Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Mann, Gerhard , Hennig, Lothar , Weinelt, Frank , Müller, Katrin , Meusinger, Reinhard , Zahn, Gernot and Lippmann, Tino(1994) 'Structure and stereodynamics of all-cis tetramethylcalix[4]arenoctol and -dodecol ethers', Supramolecular Chemistry, 3: 2, 101 — 113
To link to this Article: DOI: 10.1080/10610279408029848
URL: http://dx.doi.org/10.1080/10610279408029848

SUPRAMOLECULAR CHEMISTRY, Vol. 3, pp. 101–113
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Structure and stereodynamics of all-cis tetramethylcalix[4]arenoctol and -dodecol ethers

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(Received February 16, 1993)

Conformations of all-cis-tetramethylcalix[4]arenoctol (1), all-cis-tetramethylcalix[4]arendodecol (2), all-cis-tetrabromo-tetramethylcalix[4]arenoctol (3), and 10 different ethers of these compounds were studied by means of temperature dependent ^{1}H-NMR spectroscopy and X-ray crystallographic analysis.

INTRODUCTION

Calix[4]arenoctols and calix[4]arendodecols are macrocyclic metacyclophanes based on resorcinol and pyrogallol, which can be easily synthesized on a large scale by the acid catalyzed condensation of aliphatic or aromatic aldehydes with resorcinol[1] or pyrogallol.[2] They take a leading part in host–guest chemistry.[3–7] The presence of the alkyl or aryl substituents from the aldehydes allows the formation of four stereoisomers designated rccc (all-cis), rcct, rctt, and rtct.[1,8,9] Usually only the rccc and rctt isomers are formed in significant amounts. Especially the all-cis isomers which have in solution at higher temperatures a statistical C_{4v} symmetry of a cone-like conformation can be used as receptor molecules and have found wide applications.[7,10–12] In crystals or at lower temperatures these compounds are fixed in a boat-like conformation with nearly C_{2v} symmetry. A characteristic feature is the flattening of two opposite rings and the erecting of the other two arene moieties. The dynamic process between the two alternative boat forms can be studied by temperature dependent NMR-spectroscopy.[13] On the other hand the rctt isomers show statistical C_{2h} symmetry with chair-like conformation and no coalescence appearance.[1,14]

The object of our investigation was the study of the dynamic processes of differently substituted all-cis isomers of tetramethylcalix[4]arenoctol and -dodecol with regard to dependence of substituents.

RESULTS AND DISCUSSION

The molecular structure (X-ray) of tetramethylcalix[4]-arenoctol **1** which has been recrystallized from ethyl methyl ketone is shown in Figs 1 and 2.[17] The boat-like molecule has nearly C_{2v} symmetry and the architecture is very similar to that in crystals containing acetonitrile and water.[11c] Four nearly identical O...O distances of 288 pm are typical. Strong intramolecular hydrogen bonds force two opposite arene rings to an inclination with an angle $\alpha = 37°$ between the rings and the main plane of the macrocycle and the other two rings to an inclination with angles $\alpha = 68°$ and 71°. An instructive description of the geometry is given by the eight torsional angles between the arene rings and the tetragonal carbons of the macrocycle.[18]

In solution a rapid change between the two alternative boat C_{2v} conformations of the phenolic compounds **1–3** is observed (Scheme 1). Down to −90 °C in acetone no splitting or broadening of OH, H, or CH_3 signals in the 400 MHz ^{1}H-NMR spectra is detectable (Table 1). Thus a barrier for conformational change lower than 50 kJ/mol can be estimated.

Otherwise, alkyl substituted ethers **4–13** show a boat-like structure with a statistical C_{2v} symmetry in solution at low temperatures. In contrast to the phenolic compounds, the boat-to-boat change leads to a statistical C_{4v} symmetry at higher temperatures (Scheme 2).

Thus, at lower temperatures different signals in the

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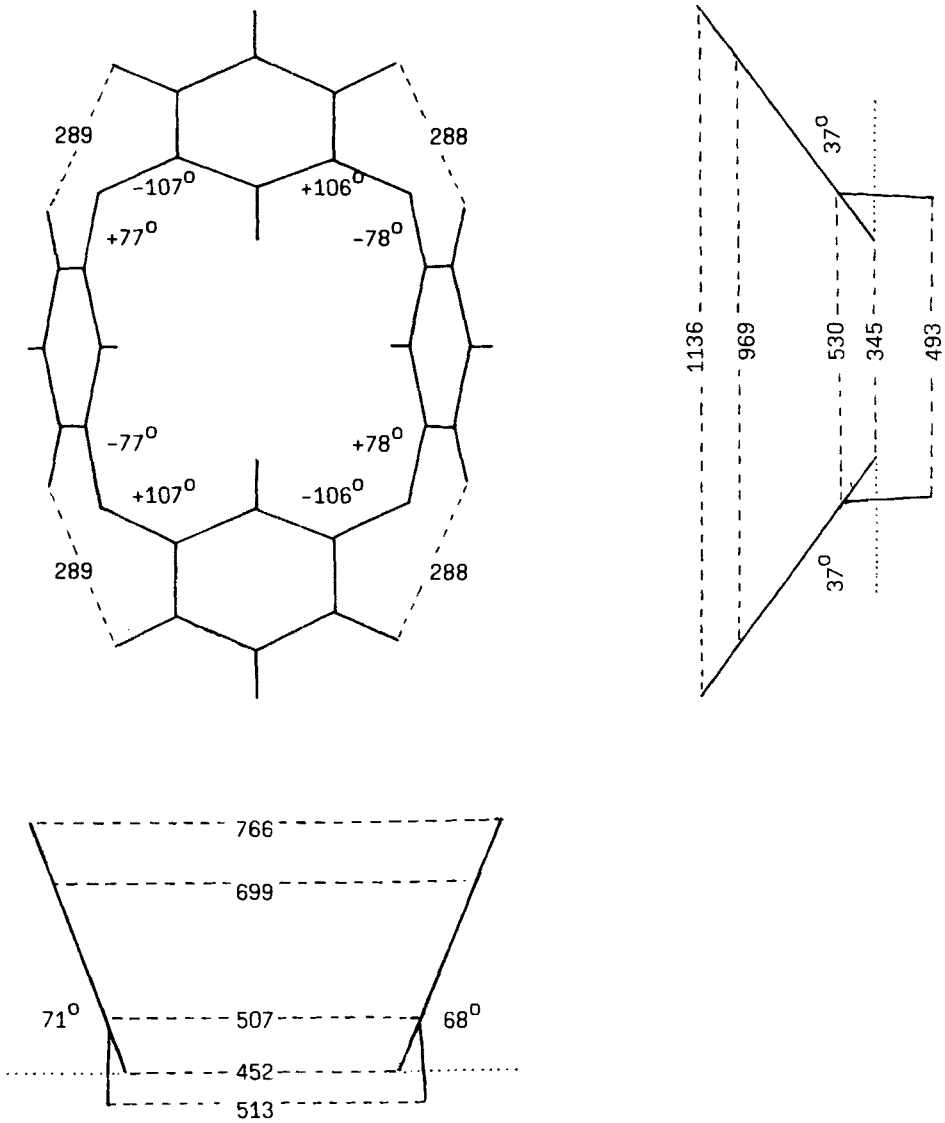
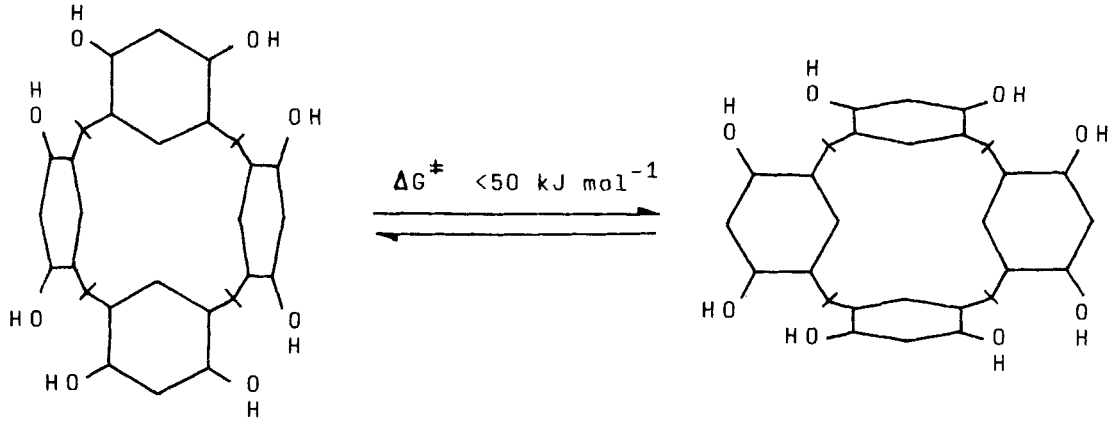


