Calix[4]arene dimers; self-assembly via hydrogen bonding at the upper rim

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The X-ray structure determination of calix[4]arene-tertcarboxylic acid unequivocally proves the self-assembled dimeric structure in the solid state. Also in apolar solvents two calix[4]arene molecules are connected via carboxylic acid moieties at the upper rim. NMR studies show that in polar solvents the calix[4]arenedicarboxylic acid is present as a monomer with a pinched cone conformation that differs from the dimeric structure in apolar solvents.

Introduction

The design of noncovalently bonded, structurally well-defined capsules, boxes and aggregates based on calix[4]arene building blocks is of increasing interest in the field of supramolecular chemistry. Very recently, Rebek et al. reported the reversible encapsulation of aromatic guest molecules in a hydrogen bonded, self-assembled calix[4]arene dimer. Four area functions at the upper rim of one calix[4]arene unit result in the formation of 16 H-bonds in the dimer. Regen et al. suggested for a calix[4]arenetetracarboxylic acid a monomeric structure with one intramolecular hydrogen bond between two diametrical carboxylic acid groups at the upper rim. However, based on VPO measurements in CHCl₃ solution, Ardini et al. recently reported that a related calix[4]arenedicarboxylic acid forms instead of one intramolecular hydrogen bonds in a dimer.

We have studied the dimerization via hydrogen bonding of appropriately functionalized calix[4]arenes in more detail. In this paper, we present the first single crystal X-ray structure of a calix[4]arene dimer (5-5) self-assembled by H-bonds at the upper rim. In solution, this calix[4]arenedicarboxylic acid 3 adopts two different and temperature-independent pinched cone conformations: in chlorinated solvents by intermolecular hydrogen bonding in a dimer and in the hydrogen bond breaking solvent (CD₂)₂SO (solvent induced stabilization) as a monomer with a different pinched cone conformation.

Results and discussion


Gross formylation of 1,3-dinitrocalix[4]arene with titanium tetrachloride and a-dichloromethyl methyl ether in CH₂Cl₂ at −10 °C and 90% yield, respectively. Subsequent oxidation of the aldehyde moieties with sodium dichromate and sulfuric acid in a chloroform-acetone mixture gave the corresponding calix[4]arenes(tri)carboxylic acids 4 and 5 in almost quantitative yield. The FAB mass spectra of the calix[4]arenedicarboxylic acids 4 (m/z 1451.6) and 5 (m/z 1538.9) using o-nitrophenyl acetyl ether (ONPBE) as a polar matrix already indicate the presence of the respective dimers. However, using m-nitrobenzyl alcohol (NBA) as a polar matrix no dimer was observed for diacid 5 (see Experimental).

X-Ray structure determination

Single crystals suitable for X-ray structure determination could only be obtained by very slow evaporation of a CHCl₃-CH₂Cl₂ solution mixture (ca. 1:2) of calix[4]arenedicarboxylic acid 5 at room temperature. Details of the X-ray analysis are given in the Experimental section. Selected bond lengths and angles are listed in Table 1.

The centrosymmetric assembly 5-5 in the solid state with non-crystallographic, idealized D₂h symmetry is depicted in Fig. 1. The dimerization results in two hydrogen bonds per calix[4]arene unit. Regen et al. reported one intramolecular hydrogen bond in a calix[4]arenetetracarboxylic acid.

The hydrogen-bonded dimer 5-5 adopts the pinched cone conformation in which the aromatic units bearing the carboxylic acid groups are oriented face-to-face whereas the other two aromatics are "flattened". The intermolecular O...O distances of the hydrogen-bonded carboxylic acid groups are O(2)...O(8) 2.644(10) and O(1)...O(1') 2.631(10) Å. The carboxylic acid groups of the 5-5 are oriented in the plane with respect to the aromatic units. To the best of our knowledge

Scheme 1 Reagents and conditions: 1. TiCl₄, CH₂CHOCH₂, CH₂Cl₂, −10 °C; 2. H₂SO₄, NaClO₄, CH₂Cl₂, acetone, room temp.
this represents the first X-ray crystal structure of a calix[4]-arene dimer hydrogen-bonded via the upper rim. The hydrogen-bonded dimers stack in layers parallel with the π-plane, cemented by layers of CHCl₃ and CH₂Cl₂ solvent molecules.

