Bridged Calix[4]arenes; X-Ray Crystal and Molecular Structures and Spectroscopic Studies

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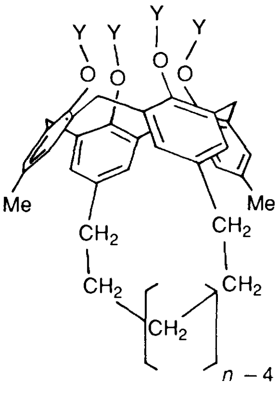
Single crystals of two macrocyclic compounds of the calix[4]arene type, in which two opposite *para*-positions are connected by an additional aliphatic chain where $n = 5$ (**1a**) or $n = 7$ (**1c**) respectively, were obtained from acetone without incorporation of solvent. Crystals of compound (**1a**) are monoclinic, space group $P2_1/n$, $a = 8.879(1)$, $b = 17.216(4)$, $c = 18.167(3)$ Å, $\beta = 98.16(1)°$, $V = 2\,748.2$ Å^3, $Z = 4$, $D_x = 1.258$ g cm^{-3}, final R-value 0.046 (2 476 unique reflections); crystals of compound (**1c**) are monoclinic, space group $P2_1/c$, $a = 18.105(3)$, $b = 9.117(2)$, $c = 19.123(2)$ Å, $\beta = 97.84(1)°$, $V = 3\,127.0$ Å^3, $Z = 4$, $D_x = 1.166$ g cm^{-3}, final R-value 0.043 (4 470 unique reflections). In both cases the arrangement of the four phenolic residues corresponds to the cone conformation. This cone is strongly distorted in the case of compound (**1a**), where two aromatic rings are nearly parallel. For the whole series of bridged calix[4]arenes ($n = 5$–14) FTIR spectra were measured in CCl_4. A decreasing OH-stretching frequency with increasing chain length n shows an increasing strength of the intramolecular hydrogen bonds. These results, which are also supported by the ^1H NMR data, are discussed in connection with the molecular conformations found in the crystalline state.

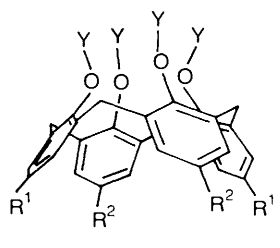
Calixarenes continue to attract interest[1,2] either as host molecules themselves or as building blocks for the preparation of more sophisticated host molecules.[3–5] These compounds are easily available in reasonable to excellent yield by direct condensation of *p*-t-butylphenol (and less frequently also from some other alkyl phenols) with formaldehyde under alkaline conditions.[6] This interest arises from their easy access as well as from the potentially large variety of compounds of this type. Many X-ray structures of calix[4]arenes[7] show that the molecule is always in the so-called cone conformation, having the four OH-groups at one side of the plane defined by the four benzylic methylene carbons. This conformation is also predominant (or exclusively found) in solution where, however, a rapid interconversion of the two opposite cone conformations is shown by the ^1H NMR spectrum at elevated temperatures.[8] To study the properties of a molecular system where this interconversion is impossible, a series of bridged calix[4]arenes (**1**) having two opposite phenolic units connected *via* their *para*-positions by an aliphatic chain of various length (n = 5–16) were recently prepared.[9]

Derivatives of calix[4]arenes with a fixed cone conformation can also be obtained by the introduction of suitable residues Y at the phenolic oxygens.[3,10] Compounds (**3**) with Y = CH_2CO_2R, CH_2COR, or CH_2CONR_2 have been shown to complex very strongly with alkali cations between their ether and carbonyl oxygen atoms.[3,11,12] Similar complexation properties have been found for tetraester derivatives (**2**) of bridged calix[4]arenes.[13] These, however, reveal a distinct switch from complexation to non-complexation in going from the chain length $n \geqslant 7$ to $n \leqslant 6$. This abrupt change in the complexation properties within a series of analogous compounds must be caused by the very small conformational differences exerted by the aliphatic bridge. For a complete interpretation, therefore, a detailed knowledge of the conform-



(**1**) Y = H
(**2**) Y = CH_2CO_2Et

	a	b	c	d	e	f	g	h
n =	5	6	7	8	9	10	12	14



(**3**) $R^1 = R^2 = Bu^t$
(**4**) Y = H, R^1 = Me, $R^2 = [CH_2]_7Me$

Table 1. Atomic co-ordinates (× 10^4) of compound (**1a**), with esds in parentheses.