Figure 1 Top view and side views of tetramethylcalix[4]arenoctol 1 in the solid state (recrystallized from ethyl methyl ketone).



Scheme 1 Dynamic behaviour of phenolic compounds 1–3 in solution.

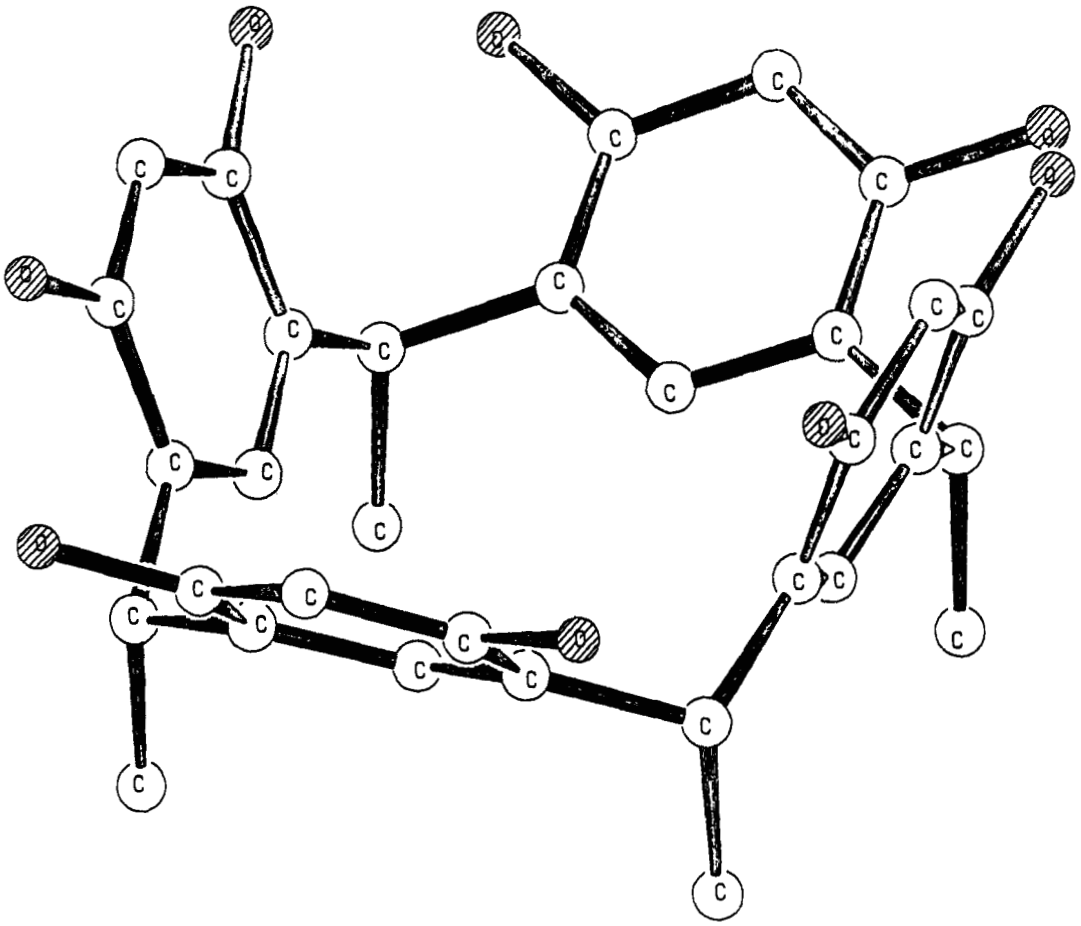


Figure 2 X-Ray crystallographic structure of compound **1**.