Conformational behaviour in solution

The different distances between the equatorial calix[4]-arene bridging methylene hydrogens (Hₓₙ) and the two different adjacent aromatic hydrogens (H₁ and H₂, Table 2) indicate that calix[4]arenediacarboxylic acid 5 also adopts a pinched cone conformation in C₆D₆Cl₂ solution.†

The respective distances (Table 2) were determined by NOESY spectroscopy using the initial rate approximation in which the distance of 1.79 Å between the equatorial and axial bridging methylene hydrogen atoms was used as a reference.† The distances determined in solution are in good agreement with the distances from the X-ray structure analysis. Generally, the respective distances for symmetrically tetrasubstituted calix[4]-arene derivatives in CDCl₃ solution are equal (time-averaged Cₛ, cone conformation).§

Calix[4]arenes in the 'cone' conformation still possess flexibility of the skeleton. The Cₛ, symmetrical cone conformation usually observed by ¹H NMR spectroscopy is in fact the result of fast interconversion between the two Cᵥ, symmetrical pinched cone conformers (time-averaged structure, Scheme 2).

Scheme 2  Cᵥ-Cₛ pinched cone interconversion of calix[4]-arenes

In CDCl₃, the ¹H NMR spectrum of the calix[4]arenediacarboxylic acid 5 shows two different singlets for the aromatic hydrogens. The aromatic hydrogens of the CO₂H-H-substituted aromatic rings absorb at unusual high field (δₛ 6.75), whereas the aromatic hydrogens of the NO₂-phenyl rings are shifted to low field (δₛ 8.14, Fig. 2).†

These characteristic shifts correspond to a pinched cone conformation of 5, which is a consequence of the hydrogen-bonded dimeric assembly of the calix[4]arenediacarboxylic acid 5. The two opposite aromatic rings substituted with the carboxylic acid groups are fixed in close proximity ('parallel') which results in shielding of these aromatic hydrogens. The 'flattened' aromatics bearing the NO₂ groups are not affected by shielding effects. These results fit nicely with what is observed in the solid state (vide supra). The characteristic shielding effects of the aromatic protons of calix[4]-arenes are a sensitive probe for con-
Table 1  Selected bond lengths (Å) and bond angles (°) for calix-
[4]arenedicarboxylic acid 5

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Table 2  Distances (Å) between the H₄⁺⁺ and the adjacent aromatic hydrogens H₂⁺ in 5 calculated from NMR data and X-ray analysis

| H⁻⁻·H₄⁺⁺ | 2.3⁻⁻ | 2.4⁻⁻ |
| H⁻⁻·H₂⁺⁺ | 2.7⁻⁻ | 2.7⁻⁻ |

*H₄⁺⁺ are the equatorial calix[4]arene bridging methylene hydrogens. *Determined by NOESY spectroscopy in CD₂Cl₂ at 243 K, 10.62 Â. *Calculated, averaged distances from the X-ray structure analysis.