Atom	x	y	z
C(01)	−3 790(4)	2 220(3)	−1 728(3)
C(02)	−3 573(5)	2 404(3)	−976(3)
C(03)	−3 184(4)	1 852(3)	−421(3)
C(04)	−2 950(5)	2 098(3)	381(3)
C(05)	−1 603(5)	2 657(3)	535(3)
C(06)	−1 799(5)	3 440(3)	683(3)
C(07)	−589(6)	3 945(3)	750(3)
C(08)	812(5)	3 676(3)	654(3)
C(09)	1 080(5)	2 899(3)	505(3)
C(10)	2 635(5)	2 643(3)	349(3)
C(11)	2 581(4)	2 382(3)	−464(3)
C(12)	2 287(4)	2 915(3)	−1 036(3)
C(13)	2 122(5)	2 695(3)	−1 772(3)
C(14)	2 347(4)	1 912(3)	−1 935(3)
C(15)	2 629(4)	1 364(3)	−1 384(3)
C(16)	2 735(5)	522(3)	−1 616(3)
C(17)	1 220(5)	251(3)	−2 034(3)
C(18)	1 014(5)	151(3)	−2 790(3)
C(19)	−372(5)	−9(3)	−3 203(3)
C(20)	−1 631(5)	−38(3)	−2 820(3)
C(21)	−1 489(5)	55(3)	−2 051(3)
C(22)	−2 877(5)	66(3)	−1 651(3)
C(23)	−3 187(4)	889(3)	−1 394(3)
C(24)	−3 620(4)	1 451(3)	−1 922(3)
C(25)	−4 056(4)	2 850(3)	−2 318(3)
C(26)	−2 739(5)	2 924(3)	−2 752(3)
C(27)	−1 185(5)	3 085(3)	−2 326(3)
C(28)	82(5)	3 096(3)	−2 817(3)
C(29)	1 658(5)	3 261(3)	−2 401(3)
C(30)	2 724(4)	1 599(3)	−642(3)
C(31)	−53(5)	177(3)	−1 677(3)
C(32)	−2 937(4)	1 108(3)	−665(3)
C(33)	−139(5)	2 401(3)	472(3)
C(34)	−821(5)	4 806(3)	919(3)
C(35)	−504(7)	−111(4)	−4 048(3)
O(1)	2 899(3)	1 094(2)	−40(2)
O(2)	212(3)	246(2)	−907(2)
O(3)	−2 372(4)	533(2)	−130(2)
O(4)	7(3)	1 610(2)	357(2)

Table 2. Atomic co-ordinates (× 10^4) of compound (**1c**), with esds in parentheses.

Atom	x	y	z
C(01)	6 525(1)	5 125(3)	−469(1)
C(02)	7 271(1)	4 990(3)	−577(1)
C(03)	7 761(1)	6 150(3)	−502(1)
C(04)	8 574(1)	5 894(3)	−598(1)
C(05)	8 995(1)	5 155(3)	45(1)
C(06)	9 104(1)	3 637(3)	54(1)
C(07)	9 455(1)	2 908(3)	645(1)
C(08)	9 700(1)	3 732(3)	1 238(1)
C(09)	9 608(1)	5 245(3)	1 256(1)
C(10)	9 834(1)	6 085(3)	1 933(2)
C(11)	9 168(1)	6 326(3)	2 326(1)
C(12)	8 894(1)	5 171(3)	2 688(1)
C(13)	8 253(1)	5 281(3)	3 007(1)
C(14)	7 894(1)	6 633(3)	2 966(1)
C(15)	8 136(1)	7 817(3)	2 606(1)
C(16)	7 699(1)	9 241(3)	2 564(1)
C(17)	7 005(1)	9 199(3)	2 030(1)
C(18)	6 308(1)	9 021(3)	2 239(2)
C(19)	5 656(2)	8 937(3)	1 757(2)
C(20)	5 728(1)	8 978(3)	1 060(2)
C(21)	6 408(1)	9 169(3)	812(1)
C(22)	6 472(1)	9 157(3)	25(1)
C(23)	6 757(1)	7 710(3)	−212(1)
C(24)	6 286(1)	6 506(3)	−307(1)
C(25)	6 038(1)	3 781(3)	−443(2)
C(26)	5 931(2)	3 430(4)	308(2)
C(27)	6 637(2)	3 286(3)	820(2)
C(28)	6 530(2)	3 204(3)	1 588(2)
C(29)	7 256(2)	3 310(3)	2 074(2)
C(30)	7 204(2)	3 502(4)	2 849(2)
C(31)	7 913(2)	3 937(3)	3 295(2)
C(32)	8 763(1)	7 634(3)	2 277(1)
C(33)	7 035(1)	9 290(3)	1 312(1)
C(34)	7 502(1)	7 493(3)	−305(1)
C(35)	9 261(1)	5 922(3)	649(1)
C(36)	9 572(2)	1 271(3)	644(2)
C(37)	4 901(3)	8 777(11)	2 016(4)
O(1)	9 003(1)	8 785(2)	1 888(1)
O(2)	7 720(1)	9 580(2)	1 094(1)
O(3)	7 991(1)	8 676(2)	−181(1)
O(4)	9 180(1)	7 447(2)	648(1)

ation of these compounds seems necessary. This may be obtained from spectroscopic data in solution or, even more precisely, from X-ray analysis for these rigid compounds.

In this paper the molecular structure of two compounds with 5 and 7 carbon atoms in the bridge (the first examples where this number is odd) is reported and the results are discussed in relation to those structures already described (n = 6, 8, 16)[9,14]. In addition a detailed FTIR study of a whole series of bridged compounds (n = 5–10, 12, 14) is compared with the X-ray results concerning the molecular shape in the solid state and with ^{1}H NMR data obtained in solution.