Table 1 ^{1}H-NMR spectra of compounds **1**–**3** (0.002 molar solutions) at 400 MHz

Compd.	*Temp. (°C)*	*Solvent*	*-OH*	*-CH_3*	*-H^a (methine protons)*	*-H^b (aromatic protons) (meta to -OH)*	*-H^c (ortho to -OH)*
1	+50	acetone	8.50 br (8)	1.90 d (12) J = 7.4 Hz	4.68 q (4) J = 7.4 Hz	7.74 s (4)	6.38 s (4)
	−90	acetone	9.75 s (8)	1.80 d (12) J = 7.2 Hz	4.32 q (4) J = 7.2 Hz	7.83 s (4)	6.32 s (4)
2	+26	acetone	8.16 br (12)	1.88 d (12) J = 7.2 Hz	4.68 q (4) J = 7.2 Hz	7.35 s (4)	—
	−80	acetone	9.00 s (8) 8.40 s (4)	1.82 d (12) J = 7.2 Hz	4.58 q (4) J = 7.2 Hz	7.43 s (4)	
3	+25	DMSO	8.48 s (8)	1.49 d (12) J = 7.0 Hz	4.71 q (4) J = 7.0 Hz	6.91 s (4)	—

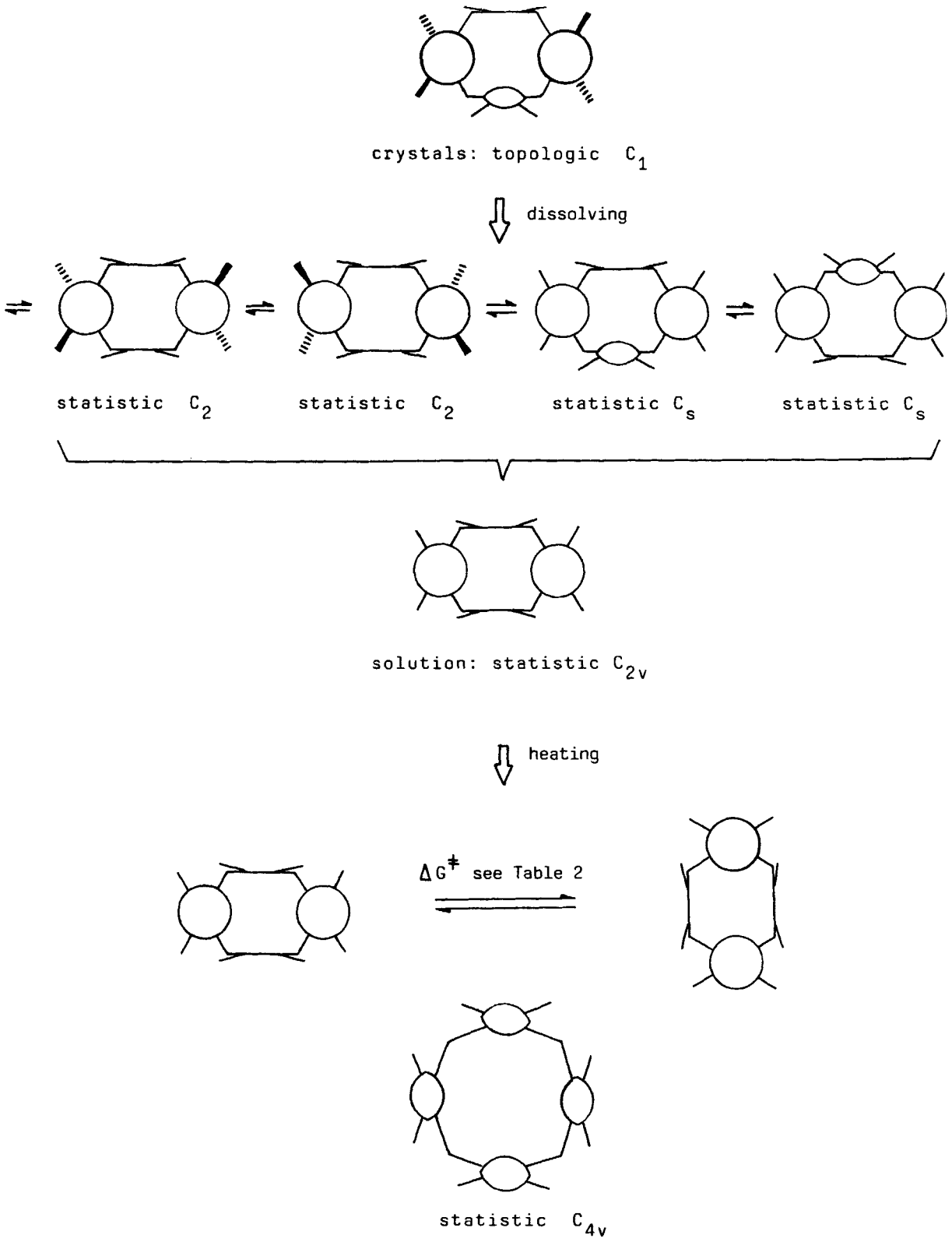
^{1}H-NMR spectra of protons which belong to the vertical (H^v) and to the horizontal (H^h) parts of the molecules can be observed. The largest differences in chemical shifts are seen at the -O-CH- protons (H^d) in ether substituents and the aromatic protons (H^b and H^c).

For all substituted ethers **4**–**13** the coalescence temperature (T_c) was determined at 400 MHz and the Gibbs energy was estimated by Eyring equation in the form of:

$$\Delta G \neq = RT_c(22{,}96 + \ln T_c/\Delta\nu)$$

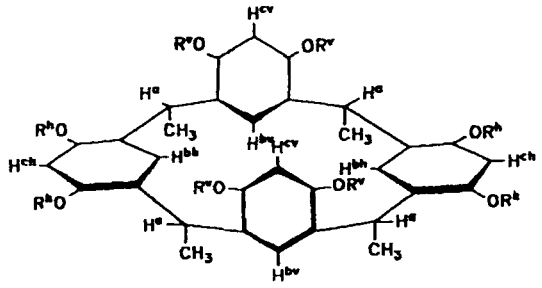
The results in Table 2 show that the energy barriers depend significantly on the size of the letter alkyl groups and on the substituents at the arene rings.

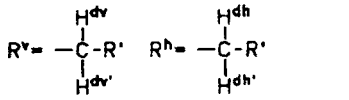
Whereas methyl ether **4** shows coalescence owing



Scheme 2 Dynamic behaviour of ethers **4–13** in solution.

