

Unusual conformations of 1,3-dialkoxythiacalix[4]arenes in the solid state

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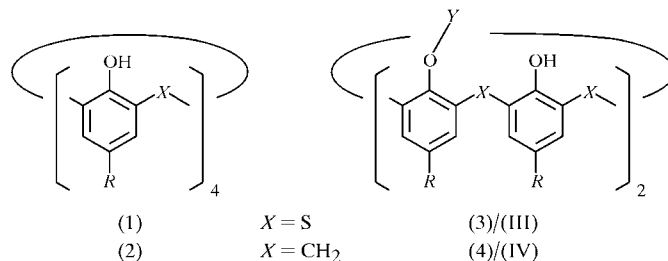
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The structures of three *syn*-1,3-dialkoxythiacalix[4]arenes with unusual conformations in the solid state are reported. The pinched cone conformation of *syn*-2²,4²-dihydroxy-1²,3²-bis(prop-2-enyloxy)thiacalix[4]arene, C₃₀H₂₄O₄S₄, (3a), is stabilized by two intramolecular hydrogen bonds, remarkably formed from both OH groups to the same ether O atom. In *syn*-2²,4²-dihydroxy-1⁵,2⁵,3⁵,4⁵-tetranitro-1²,3²-bis(prop-2-enyloxy)thiacalix[4]arene acetone disolvate, C₃₀H₂₀N₄O₁₂S₄·2C₃H₆O, (3b1), the molecule is found in the 1,3-alternate conformation. The crystallographic C₂ symmetry is due to a twofold rotation axis running through the centre of the calixarene ring. The hydroxy groups cannot form intramolecular hydrogen bonds as in (3a) and both are bonded to an acetone solvent molecule. The molecule of the pseudopolymorph of (3b1) in which the same compound crystallized without any solvent, *viz.* (3b2), is located on a crystallographic mirror plane. Only one of the two hydroxy groups forms a hydrogen bond, and this is with a nitro group of a neighbouring molecule as acceptor. Molecular mechanics calculations for *syn*-1,3-diethers suggest a preference of the 1,3-alternate over the usual cone conformation for thiacalix[4]arene *versus* calix[4]arene and for *para*-nitro *versus* *para*-H derivatives.

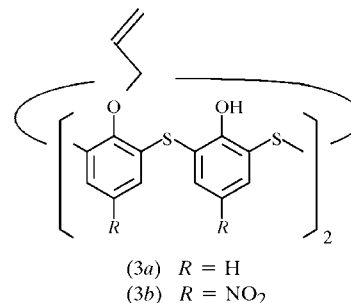
Comment

In principle, thiacalix[4]arenes, (1) (see scheme), can undergo analogous chemical modifications to calix[4]arenes, (2), on their wide rim (*e.g.* transbutylation and electrophilic substitutions) and on their narrow rim (*e.g.* O-alkylation) (Böhmer,

1995). Subtle differences are found, however, between the two cases. Ether residues introduced to (1) must be larger than propyl (Lang *et al.*, 1999; Lhotak, 2004) [which is sufficient for (2) (Böhmer, 1995)] to prevent a rotation through the annulus, and the introduction of four ether groups leads usually to derivatives in which the 1,3-alternate conformation is fixed (Lhotak *et al.*, 1998; Lhotak, 2004). Derivatives in the cone conformation are only formed with alkylating agents of the type X-CH₂-C(O)-R (Iki *et al.*, 1998; Akdas *et al.*, 1999) or X-CH₂-Ar (Yamato *et al.*, 2002) in the presence of sodium cations. For both calix[4]arenes, 1,3-diethers with a *syn* orientation of the ether residues are easily obtained with a variety of alkylating agents. The conformational analysis of thiacalixarenes and their derivatives in solution is complicated by the fact that the spectroscopic information given by methylene H atoms is not available in the ¹H NMR spectra. The ¹³C chemical shift of the methylene bridges, often useful for conformational assignment (Jaime *et al.*, 1991), is also lacking. This makes conformational information from the crystalline state more important.



All five X-ray structures reported for the *syn*-1,3-diether derivatives (3) (Dudic *et al.*, 2003, 2004; Clemente, 2003; Bhalla *et al.*, 2004) show the compounds in the cone conformation. 103 structures of *syn*-1,3-diethers (4) (metal complexes are not included) are found in the Cambridge Structural Database (CSD; Version 5.27 plus one update; Allen, 2002), among which only one example has a 1,3-alternate conformation (Simaan *et al.*, 2003), while the rest assume the (pinched) cone conformation. (From 15 structures of *syn*-1,3-diethers, two partial cone conformations and one 1,3-alternate conformation are found.) The reason for this disparity is usually searched for in the stabilization of the cone conformation by intramolecular hydrogen bonds between the phenol hydroxy groups and the adjacent ether O atoms. From further O-alkylation products, it can be deduced, however,



that the molecules can assume the partial cone or the 1,3-alternate conformation by passing of the OH groups through

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the annulus. We recently prepared (Böhmer & Kasyan, 2006) the 1,3-diallylethers (3a) and (3b), and we report their crystal structures here. For (3b), which was crystallized from different solvents, two pseudo-polymorphs, (3b1) and (3b2), were obtained.

