of the p*K*-values was achieved by measuring the UV-spectra (Perkin Elmer UV–VIS-spectrometer Lambda 17) as a function of the apparent pH, following a procedure described in detail before.[22]

Crystallography

Single crystals suitable for X-ray analysis were grown at room temperature from a DMSO solution of **2a** after the addition of some drops of $Ca(HCO_3)_2$ containing water: $C_{58}H_{42}N_4O_{16}Ca\cdot 2H_2O\cdot 10(CH_3)_2SO$, $M = 1908.35$, monoclinic, space group $C2/c$, $a = 35.329(1)$, $b = 14.001(1)$, $c = 23.445(1)$ Å, $\beta = 127.72(1)°$, $V = 9173.5(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.382$ g cm^{-3}, μ(Mo-Kα) = 0.373 mm^{-1}; determination of the cell constants and data collection at room temperature with a computer controlled three circle diffractometer {rotating anode: 0.5 × 5 mm^2 focus, 50 kV, 120 mA, λ(Mo-Kα) = 0.71073 Å, graphite monochromator; CCD-detector; ω-scan with steps of 0.3° and 30 s radiation per step}; 17243 reflections ($\theta_{min} = 1.46$, $\theta_{max} = 20.82°$, $-34 < h < 35$, $-14 < k < 14$, $-23 < l < 23$) resulting in 4792 symmetry independent reflections ($R_{int} = 0.035$, $R_\sigma = 0.033$) which were used for the structure analysis. Absorption correction and data reduction with SADABS and XPREP (G. M. Sheldrick, university of Göttingen 1996); solution of the phase problem by SHELXS90 (G. M. Sheldrick, university of Göttingen 1990); only the coordinates of the hydrogen of two DMSO molecules could not be found experimentally, and had to be calculated. Refinement of parameters with SHELX93 (G. M. Sheldrick, university of Göttingen, 1993) {minimisation of $(F_o^2 - F_c^2)^2$, 775 parameters, $R = 0.064$ [0.0499 for 3763 reflections > $4\sigma(F_o)$], $R_w = 0.1339$, $S = 1.055$, weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0566 \times P)^2 + 19.966 \times P]$, where σ results from the counting statistics and P is the function $[(\max(F_o2,0) + 2 \times F_c^2)/3]$. Largest change of parameters during the last refinement cycle: 0.001/esd, maximal and minimal electrodensity in the final Fourier synthesis: −0.37 and 0.28 electrons/Å^3}. The mean standard deviations are: C–C bond: 0.006 Å, S–C bond: 0.01 Å; C–C–C bond angle: 0.4°; C–C–C–C-torsion angle: 0.4°. Calculation of the molecular geometry and the drawings were done with SHELXTL-PLUS, release 5.03 (G. M. Sheldrick, university of Göttingen 1994). For all calculations a DEC 3000/900 AXP computer with VMS processing system was used.

Acknowledgements

We are grateful for financial support from the Deutsche Forschungsgemeinschaft and the German-Israeli Foundation.

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Paper 7/08088C