Table 2 Coalescence temperatures at 400 MHz and barriers between the alternative boat conformers of ethers **4–13**





R^{v}= $-\overset{H^{dv}}{\underset{H^{dv'}}{\overset{|}{\underset{|}{C}}}}-R'$ R^{h}= $-\overset{H^{dh}}{\underset{H^{dh'}}{\overset{|}{\underset{|}{C}}}}-R'$

R'= CH_3, CH_2CH_3, $CH_2CH_2CH_3$

Compound	*v (ppm)*	T_c *(K)*	*G (kJ/mol)*	*Mean value*
4	1.39 (H^{bv}; H^{bh})	265	62.4	
	0.51 (OCH_3^v; OCH_3^h)	255	61.8	62
	0.34 (H^{cv}; H^{ch})	248	60.8	
5	1.35 (H^{bv}; H^{bh})	297	70.1	
	0.79 (OCH_3^v; OCH_3^h)	283	69.2	70
6	1.44 (H^{bv}; H^{bh})	303	71.4	
	0.73 (OCH_3^v; OCH_3^h)	300	72.4	72
7	1.34 (H^{bv}; H^{bh})	318	75.1	
	0.53 ($-CH_3^v$; $-CH_3^h$)	308	75.1	75
	0.44 (H^{cv}; H^{ch})	307	75.3	
8	1.40 (H^{bv}; H^{bh})	308	72.7	
	0.53 ($-CH_3^v$; $-CH_3^h$)	303	73.9	73
	0.44 ($-CH_3^v$; $-CH_3^h$)	293	73.2	
9	1.25 (H^{bv}; H^{bh})	325	77.2	77
10	1.33 (H^{bv}; H^{bh})	331	78.5	
	0.43 ($-CH_2^v-$; $-CH_2^h-$)	322	79.2	79
	0.37 (H^{cv}; H^{ch})	319	78.9	
11	1.22 (H^{bv}; H^{bh})	327	77.4	
	0.60 (OCH^v-; OCH^h-)	320	77.8	78
	0.27 (H^{cv}; H^{ch})	310	77.4	
12	1.32 (H^{bv}; H^{bh})	>333		
	0.85 (OCH_2^v-; OCH_2^h-)	333	80.2	81
	0.37 (OCH_2^v-; OCH_2^h-)	327	80.9	
13	1.26 (H^{bv}; H^{bh})	348	82.8	
	1.07 (OCH_2^v-; OCH_2^h-)	348	83.3	83
	0.40 ($=CH_2^v$; $=CH_2^h$)	333	82.6	

to the change from C_{2v} to C_{4v} symmetry just at -25 °C, butyl ether **12** reaches an analogous flexibility only at $+60$ °C. That means a difference in the barriers of conformational change of ca. 20 kJ mol^{-1}. The strongest bias in favor of the boat-like conformation is obtained with allyl substituents at the oxygen atoms, with bromo substituents in the arene rings or with ethers of pyrogallol-derived metacyclophanes.

Correct assignment of the ^1H- and ^{13}C-NMR signals was achieved by two-dimensional methods (H,H-COSY, HETCOR). It was necessary to determine the homogeneity of protons which convert one into another at higher temperatures. In the state of rapid exchange the broad line shapes do not allow an exact determination in some cases. Hence, the two-dimensional NOESY-experiment in a phase sensitive mode was made. Figure 3 shows a part of the NOESY spectra from *n*-propylether **10** at -30 °C in $CDCl_3$. Cross peaks in this experiment are produced either by exchange processes or by nuclear Overhauser effects (NOE). In the first case the sign of the cross peaks is the same as in the diagonal peaks (Fig 3a:

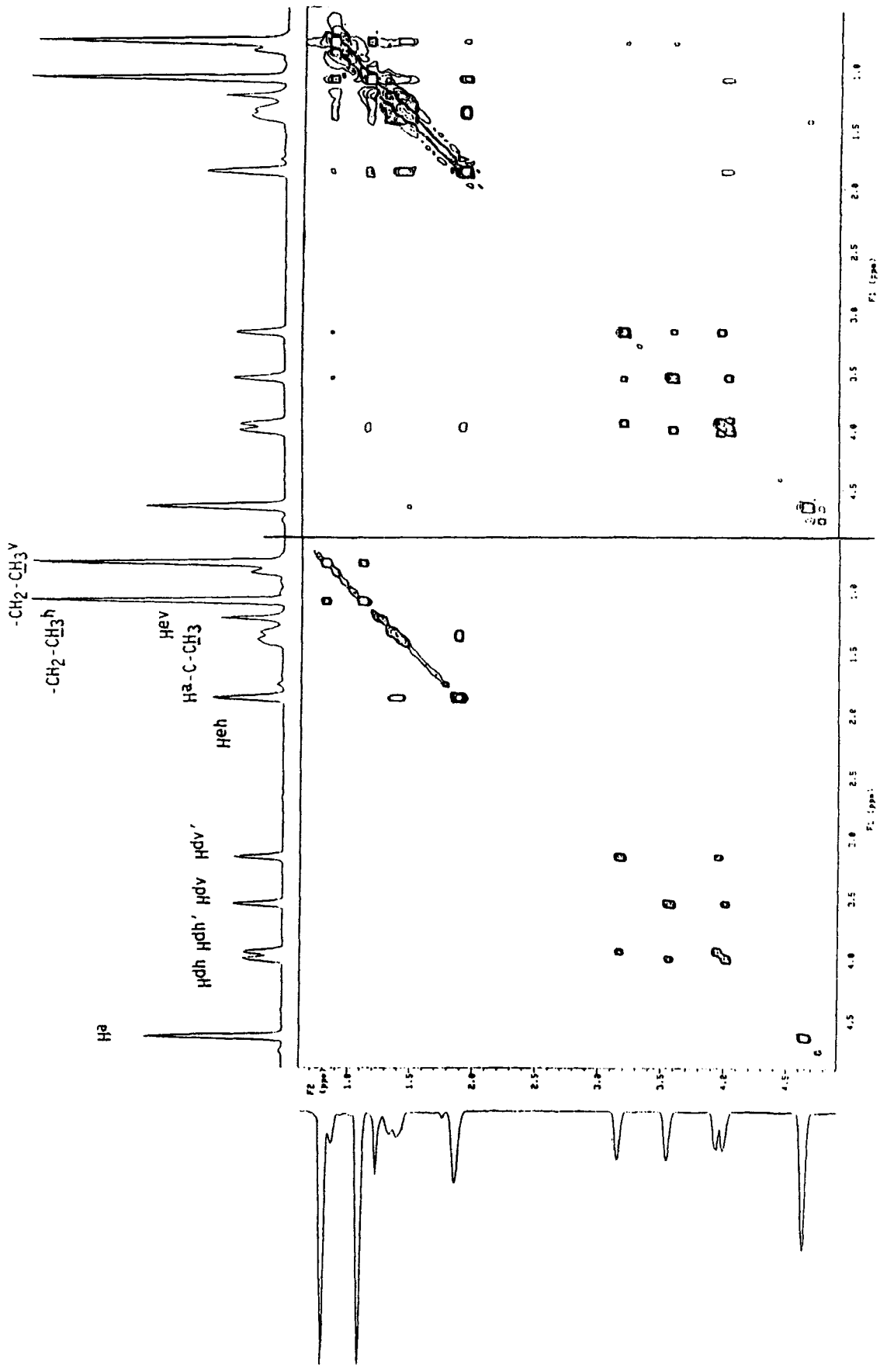


Figure 3 Aliphatic part of the phase sensitive NOESY spectra of compound **10** at −30 °C (400 MHz, $CDCl_3$, mixing time 0.8 s, acquisition time 6.8 h). (a) positive signals only; (b) positive and negative signals.