due to a cooperative effect. For comparison, the dimerization constant for benzoic acid in CHCl₃ is 400 dm³ mol⁻¹. 13 The cooperative effect may be due to a large positive entropic contribution as we recently discussed for the self-association of diuril containing calix[4]arenes.14 Concentration dependent FTIR studies clearly demonstrated the presence of the dimeric structure of 5. Both at 2.0 × 10⁻³ and 2.0 × 10⁻⁴ m in CHCl₃ a characteristic absorption at 1700 cm⁻¹ (C=O) was present pointing to dimer formation;15 no signal of the monomer (expected at ca. 1725 cm⁻¹)15 could be observed. The ¹H NMR spectrum of the corresponding monocarboxylic acid derivative 4 shows conformational mobility in CDCl₃ (time-averaged structure). The aromatic hydrogens of the NO₂- and the CO₂H-substituted rings are almost at the same position (δH 7.49 and 7.41, respectively). For the monocarboxylic acid 4, a conformational restriction (pinched cone conformation) is not a prerequisite for dimerization. In (CD₃)₂SO as a hydrogen bond breaking solvent (consequentially no dimer formation is possible) the calix[4]arenedicarboxylic acid 5 shows a different pinched cone conformation (Fig. 2). The ¹H NMR spectrum of calix[4]arenedicarboxylic acid 5 in (CD₃)₂SO at room temperature exhibits the signal for the aromatic hydrogens of the carboxylic acid phenyl rings downfield shifted to δH 7.91 (cf. 7.63 in CD₂Cl₂), while the aromatic protons of the nitro phenyl rings are positioned at δH 6.88 (cf. 8.14 in CDCl₃).16 The OCH₃ hydrogen resonances are 0.28 ppm apart. Variable temperature ¹H NMR experiments with 5 in (CD₃)₂SO show no pinched cone interconversion in a range of -20 to +15 °C (δΔH = 0.1). We explain the presence of this different pinched cone conformation of monomeric calix[4]arenedicarboxylic acid 5 (solvent induced stabilization) to a combination of two effects: (a) a more favourable solvation (hydrogen bonding) of the carboxylic acid groups by the Me₂SO molecules when the respective aromatic units are oriented in a 'flattened' position, and (b) a preferred 'parallel' orientation of the NO₂- aromatic units in Me₂SO as a solvent. The ¹H NMR spectrum of monocarboxylic acid 4 in (CD₃)₂SO indicates that the aromatic unit bearing the carboxylic acid group prefers a 'flattened' orientation due to the low-field shift (δH 7.72, cf. δH 7.49 in CDCl₃) like calix[4]arenedicarboxylic acid 5, but less pronounced.

† Auresdi et al. reported that a related dicarboxylic acid is conformationally mobile in CD₂OD as a hydrogen bond breaking solvent.‡ The chemical shifts of the aromatic protons of reference compound 2,6-dimethyl-4-nitro-1-propoxybenzene in CD₂Cl₂ or (CD₃)₂SO as a solvent differ only very little (Δδ = 0.03) in the ¹H NMR spectra. The difference in chemical shifts of the same aromatic protons in the carboxylic acids 4 and 5 is the result of the shielding effects of the opposite aromatic rings in a pinched cone conformation.** Also the in the ¹H NMR spectrum of 1,3-dinitrocalix[4]arene 1 in (CD₃)₂SO, the respective high-field shift indicates that the NO₂- aromatic rings (δH 6.88) are in close proximity, more than in CDCl₃ solution (δH 7.42, time-averaged structure in CDCl₃).

formational studies.66 Also the chemical shifts of the OCH₃ hydrogens, which are 0.44 ppm apart, are in agreement with the pinching in CD₂Cl₂.6

Variable temperature ¹H NMR experiments with 5 in a range of -20 to +115 °C in CD₂Cl₂ show no chemical shifts, implying that the pinched cone conformation and consequently the dimeric structure of 5 is stable up to at least 115 °C in solution. Corresponding behaviour of the pinched cone conformation has been observed for 5.17b-[N(4)-[R-ureido]-25,26,27,28-tetraakis[ethenoxycarbonyl]-methoxy]calix[4]arenes which proved to be stable in CD₂Cl₂ up to at least 120 °C.6 Also dilution experiments of the calix[4]arenedicarboxylic acid 5 in CD₂Cl₂ (from 0.6 x 10⁻³ to 1.2 x 10⁻⁴ m) show no shifts in the ¹H NMR spectra which is in agreement with a high dimerization constant

Conclusions
For the first time, the solid state structure of a calix[4]arene dimer 5-5 hydrogen bonds could be confirmed by X-ray structure determination. The calix[4]arene units of the self-assembled dimer adopt a pinched cone conformation in the solid state.

Further, we have demonstrated that in chlorinated hydrocarbons the calix[4]arenedicarboxylic acid 5 is present as a dimer. Calix[4]arenedicarboxylic acid 5 adopts the same pinched cone conformation, as was determined by X-ray structure analysis, due to intramolecular hydrogen bonding between the carboxylic acid functions. The conformation is stable up to at least 115 °C in CD2Cl2.