Experimental

The synthesis of all compounds studied here has been described elsewhere.[9] Single crystals of compounds (**1a**) and (**1c**) were obtained by recrystallization from acetone.

X-Ray Structure Analyses.—Single crystals [compound (**1a**) 0.55 × 0.13 × 0.13 mm; compound (**1c**) 0.45 × 0.45 × 0.10 mm] were sealed in Lindemann-glass capillaries; 25 reflections with $2\theta > 14°$ were used for cell refinement. One standard reflection for the intensity measurements, reflections with $I > 1\sigma(I)$ [(**1a**) 2 476 of 2 885 unique reflections; (**1c**) 4 470 of 5 554 unique reflections] were used for structure analysis; Nicolet R3 computer-controlled diffractometer, Mo-K_α, μ = 0.7 cm^{-1}, $2\theta/\theta$ scan for compound (**1c**), the poor crystal quality of compound (**1a**) necessitated an ω-scan, $2\theta_{\max}$ = 44 for (**1a**) and 50 for (**1c**), speed 4–20° min^{-1}; T 293 K; no corrections for absorption or extinction; $[-9\ (\mathbf{1a});\ -21\ (\mathbf{1c})] \leqslant h \leqslant 3$, $0 \leqslant k \leqslant [18\ (\mathbf{1a});\ 10\ (\mathbf{1c})]$, $[-19\ (\mathbf{1a});\ -22\ (\mathbf{1c})] \leqslant l \leqslant [19\ (\mathbf{1a});\ 22\ (\mathbf{1c})]$.

The solution of the phase problem by direct methods was quite simply obtained in both cases by the default input to the SHELXTL program.[15] The co-ordinates of all the non-hydrogen atoms were obtained from an E-map. After a few cycles of least-squares refinement on F all the hydrogen atoms were shown in a difference electron-density map. The carbon and oxygen atoms were refined anisotropically, the hydrogen atoms isotropically [(**1a**) 1 981 degrees of freedom, 495 parameters; (**1c**) 3 932 degrees of freedom, 531 parameters]. The weighting system was according to the counting statistics of the measured intensities: $w = 1/\sigma^2\ (F)$. The final $R(1)$- and $R(2)$-values [(**1a**) 8.74, 4.58%; (**1c**) 9.06, 4.32%] are quite different, because the weighted $R(2)$-value takes into account the fact that *ca.* 20% of the reflections have intensities between σ and 4σ, thus leading to a relative large deviation between observed and calculated values. The biggest change of a parameter in the last least-squares cycle was < 10% of its standard deviation. At the end of the refinements a difference electron-density map was

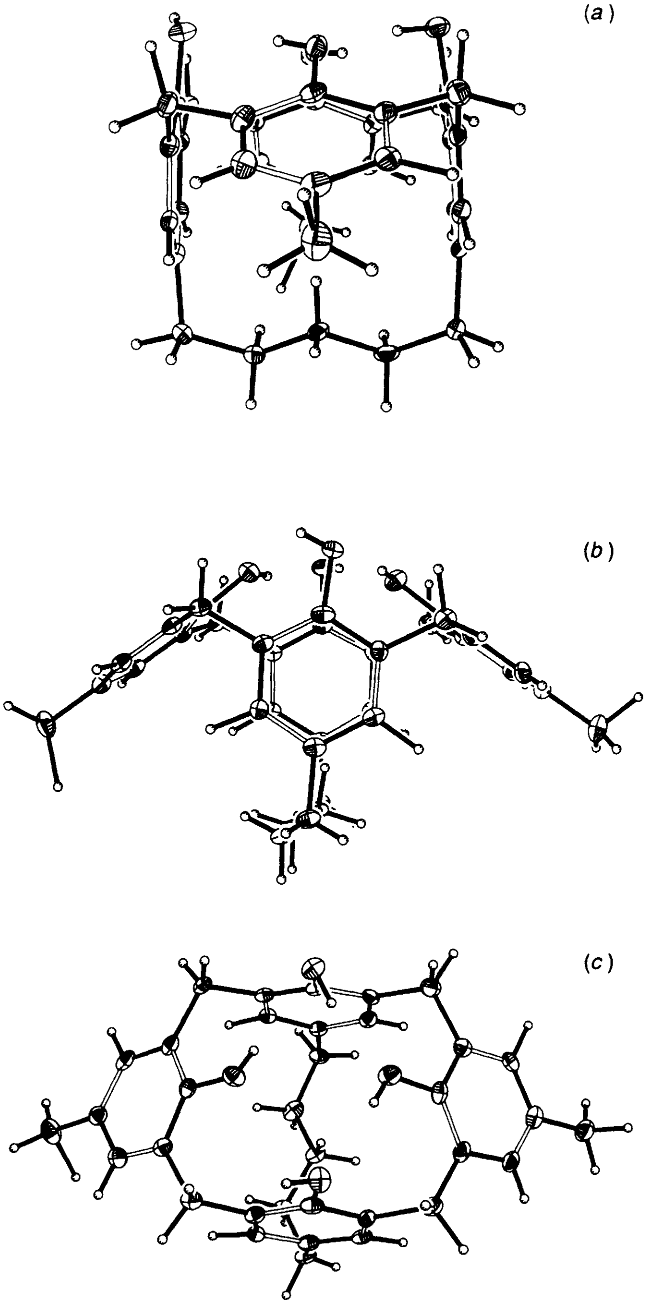


Figure 1. Molecular conformation of compound (**1a**) (n = 5), seen from 3 different, orthogonal directions.