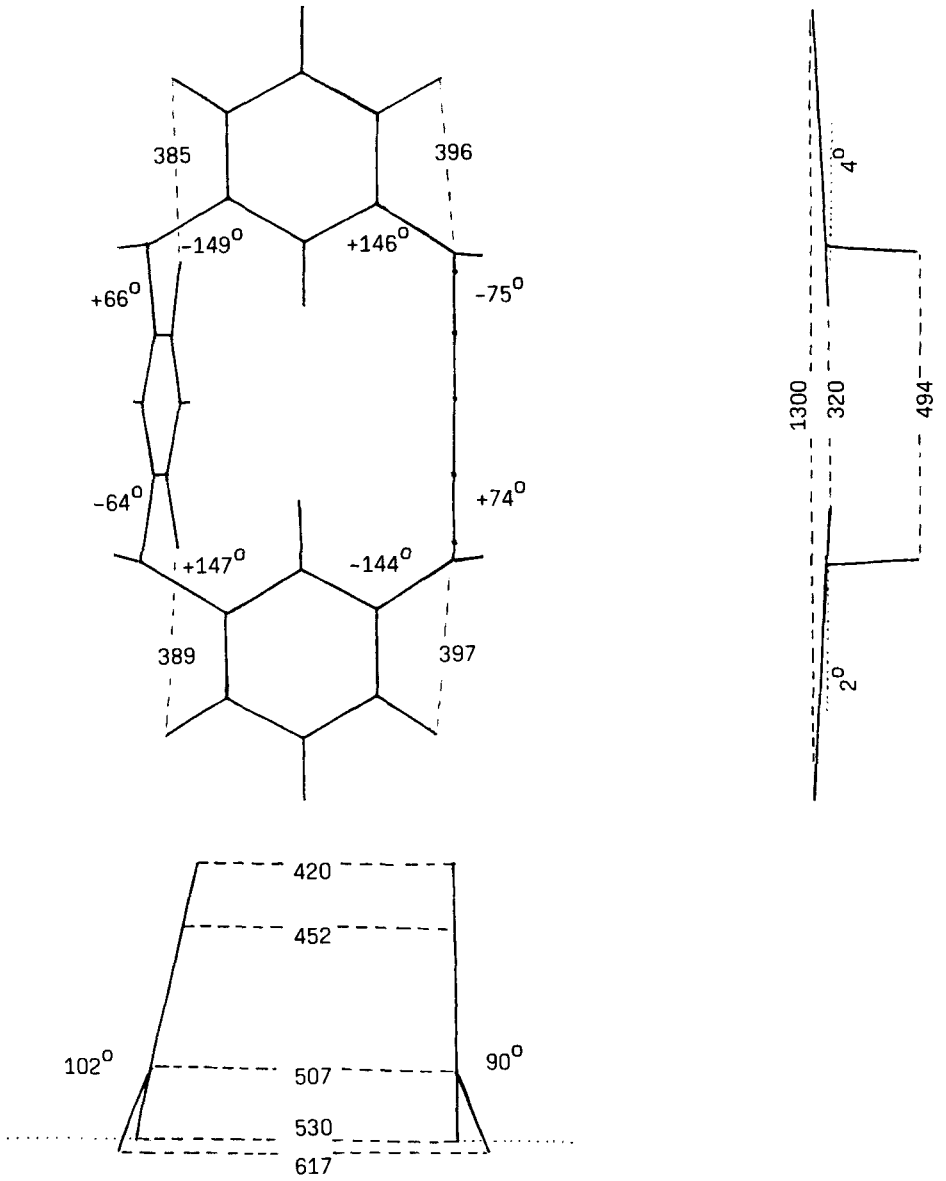


Figure 4 Top view and side views of tetramethylcalix[4]arenoctaethyl ether 7 in the solid state (recrystallized from dimethylformamide).

positive signals only). NOE signals have in most cases negative signs (direct NOE) and therefore they are distinguishable from exchange processes.

Diastereotopic O-CH_2 protons (H^d and $H^{d'}$) exist in the vertical (H^{dv} and $H^{d'v}$) and horizontal (H^{dh} and $H^{d'h}$) arene rings, (4 signals between 3 and 4 pm in Fig 3). Figure 3a clearly shows cross peaks only between two H^d protons in each case in this region. They are the result of the conversion $H^{dv} \Leftrightarrow H^{dh}$ and $H^{d'v} \Leftrightarrow H^{d'h}$, respectively. Analogous effects can be seen for the other methylene protons (H^e) and for the methyl protons (CH_2-CH_3). NOE effects are shown in Fig 3b. Thus, the assignment of protons of the vertical and horizontal molecular parts was achieved.

The crystal structure of tetramethylcalix[4]-arenoctaethyl ether 7 is shown in Fig 4 and 5.[19] This structure is characterized by an approximate C_s symmetry. Owing to the absence of hydrogen bonds and the introduction of bulky ethyl groups the O...O distance increases from 288 pm to 387 and 397 pm. Two equatorial arene rings are now nearly in the plane of the macrocycle. The other two arene rings are directed axially upwards, nearly perpendicular to the plane of the molecule but with different inclinations. In contrast to the phenolic compounds[11c,17] no solvent molecules are found in the cavities of the crystalline ethers. The torsion angles sideward of the perpendicular arene rings are 65° and 75°, respectively, and those sideward of the horizontal arene rings are between 144° and 149°.