In CD2Cl2 as a solvent the 'reversed' pinched cone conformation for the monomeric calix[4]arenedicarboxylic acid 5 was observed (solvent induced stabilization). Also this conformation showed no interconversion in a range of +60 to +115 °C in solution.

Experimental
General
Melting points were determined using an electrothermal apparatus and are uncorrected. 1H NMR and 13C NMR spectra were recorded on Bruker spectrometers at 250 and 400 MHz with SiMe4 as an internal standard. Chemical shifts are reported in ppm (δ). J values are given in Hz. The assignments of the respective aromatic hydrogens of 5 in CD2Cl2 or CD2Cl2·D2O as a solvent were performed by HMOC and HMBC NMR experiments. NOESY, HMOC, HMBC and temperature-dependent 1H NMR spectra were recorded on the 400 MHz spectrometer. FAB mass spectra were recorded with a Finnigan MAT90 using m-nitrobenzyl alcohol (NBA) or o-nitrophenyl octyl ether (ONPOE) as a matrix. FTIR spectra were recorded with a BIO-RAD FTS-60 spectrophotometer. CHCl3 was obtained from Merck (Unasol). Commercial CH2Cl2 was distilled over CaCl2 and then stored for at least 3 h over molecular sieves (3 Å). All other solvents and chemicals were used without purification. Analytical TLC were performed on precoated silica plates (SiO2, Merck, 60F254). Silica gel (particle size 0.040-0.063 mm, 230-240 mesh) was obtained from Merck. All reactions were carried out under an argon atmosphere. For convenience the name calix[4]arene is used instead of the more systematic name penta-cyclo[10.3.1.17,13,18,13]pentaicosan-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene. Before the elemental analysis the samples were dried overnight over P2O5 at 80 °C in vacuo.

5.17-Dinitro-25,26,27,28-tetrapropoxycalix[4]arene 1
5.17-Dinitro-25,26,27,28-tetrapropoxycalix[4]arene was prepared as described in ref. 8, 5a (250 MHz; CDCl3). 7.42 (4 H, d, J = 13.7, Ar, CHAr), 3.91 and 3.86 (8 H, 2t, J = 7.2 and 7.9, OCH2), 3.24 (4 H, d, J = 13.7, Ar, CHAr), 1.90-1.85 (8 H, m, OCH2CH2CH3), 1.03 and 0.97 (12 H, 2t, J = 7.5 and 7.2, OCH2CH2CH2), δ (50 MHz; CDCl3) 7.20 (4 H, d, J = 7.3, Ar, CHAr), 7.02-6.99 (2 H, m, ArH), 6.99 (4 H, s, Ar-NO2), 4.38 (4 H, d, J = 13.5, Ar, CHAr), 3.95 and 3.81 (8 H, 2t, J = 7.6 and 6.4, OCH2), 3.39 (4 H, d, J = 14.2, Ar, CHAr), 1.89-1.83 (8 H, m, OCH2CH2CH3), 1.09 and 0.91 (12 H, 2t, J = 7.2 and 7.1, OCH2CH2CH2).

Formation of calix[4]arenes
A solution of dinitrocalix[4]arene 1 (0.68 g, 1.0 mmol) in CH2Cl2 (25 cm3) was rapidly added to a mixture of a,a-dichloromethyl methyl ether (1.15 cm3, 13 mmol) and freshly distilled TiCl4 (0.53 cm3, 4.8 mmol) in CH2Cl2 (25 cm3) at -10 °C, and was stirred for 30 min at this temperature. The reaction was quenched by addition of a mixture of 2 m HCl (30 cm3) and MeOH (30 cm3). The organic layer was separated, washed with water to neutrality, dried over Na2SO4, and evaporated to dryness.
(ArCH₂Ar), 23.3 and 23.2 (OCH₂CH₂CH₂), 10.2 (OCH₂CH₂CH₂); m/z (FAB, ONPOE, negative) 725.5 [(M - H)⁻, 100%], 1451.6 [(2M - H)⁻, 5%].