obtained, where the 10 biggest maxima were between 0.2–0.3 electrons Å^{-3} in both cases. All calculations were performed using a Nova 3/12 computer and SHELXTL.

FTIR Measurements.—1 mmol dm^{-3} solutions of compounds (**1a**)–(**1h**) were prepared in high-purity CCl_4 (Burdick and Jackson) and were examined on a Nicolet 20SXB FTIR spectrometer with data collected at 128 scans and 1 cm^{-1} resolution. A Wilk's heated cell and, for low-temperature measurements, a specially designed carbon dioxide expanded-gas-cooled cell were used to produce a 0–55 °C temperature range. The solutions were contained in a 0.5 cm cell with NaCl windows. The external cell temperatures were measured with a digital thermometer (Digitec) to ± 0.1 °C; however, the actual internal solution temperatures were only accurate to ± 1 °C.

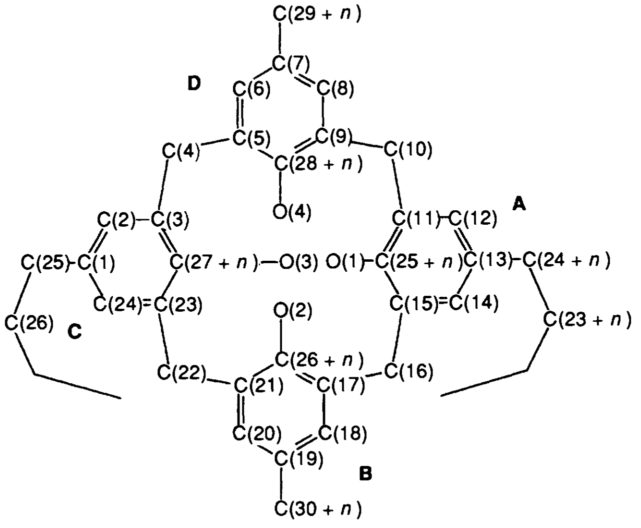
Final spectra were obtained by subtraction of the CCl_4 solvent spectra at the temperature in question. The broad OH band in many cases clearly showed multiple peaks that had temperature-dependent intensities. Consequently, in this study the OH band frequency was recorded for the centre of the major peak. In all cases, except for compound (**1e**) at 55 °C, the band frequency showing the greatest intensity is reported.

Results and Discussion

X-Ray Analysis.—Crystal data for compound (**1a**): $C_{35}H_{36}O_4$, M = 520.67, monoclinic, space group $P2_1/n$, a = 8.879(1), b = 17.216(4), c = 18.167(3) Å, β = 98.16(1)°, V = 2 748.2 Å^3, Z = 4, D_x = 1.258 g cm^{-3}.

Crystal data for compound (**1c**): $C_{37}H_{40}O_4$, M = 548.73, monoclinic, space group $P2_1/c$, a = 18.105(3), b = 9.117(2), c = 19.123(2) Å, β = 97.84(1)°, V = 3 127.0 Å^3, Z = 4, D_x = 1.166 g cm^{-3}.

Fractional atomic co-ordinates for both compounds are listed in Tables 1 and 2.* Carbon atoms are numbered closely following that numbering of the systematic names † as indicated below, where the chain of methylene groups connects the *para*-positions of phenolic residues A and C behind a plane with the oxygens O(1)–O(4) (phenolic units A–D) arranged in a clockwise order. All bond distances and bond angles have the usual values found in similar cases.



The general results show the molecular structure of the calix[4]arene part of the molecule in both compounds is in the cone conformation, even though with the bridges present the partial cone and the 1,3-alternate conformation would be possible, too. This cone conformation is strongly distorted in the case of compound (**1a**) with n = 5 (see Figure 1). Several parameters which are tabulated and compared in Table 3 may be used to describe this distorted conformation.

First, it should be noted that the four benzylic methylene carbons C(4), C(10), C(16), and C(22) connecting the phenolic

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* Lists of structure factors, anisotropic temperature factors and hydrogen atom co-ordinates, bond distances bond angles and torsion angles are deposited at the *Fachinformationszentrum* H. Karlsruhe, *Gesellschaft für wissenschaftlichtechnische information mbH* D-7514 Eggenstein-Leopoldshafen 2. The full literature citation of this publication and the code number CSD-54765 should accompany the request.