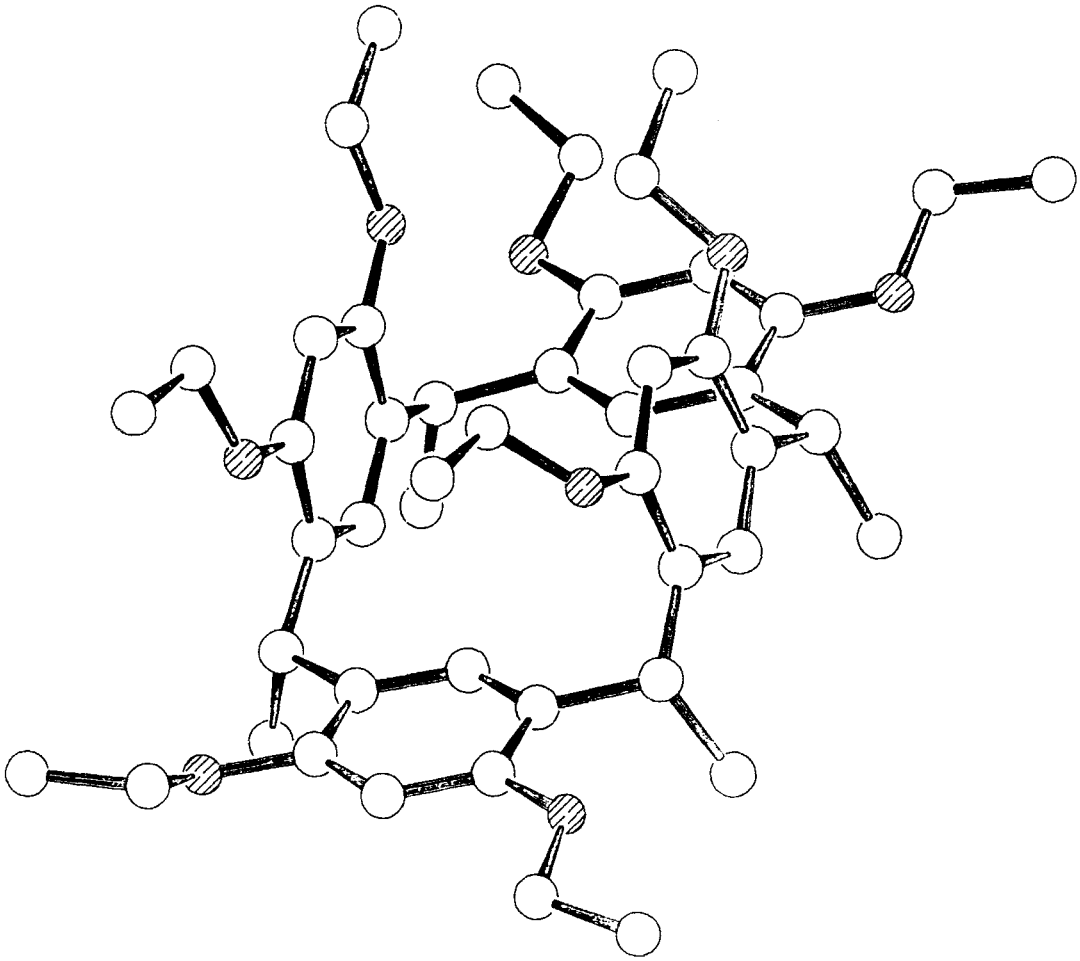
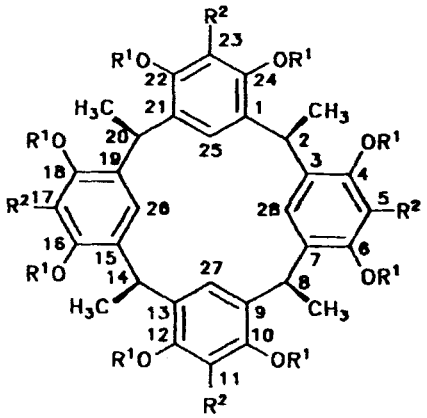


Figure 5 X-Ray crystallographic structure of compound 7.



Compd.	R^1	R^2
1	H	H
2	H	OH
3	H	Br
4	CH_3	H
5	CH_3	OCH_3
6	CH_3	Br
7	CH_2CH_3	H
8	CH_2CH_3	OCH_2CH_3
9	CH_2CH_3	Br
10	$CH_2CH_2CH_3$	H
11	$CH(CH_3)_2$	H
12	$(CH_2)_3CH_3$	H
13	$CH_2CH{=}CH_2$	Br

Chart 1

Table 3 Analytical data from compounds 4–13

Compd.	Procedure (reagens)	mp (°C)	IR (KBr)		Calcd.	Found
4	A (methyl iodide)	334–36	2950, 2830 1620, 1580, 1500 1300, 1200, 1040	$C_{40}H_{48}O_8$	C: 73.15 H: 7.37 O: 19.49	C: 72.98 H: 7.18 O: 19.41
5	A (methyl iodide)	290–95	2950, 2830 1480, 1450, 1410 1310, 1100, 1050, 1000	$C_{44}H_{56}O_{12}$	C: 68.02 H: 7.27 O: 24.71	C: 68.40 H: 7.64 O: 23.07
6	A (methyl iodide)	>360	2950 1480, 1420 1300, 1050, 1000	$C_{40}H_{44}O_8Br_4$	C: 49.39 H: 4.56 O: 13.16 Br: 32.89	C: 49.84 H: 4.87 O: 13.20 Br: 32.71
7	A (ethyl iodide)	254–56	2870 1620, 1580, 1500 1400, 1300, 1180, 1120, 1050	$C_{48}H_{64}O_8$	C: 74.97 H: 8.39 O: 16.64	C: 74.62 H: 8.08 O: 16.68
8	A (ethyl iodide)	243–46	2900 1430 1350, 1300, 1100, 1040, 900	$C_{56}H_{80}O_{12}$	C: 71.16 H: 8.53 O: 20.31	C: 70.82 H: 8.24 O: 19.93
9	A (ethyl iodide)	319–22	2950 1450 1380, 1300, 1100, 1050, 900	$C_{48}H_{60}O_8Br_4$	C: 53.16 H: 5.58 O: 11.80 Br: 29.46	C: 52.78 H: 5.56 O: 12.21 Br: 28.98
10	B (*n*-propyl bromide)	179–83	2960 1620, 1580, 1500 1300, 1200, 1120, 1070, 980	$C_{56}H_{80}O_8$	C: 76.32 H: 9.15 O: 14.43	C: 76.41 H: 9.15 O: 14.13
11	B (*i*-propyl bromide)	233–36	2980 1620, 1580, 1500 1300, 1200, 1120, 950	$C_{56}H_{80}O_8$	C: 76.32 H: 9.15 O: 14.53	C: 75.88 H: 9.38 O: 14.15
12	B (*n*-butyl iodide)	185–89	2960 1620, 1580, 1500, 1480, 1400 1300, 1180, 1120, 980, 920	$C_{64}H_{96}O_8$	C: 77.38 H: 9.74 O: 12.88	C: 77.51 H: 9.63 O: 12.79
13	A (allyl bromide)	192–95	2920 1650, 1450, 1400 1300, 1100, 985, 920	$C_{56}H_{60}O_8Br_4$	C: 56.95 H: 5.12 O: 10.84 Br: 27.09	C: 56.80 H: 5.62 O: 10.60 Br: 26.59