5.17-Dinitro-25,26,27,28-tetrapropoxycaix[4]arene-11,23-dicarboxylic acid was prepared as described for compound 4 starting from calix[4]arene 3 (185 mg, 0.25 mmol). The procedure was performed twice to afford dicarboxylic acid 5 as a light-yellow powder (183 mg, 85%); mp >320°C (Found: C, 65.15; H, 6.06; N, 3.74. Calc. for C₃₃H₂₄N₂O₁₂: C, 65.44; H, 6.02. N, 3.63%); δₐ (400 MHz; CDCl₃) 12.65 (2 H, s, CO₂H), 8.14 (4 H, s, Ar-CH₃), 6.75 (4 H, s, Ar=CH₂CO₃H), 4.47 (4 H, d, J=13.9, ArCH₂Ar), 4.14 and 3.70 (8 H, 2t, J=8.1 and 6.7, OCH₂)
3.34 (4 H, d, J=14.0, ArCH₂Ar), 1.92-1.85 (8 H, m, OCH₂CH₂CH₂)
1.09 and 0.87 (12 H, 2t, J=7.3 and 7.4, OCH₂CH₂CH₂); m/z (FAB, ONPOE, positive) 752.2 [(M + OH)⁺, 100%], 1539.2 [(2M + H)⁺, 4%]; m/z (FAB, NIBA, positive) 793.7 [(M + Na⁺), 100%].

X-Ray crystallography
Crystal data for 5. C₃₃H₂₄N₂O₁₂·3CH₂CH₂Cl₂
M= 1213.90. Triclinic, space group Pi, a = 136.60(3), b = 189.33(3), c = 242.36(3), γ = 73.10(2), β = 80.41(2), θ = 76.13(2)°, V = 2710.4(1) Å³ found by least-squares treatment (SET4) of 25 centred reflections with 10.17° < θ < 13.76°, λ = 0.71073 Å; Z = 2, Dc = 1.480 g cm⁻³. Colourless plate shaped (twinned) crystal, crystal decomposition by contact with air due to the loss of the cocrysallized solvent molecules. Crystal dimensions: 0.18 x 0.65 x 0.65 mm, μ(Mo-Kα) = 6.2 mm⁻¹.

Data collection and processing: X-Ray data were collected for an inert-oil-covered fresh crystal taken from the mother liquor and transferred directly into the cold nitrogen stream of a CAD4 diffractometer with rotating anode, ω-scan mode with ω = (0.97 ± 0.35) tan θ₀, graphite-monochromated Mo-Kα radiation; 9276 reflections (T = 150 K, 1.28 < θ < 25.35°; h = 0 to 15; k = -14 to 15; l = -20 to 20) were collected for one of the twin-lattices and were corrected for a linear decay (18% during 27 h of the X-ray exposure time) of the intensity control reflections and for absorption (DIFABS) and merged into a dataset of 8852 unique reflections.

Structure analysis and refinement. Structure solved with direct methods (SIR-90). Full-matrix least-squares refinement on F² with all 8852 unique reflections and 632 parameters with all non-hydrogen and non-disordered atoms anisotropic. Atoms C(38) and C(39) were found to be disordered in a 0.56(3):0.44(3) ratio; in view of the limited quality of the data, these atoms were refined with isotropic thermal parameters.

H-atoms were included on calculated positions and refined in riding mode with thermal parameters related to the U₁₁ of their carrier atoms. The slight non-linearity in the carboxyl bridge is probably a refinement artefact. Final R₁ = [Σ(|F₁| - |F₀|)]/Σ|F₁| for 4257. F₂ = 2.04 and wR₂ = 0.1241, w = [Σ(w/F₂²)]⁻¹ for the 8852 refined reflections; 0.3685 and S = [Σ(w(F₂² - F₁²))/Σ(w(F₂²))]² = 0.42 for the 8852 refined reflections; weighting scheme: w = 1/[σ²(F₂) + (0.2 F₂)²]; F₀ from counting statistics. Neutral-atom scattering factors and anomalous dispersion factors were taken from ref. 17. All calculations were performed with SHELXL-97 and the

PLATON package (geometrical calculations and illustrations) on a DEC-5000 cluster.

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