† The systematic name for (**1a**) is 7,19-dimethylhexacyclo-[11.11.5.$1^{3,23}$.$1^{5,9}$.$1^{11,15}$.$1^{17,21}$]triatriaconta-1,3(32),5,7,9(33),11,13,15(30),17,19,21(31),23-dodecaene-30,31,32,33-tetraol.

Table 3. Comparison of the shape of the calixarene part of different bridged calixarenes, as determined by X-ray analysis. For three characteristic quadrangles (see text) distances (in Å) and angles (in °) are given. The different shape is characterized further by the inclination of the phenolic rings relative to the plane of the benzylic methylene carbons.

Compound	(**1a**)	(**1b**)	(**1c**)	(**1d**)	(**1d′**)
Quadrangle of benzylic methylene carbons					
C(4)–C(10)	5.055	5.026	5.063	5.101	5.094
C(10)–C(16)	5.115	5.105	5.095	5.161	5.144
C(16)–C(22)	5.035	5.006	5.056	5.022	5.082
C(22)–C(4)	5.093	5.078	5.098	5.094	5.094
C(4)–C(16)	7.155	7.169	7.141	7.166	7.228
C(10)–C(22)	7.196	7.125	7.221	7.244	7.205
C(4)–C(10)–C(16)	89.4	90.1	89.3	88.6	89.8
C(10)–C(16)–C(22)	90.3	89.6	90.7	90.7	89.6
C(16)–C(22)–C(4)	89.9	90.6	89.4	90.2	90.5
C(22)–C(4)–C(10)	90.3	89.7	90.6	90.5	90.0
Quadrangle of oxygen atoms					
O(1)–O(2)	3.04	2.758	2.694	2.630	2.625
O(2)–O(3)	2.90	2.777	2.681	2.692	2.681
O(3)–O(4)	2.86	2.819	2.732	2.723	2.679
O(4)–O(1)	2.90	2.762	2.724	2.665	2.627
O(1)–O(3)	4.759	4.318	4.127	4.029	3.902
O(2)–O(4)	3.308	3.449	3.479	3.503	3.558
O(4)–O(1)–O(2)	67.6	77.3	79.9	82.8	86.2
O(1)–O(2)–O(3)	106.5	102.6	100.3	98.4	94.7
O(2)–O(3)–O(4)	70.1	76.1	80.0	80.6	84.0
O(3)–O(4)–O(1)	111.4	101.4	98.3	96.8	94.7
Quadrangle of carbon atoms attached to *para*-positions [C(A) = C(24 + *n*), C(B) = C(30 + *n*), and so on]					
C(A)–C(B)	6.686	6.623	7.181	6.705	6.934
C(B)–C(C)	6.972	6.889	7.053	7.278	7.364
C(C)–C(D)	7.026	6.876	6.846	7.283	7.434
C(D)–C(A)	7.215	6.953	6.691	6.773	6.753
C(A)–C(C)	5.146	6.246	7.485	8.202	8.412
C(B)–C(D)	12.403	11.812	11.458	11.212	11.328
C(D)–C(A)–C(B)	128.3	120.9	111.3	112.6	111.7
C(A)–C(B)–C(C)	44.2	55.0	63.4	71.7	72.0
C(B)–C(C)–C(D)	124.8	118.2	111.0	100.7	99.9
C(C)–C(D)–C(A)	42.3	53.7	67.1	71.3	72.5
Inclination relative to the plane of the benzylic methylene carbons					
Ring A	91.8	101.9	108.9	115.9	119.8
Ring B	141.7	139.1	138.1	133.7	132.0
Ring C	92.2	98.9	108.7	107.6	108.4
Ring D	145.9	136.6	132.2	130.7	133.0

Table 4. The variation of OH frequency (cm^{-1}) with temperature and chain length *n* for bridged calix[4]arenes in CCl$_4$.

Compound	*n*	Temperature			Difference
		0 °C	25 °C	55 °C	$(\nu_{55} - \nu_0)$/cm^{-1}
(**1a**)	5	3 391	3 395	3 399	8
(**1b**)	6	3 334	3 339	3 344	10
(**1c**)	7	3 284	3 289	3 294	10
(**1d**)	8	3 249	3 255	3 258	9
(**1e**)	9	3 201	3 205	3 212	11
(**1f**)	10	3 192	3 196	3 200	8
(**1g**)	12	3 187	3 190	3 194	7
(**1h**)	14	3 173	3 179	3 189	16
(**4**)		3 161	3 164	3 169	8

units in all cases described here and formerly[9,14] are situated at the corners of a regular square. The maximum deviation of the best plane through these carbons is 0.048 Å for compound (**1a**) and 0.029 Å for compound (**1c**). Therefore it is reasonable to take this plane (in the special cases discussed here and generally for calix[4]arenes) as a reference plane describing their conformation.