EXPERIMENTAL

Materials

The starting all-cis compounds 2,8,14,20-tetramethylcalix[4]aren-4,6,10,12,16,18,22,24-octol 1[1] and 2,8,14,20-tetramethylcalix[4]aren-4,5,6,10,11,12,16,17,18,22,23,24-dodecol 2[2] were synthesized from the acetaldehyde and resorcinol or pyrogallol, respectively. 5,11,17,23-Tetrabromo - 2,8,14,20 - tetramethylcalix[4]aren-4,6,10,12,16,18,22,24-octol 3 was obtained by bromination of 1 with *N*-bromsuccinimide[15] or bromine.[16] Alkylation of the hydroxy compounds with methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, and allyl halogenides resulted in ethers 4–13 which were recrystallized from dimethylformamide (Chart 1).

NMR spectra were recorded on a VARIAN UNITY 400 spectrometer at 400 MHz ^{1}H- and at 100.6 MHz ^{13}C resonance frequencies. The dynamic NMR studies with five degree steps in the range of −50 °C to +90 °C and one degree steps near the coalescence temperatures were carried out with solutions of 5% samples in $CDCl_3$ or nitrobenzene (see Table 4) with TMS as an internal standard. The NOESY experiments were performed in 5 mm tubes at approximately 0.05 M solutions in $CDCl_3$ at −30 °C with a mixing time of 0.8 s. Elemental analysis were performed with an elemental analysator CHNO Rapid from Heraeus. IR spectra were measured with a Carl Zeiss JENA specord M 80.

Crystal structure data

Compound 1 crystallizes from methyl ethyl ketone as colourless crystals. $C_{32}H_{32}O_8$ 4 $CH_3COCH_2CH_3$;

Table 4 ^{1}H-NMR spectra of compounds 4–13 in $CDCl_3$ (0.002 molar solutions) at 400 MHz (-O-CH^d-CH^e-CH^f-CH^g)

Compd.	*Temp. (°C)*	*-CH$_3$*	*-H^a*	*-H^b*	*-H^c*	*-H^d*		*-H^e*		*-H^f*	*-H^g*
4	+60	1.43 d (12) J = 7.2 Hz	4.58 q (4) J = 7.2 Hz	6.60 s (4)	6.33 s (4)	3.62 s (24)		—		—	—
	−50	1.48 d (12) J = 7.2 Hz	4.53 q (4) J = 7.2 Hz	5.91 s (2)	6.21 s (2)	3.47 s (12)					
				7.30 s (2)	6.55 s (2)	3.98 s (12)					
5	+50	1.49 d (12) J = 7.2 Hz	4.68 q (4) J = 7.2 Hz	6.50 br (4)	—	3.82 s (24)	3.69 s (12)	—		—	—
	−50	1.50 d (12) J = 7.1 Hz	4.63 q (4) J = 7.1 Hz	5.80 s (2)		3.28 s (12)	3.61 s (6)				
				7.15 s (2)		4.07 s (12)	4.04 s (6)				
6	+40	1.46 d (12) J = 7.4 Hz	4.59 q (4) J = 7.4 Hz	6.40 coll.	—	3.66 br (24)		—		—	—
	+10	1.55 d (12) J = 7.3 Hz	4.54 q (4) J = 7.3 Hz	5.80 s (2)		3.29 br (12)					
				7.24 s (2)		4.02 s (12)					
7	+60	1.43 d (12) J = 7.2 Hz	4.64 q (4) J = 7.2 Hz	6.00 coll.	6.22 s (4)	3.70 br (8)	3.90 br (8)	1.21 t (24)		—	—
	−50	1.43 d (12) J = 7.2 Hz	4.57 q (4) J = 7.2 Hz	5.89 s (2)	6.02 s (2)	3.10 dq (4) J = 7.2 Hz	3.67 dq (4) J = 7.2 Hz	0.94 t (12) J = 7.2 Hz			
				7.23 s (2)	6.46 s (2)	4.10 dq (4) J = 7.2 Hz	4.08 dq (4) J = 7.2 Hz	1.47 t (12) J = 7.2 Hz			
8	+55	1.40 d (12) J = 7.2 Hz	4.65 q (4) J = 7.2 Hz	6.40 s (4)	—	3.60 br (12)	4.00 br (12)	1.35 m (24)	1.11 m (12)	—	—
	−60	1.48 d (12) J = 7.2 Hz	4.54 q (4) J = 7.2 Hz	5.60 s (2)		3.05 m (4)	4.02 m (4)	1.48 t (12) J = 6.8 Hz	1.48 t (6) J = 6.8 Hz		
				7.00 s (2)		3.73 m (4)	4.20 m (4)	0.95 t (12) J = 6.8 Hz	1.23 t (6) J = 6.8 Hz		
						3.81 m (4)	4.22 m (4)				

9	+50	1.56 d (12) J = 7.3 Hz	4.65 q (4) J = 7.3 Hz	6.60 coll.	—	4.05 br (8)	3.20 br (8)	1.36 br (24)		—		—
	+25	1.60 d (12) J = 7.2 Hz	4.60 q (4) J = 7.2 Hz	5.95 s (2)		3.00 br (4)	3.20 br (4)	1.30 br (24)				
				7.20 s (2)		3.80 br (4)	4.20 br (4)					
10	+60	1.42 d (12) J = 7.2 Hz	4.66 q (4) J = 7.2 Hz	7.10 coll.	6.25 br	3.60 br	3.80 br	1.60 br		0.95 br		—
	−60	1.45 d (12) J = 7.2 Hz	4.66 q (4) J = 7.2 Hz	5.93 s (2)	6.06 s (2)	3.17 dt (4) J = 7.4 Hz	3.57 dt (4) J = 7.4 Hz	1.43 m (8)		0.81 t (12) J = 7.4 Hz	1.11 t (12) J = 7.4 Hz	
				7.26 s (2)	6.43 s (2)	4.01 dt (4) J = 7.4 Hz	3.97 dt (4) J = 7.4 Hz	1.88 br (8)				
11	+60	1.42 d (12) J = 7.2 Hz	4.60 q (4) J = 7.2 Hz	6.80 coll.	6.25 s (4)	4.25 br (8)		1.25 br (24)	1.05 br (24)	—		—
	0	1.42 d (12) J = 7.2 Hz	4.59 q (4) J = 7.2 Hz	6.04 s (2)	6.15 s (2)	3.88 m (4)		0.75 d (12) J = 6.8 Hz	1.06 d (12) J = 6.8 Hz			
				7.26 s (2)	6.42 s (2)	4.48 m (4)		1.43 d (12) J = 6.8 Hz	1.42 d (12) J = 6.8 Hz			
12	+60	1.42 d (12) J = 7.2 Hz	4.64 q (4) J = 7.2 Hz	7.10 coll.	6.21 s (4)	3.40 br (8)	3.82 br (8)	1.66 br (16)		1.40 br (16)		0.95 br (24)
	0	1.41 d (12) J = 7.2 Hz	4.64 q (4) J = 7.2 Hz	5.91 s (2)	6.03 s (2)	3.20 dt (4) J = 7.4 Hz	3.97 dt (4) J = 7.4 Hz	1.54 m (8)		1.22 m (8)		0.84 t (12) J = 7.4 Hz
				7.23 s (2)	6.42 s (2)	3.60 dt (4) J = 7.4 Hz	4.05 dt (4) J = 7.4 Hz	1.83 m (8)		1.32 m (8)		0.99 t (12) J = 7.4 Hz
13	+95[1)]	1.38 d (12) J = 7.2 Hz	4.55 q (4) J = 7.2 Hz	6.60 br (4)	—	4.15 br (8)	4.38 br (8)	5.90 br (8)		5.00 d (8) J = 17.2 Hz	5.22 d (8) J = 10.7 Hz	—
	−60	1.59 d (12)	4.66 q (4)	5.70 s (2)		3.50 br (4)	4.53 dd (4)	5.80–5.95 m (4)		5.05 d (4)	5.15 d (4)	
				7.30 s (2)		4.23 dd (4)	4.78 dd (4)	6.10–6.25 m (4)		5.35 d (4)	5.61 d (4)	

[1)] Nitrobenzene.

Table 5 ^{13}C-NMR spectra from compounds 1–13 in $CDCl_3$ (0,002 molar solutions, assignment with APT-experiments) at 100 MH (-O-CH^d-CH^e-CH^f-CH^g)

Compd.	Temp. (°C)	-CH$_3$	-CH^a (2,8, 14,20)	Aromatic protons (1,3,7,9,13, 15,19,21)	(25,26 27,28)	(4,6,10,12, 16,18,22,24)	(5,11, 17,23)	-CH^d	-CH^e	-CH^f	-CH^g
1	+30[1]	20.66	29.07	126.52	125.49	152.72	104.02	—	—	—	—
2	+25[1]	20.28	29.63	114.44	127.12	140.14	133.97	—	—	—	—
3	+25[2]	21.05	31.03	125.66	123.63	148.84	101.95	—	—	—	—
4	+60	20.13	30.75	128.07	125.73	155.94	95.55	56.33	—	—	—
	−55	19.68	30.48	125.85	124.14	154.38	93.55	55.61			
				127.50	124.36	155.77	95.98	56.04			
5	+25	21.37	31.55	137.46	119.64	149.28	145.98	60.34; 60.21	—	—	—
	−50	21.48	31.41	132.08	119.09	148.19	145.56	59.78; 60.32			
				137.24	119.97	149.04	146.21	61.11; 60.94			
6	+25	21.06	29.96	collapsed	125.04			60.99	—	—	—
7	+45	19.99	30.46	125.29	127.00	154.76	98.68	64.27	14.88	—	—
8	−50	21.35	32.26	132.09	119.49	144.74	148.43	68.60; 68.37	16.00; 16.26	—	—
				136.89	120.27	145.44	149.68	69.33; 68.92	16.59; 16.41		
9	+50	21.04	33.75	125.20	collapsed	153.50	95.00	69.22	15.61	—	—
10	+40	20.09	30.68	125.56	125.47	154.57	96.00	70.04	23.05	10.68	—
					129.38	154.96	98.00				
	−20	19.86	30.31	125.30	124.90	154.06	94.95	69.22	22.70	10.46	
				125.48	125.48	155.15	98.16	69.66	22.98	11.07	
11	+50	20.86	30.59	125 coll.	125 coll.	153.42	95.80	70.23	20.39	—	—
						153.46					
12	+30	20.01	31.93	126 br	125 br	154	96	67.94	30.65	19.23	14.04
					129 br	156	99	68.29			
13	+25	20.88	33.95	138.82	125.28	153.92	117.16	74.19	134.09	117.63	—

[1] Acetone.
[2] DMSO.

monoclinic; a = 10.039 (2) Å; b = 13.780 (3) Å; c = 15.257 (3) Å; β = 101.30 (9)°, Space group $P2_1/m$; $Z = 2$; Diffractometer type: Stoe STADI 4; $R = 0.049$.[17]

Compound 5 crystallizes from dimethylformamide as colourless crystals. $C_{48}H_{64}O_8$; monoclinic; a = 19.106 (3) Å; b = 15.287 (3) Å; c = 16.531 (3) Å; β = 111.56 (1)°, Space group $P2_1/c$; $Z = 4$; Diffractometer type: Huber; $R = 0.057$.[19]

Alkylation procedures

Procedure A. 0.002 mol of pure rccc isomer from compounds 1, 2 or 3 were dissolved in 50 mL acetone and added to 0.08 mol anhydrous potassium carbonate in 50 mL acetone during two hours. The solution was stirred and heated under reflux and 0.08 mol of alkyl halide were added dropwise to the suspension. The mixture was stirred and refluxed for 30–45 hours. At the end of the reaction time the mixture was cooled, filtered and the residue was washed with 100 mL water and extracted with 50 mL chloroform. The combined organic layers were washed with a solution of 10% $NaHCO_3$, water and dried over $MgSO_4$. The solvent was evaporated and the resulting solid recrystallized from dimethylformamide. Yields of products were between 50 and 70% of theory.

Procedure B. To a suspension of 0.08 mol NaH (60% dispersion in oil) in 50 mL anhydrous tetrahydrofuran was added 0.002 mol of pure cccc isomer of compound 1 dissolved in 50 mL tetrahydrofuran. The mixture was stirred under a atmosphere of nitrogen, 0.08 mol of the alkyl halide was added during two hours, and the reaction mixture was refluxed for 35 hours. The product mixture was cooled and added to 150 mL of ice water followed by 50 mL of chloroform. The organic layer was separated, washed with $NaHCO_3$, water and dried over $MgSO_4$. The solvent was evaporated and the resulting solid recrystallized from dimethylformamide. Yields were between 25 and 55% of theory.

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