Second, the inclination of the phenolic rings with respect to this reference plane may be used as a structural parameter and is also included in Table 3. For decreasing length of the connecting chain, the angles of the phenolic rings A and C (connected by this chain) decrease and consequently the angles for rings B and D increase. Thus, the whole conformational change brought about through varying the chain length of the bridge may be described by rotation of the phenolic units around axes through both *ortho*-methylene carbons which act as fixed points or hinges. For the shortest chain ($n = 5$) rings A and C are nearly parallel (dihedral angle 4.8°) while rings B and D intersect at an angle of 107.6° (see also Figure 1). This situation should be compared with the inclination angle of 123° found for an 'undistorted' calix[4]arene (**3**) in the cone conformation with four-fold symmetry[7a] or with inclination angles between 122–126° found for the calix[4]arene (**4**) (Y = H) which may be regarded as 'open-chain' analogue of compound (**1**).[7f]

Third, the distortion of the 'perfect' cone conformation can be described by the quadrangle of the four oxygen atoms. The rotation of the phenolic rings mentioned above results in an upward movement of the oxygens O(1) and O(3) and a downward movement of oxygens O(2) and O(4) for decreasing chain length (seen from the oxygen atoms at the 'top' of the molecule). Thus, the whole quadrangle deviates more and more from a plane and shows a rhombic shape, which of course is most pronounced for $n = 5$. In connection with the spectral data discussed below, it should be noted that the average distance of adjacent oxygen atoms increases from 2.68/2.65 *via* 2.71 and 2.78 to 2.93 Å when *n* goes from 8 to 5.

Finally, the quadrangle of the four carbon atoms in *para*-positions or, as shown in Table 4, the quadrangle of the carbon atoms attached to these *para*-positions may also be used for structural interpretation. Here the analogous deformation is observed but in the opposite direction from that discussed in detail above. For this quadrangle angles as low as 42° and as high as 128° are found for $n = 5$ and the deviation of these C-atoms from their best plane is between −0.97 Å and +0.98 Å. With respect to the drastic change in the complexation behaviour of the tetraester derivatives (**2b**) and (**2c**) [derived from compounds (**1b**) and (**1c**)][13] it is interesting to note that the distance between these carbon atoms [C(A)–C(C)] is only 1.3 Å longer for compound (**1c**) than that for compound (**1b**). This means that any bridge where this distance can be varied or switched in this range (*e.g.*, by light, by complexation with another guest molecule, *etc.*) would lead to a system where this switch is answered by the uptake or release of Na$^+$ ions, for example.

The conformation of the connecting chain is best characterized by the torsion angles, which are 112/−57/176/180/56/−112 for compound (**1a**) and 104/−53/170/−171/170/−167/53/−108 for compound (**1c**) [in the order C(2)–C(1)–C(25)–C(26) to C(23 + *n*)–C(24 + *n*)–C(13)–C(12) in both cases]. This means that this chain ('the handle of the basket') is bent towards an unconnected phenolic unit in both cases.

In contrast with all the other bridged calix[4]arenes which have been characterized by X-ray analysis,[9,15] compound (**1c**) ($n = 7$) has a non-crystallographic symmetry plane through atoms O(4), C(7), C(28), C(37), O(2), which is perpendicular to the bridge. Obviously such a symmetry plane is not found for compounds with an even number of carbon atoms in the bridge, since this would afford two carbon atoms in a fully eclipsed arrangement in the middle of the bridge. The reason that this

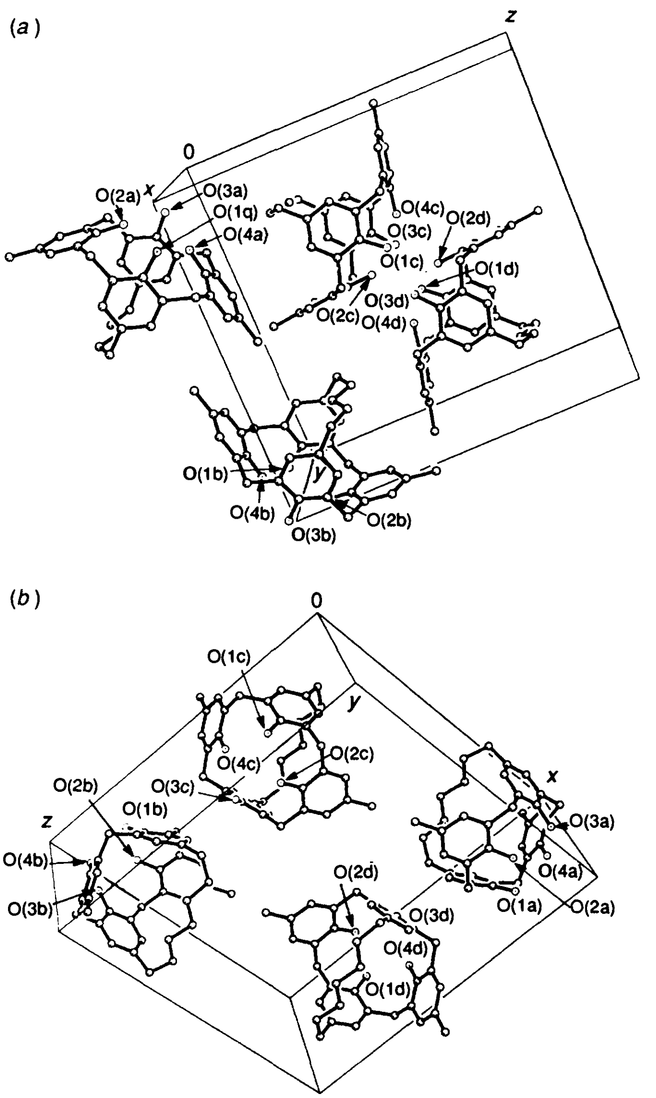

Figure 2. Comparison of the molecular arrangement of (*a*) compound (**1a**) and (*b*) compound (**1c**). No intermolecular contacts between hydroxy-group functions are observed in the latter case. (All hydrogen atoms are omitted for clarity.)

symmetry is not so pronounced for compound (**1a**) ($n = 5$) may be found in the stronger strain and in the special packing discussed below.

Compound (**1c**) forms a pure molecular lattice, where no intermolecular interactions between the phenolic OH-groups are observed [see Figure 2(*b*)]. Obviously, the cyclic array of intramolecular hydrogen bonds is still strong enough to make the molecule as a whole non-polar. This situation changes for compound (**1a**), where the short chain of five C-atoms has weakened the intramolecular hydrogen bonds to such an extent that intermolecular hydrogen bonds become possible. Thus, the molecules are arranged in pairs in the crystal lattice [see Figure 2(*b*)]. Intermolecular O–O-distances [O(3)–O(1)′ 2.86 Å and O(3)–O(2)′ 2.83 Å] which are even shorter than the average for the intramolecular O–O-distances (2.93 Å) may be interpreted in terms of intermolecular hydrogen bonding, although in general there remains an uncertainty for the positions of hydrogen atoms; *e.g.* the oxygen atom O(3) of one molecule is linked to O(1) and O(2) of the other molecule by a kind of 'three-centre' or 'bifurcated' hydrogen bond[16] and *vice versa.* This arrangement may be also the reason for the quite different intramolecular O–O-distances (2.90, 3.04, 2.90, 2.86 Å, see Table 3) and the distortion of the C_2-symmetry of the whole molecule (see above).

Similar intermolecular O–O-distances shorter than 3 Å have been observed only for the bridged calix[4]arene with $n = 6$ and with t-butyl as the *para*-substituent instead of methyl,[9] while in all other cases studied, including compound (**1b**), intermolecular O–O-contacts are absent in the crystal lattice. This is consistent with the general picture that intermolecular hydrogen bonding occurs only in those cases where the intramolecular hydrogen bonds are weakened due to a short bridge between opposite *para*-positions.

Spectroscopic Studies.—The IR frequency assignments for the bridged calix[4]arenes (**1a**)–(**1h**) are shown in Table 4 for three temperatures; also included is the frequency change between 0–55 °C. The dimethyl dioctylcalix[4]arene (**4**), as an open-chain analogue which may be also regarded as representing a long-chain bridged structure, is included for comparison. In Figure 3(*a*) this OH stretching frequency is plotted *versus* the number of CH_2 groups in the bridging chain.

Several things are apparent from these results. It is known from a previous temperature–concentration study that at this low concentration of 1 mmol dm^{-3} the hydrogen-bonding interactions are intramolecular.[17] When the calix[4]arene system is bridged with the short C_5-alkane chain, the aromatic rings are severely restricted and the OH groups are pulled away from each other in order to reduce greatly any intramolecular hydrogen bonding. Consequently, the OH band frequency shifts by >200 cm^{-1} toward the free OH stretching wavenumber which would be *ca.* 3 600 cm^{-1}. As this restriction is reduced by increasing the alkane chain length, the O–O atom separation decreases and a tightly intramolecular OH hydrogen-bonded array is formed. This is nicely illustrated in Figure 3(*a*) where the OH frequency is extrapolating toward the dimethyldioctylcalix[4]arene OH frequency of 3 164 cm^{-1} at 25 °C. This value is somewhat higher than the OH frequency of 3 138 cm^{-1} found for *p*-t-butylcalix[4]arene, a difference which must be seen as a substituent effect since both molecules show the usual ring inversion of free calix[4]arenes.

It is tempting to interpret the data in Figure 3(*a*) by two straight lines, crossing just at the chain length of $n = 9$; however, there is no reasonable theoretical model in favour of this interpretation. Clearly the compounds with shorter chains are more or less rigid, while the compounds with chain lengths greater than 9 gain an increasing flexibility of the methylene chain as well as of the calix[4]arene moiety. However, there should be a somewhat gradual change, as suggested already by the photo-CIDNP spectra of these compounds,[18] and as is also reflected by the change in chemical shift of the OH-groups shown in Figure 3(*b*).

The temperature dependence of the OH band frequency provides another interesting result. With the very short C_5 chain, the apparent change in the frequency between 0 and 55 °C is very small, *e.g.* 8 cm^{-1}. However, even though there is some suggestion that there are greater frequency shifts with longer chains (note the value of 16 cm^{-1} for $n = 14$), no systematic trend is observed, and a change of 8 cm^{-1} is found also for the open-chain analogue. (The error in these values could be ± 2 cm^{-1}.) This would suggest that most of the OH band frequency shift arises from similar OH torsional motion and that the aromatic groups must remain relatively immobile upon temperature change. Furthermore, the increasing frequency with increasing temperature suggests a strengthening of the O–H bond, which is to be expected with a decrease in intramolecular hydrogen bonding.

The ^1H NMR chemical shifts shown in Figure 3(*b*) as

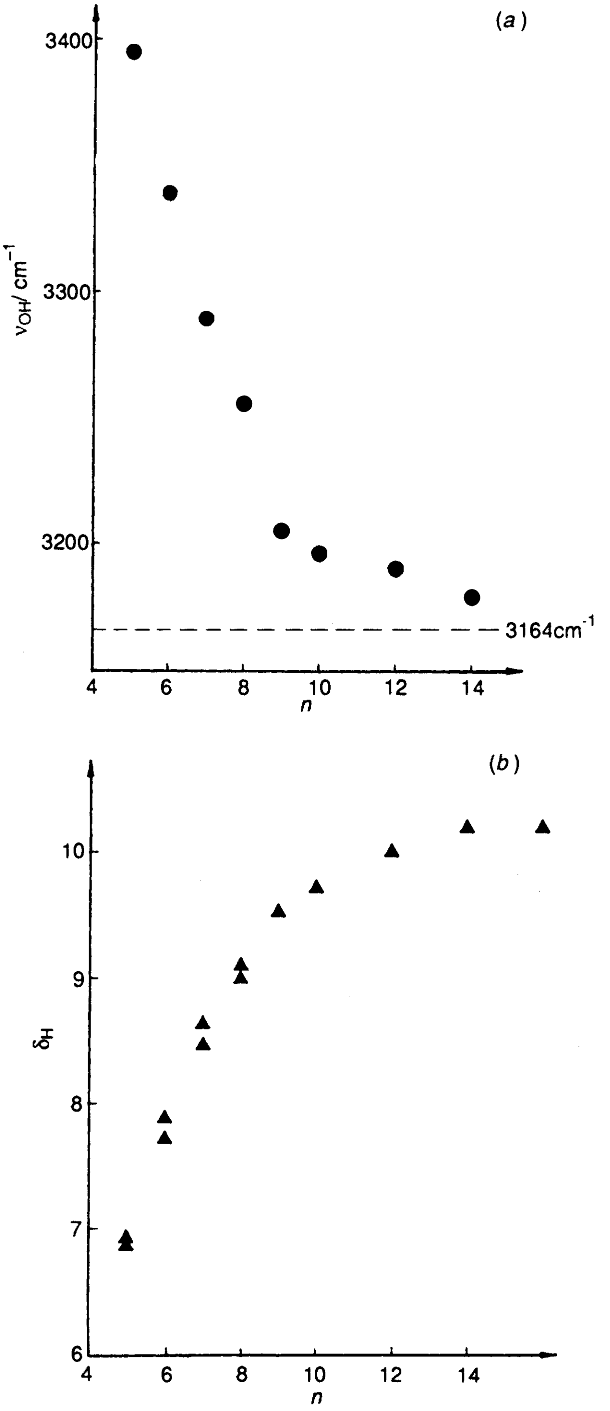

Figure 3. (*a*) OH-stretching frequency (CCl_4; 25 °C) as a function of the chain length *n*. (*b*) Chemical shift of the OH-signal ($CDCl_3$; 200 MHz) as a function of the chain length.

function of the chain length *n* also reflect the increasing strength of the intramolecular hydrogen bond system with increasing value of *n*. This change causes a low-field shift of the OH signal (*i.e.*, to higher δ-values). The whole dependence here looks more like a continuous curve gradually approaching the value for the open-chain analogues (**4**), which state is apparently reached for $n = 14$. For the shorter chains ($n = 5$–8) two different signals for the OH protons appear, indicating the two different types of hydroxy groups. While, in general, sharp signals are observed for the OH-groups the two lines are slightly broadened for $n = 7$, and two broad and largely overlapping signals are found for $n = 8$. However, this observation, as well as the fact that the difference in δ-values is somewhat larger for $n = 6$ and 7 (0.16 and 0.18 ppm) than for $n = 5$ and 8 (0.06 and 0.11 ppm) should not receive too much emphasis, since these OH-signals could be rather sensitive to trace amounts of adventitious water present.

In conclusion it can be said that the typical spectroscopic behaviour of the cyclic hydrogen-bonded array of the hydroxy groups in calix[4]arenes is not necessarily connected with the possibility of complete ring inversion. Bridged calix[4]arenes show 'exactly' the same spectroscopic properties if this bridge is sufficiently long to allow the calix[4]arene moiety to assume an undistorted cone conformation.

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