Perspective views of (3a), (3b1) and (3b2) are shown in Figs. 1–3. Bond lengths and angles can be regarded as normal (CSD; *MOGUL*, Version 1.1; Allen, 2002).

Single crystals of (3a) were obtained from acetonitrile. As expected, the molecule is found in a pinched cone conformation, with the ether units bent towards the cavity and the phenol units bent outwards. In Table 4, the angles between the mean planes through the aromatic rings and the reference/mean plane defined by the four S atoms are listed and used to characterize the conformation. One of these angles is even smaller than 90° , which means that this plane is oriented 'into' the cavity, while the opposite plane is oriented outwards. Thus, the planes of the ether-substituted benzene rings are almost coplanar [$6.53(8)^\circ$], a situation also found for other 1,3-diethers of (1). The packing of the molecules is obviously determined by π - π stacking of aromatic units. Chains of molecules with alternating orientation extend along the *c* axis (Fig. 4), with aryl-aryl contacts between the phenolic rings [the distance between the centroids of the aromatic rings C21–C26 and C41ⁱⁱⁱ–C46ⁱⁱⁱ is 3.980 Å; symmetry code: (iii) $x, \frac{3}{2} - y, \frac{1}{2} + z$], while along the *a* axis contacts between the phenoxy units exist [the distance between the centroids of the aromatic rings C11–C16 and C31^{iv}–C36^{iv} is 4.204 Å; symmetry code: (iv) $-1 + x, y, z$]. It is remarkable that both OH groups form hydrogen bonds to the same ether O atom, O32 (Table 1).

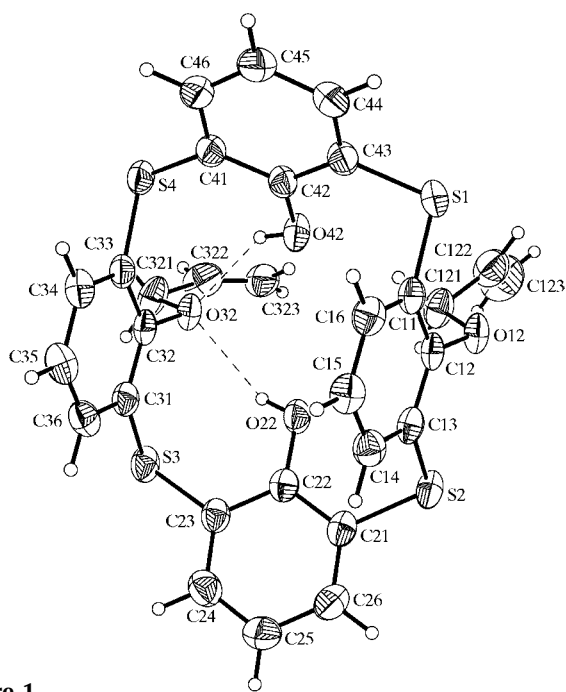


Figure 1

A perspective view of (3a), showing the atom numbering. Displacement ellipsoids are drawn at the 50% probability level and atoms of the minor disordered component have been omitted for clarity. Hydrogen bonds are shown as dashed lines.

Single crystals of (3b) were obtained from acetone and from ethanol/methylene chloride, resulting in two different crystal structures, *viz.* (3b1) and (3b2), respectively. The crystals of (3b1) include two molecules of acetone per calixarene molecule. Surprisingly, and in contrast to (3a), here the molecules assume a 'perfect' 1,3-alternate conformation with crystallographic twofold symmetry (see Fig. 2).

Although the quality of (3b2) was not as good, the crystal structure clearly shows the molecules, which are located on a crystallographic mirror plane, in the 1,3-alternate conformation again. Small differences in shape are evident from the values collected in Table 4 and the least-squares fit (Fig. 5). However, the overall conformations of (3b1) and (3b2) are very similar.

In contrast to (3a), interactions *via* π - π stacking are not pronounced in the structures of either (3b1) or (3b2). For (3b1), molecular columns of head-to-tail-oriented molecules are found along the *c* axis. Subsequent molecules are alternately turned by 72.8° around the column axis. As seen in Fig. 6, adjacent columns have the opposite direction.

Fig. 7 suggests a similar arrangement into columns along the *a* axis for (3b2). However, subsequent molecules are not directly stacked above one another but shifted by $c/2$ with respect to each other.

The structures of (3b1) and (3b2) are the first examples in which a derivative of type (3) is found in the 1,3-alternate conformation (see above). The question arises why the molecule does not assume a cone conformation, which should be stabilized by intramolecular hydrogen bonds. For the 1,3-

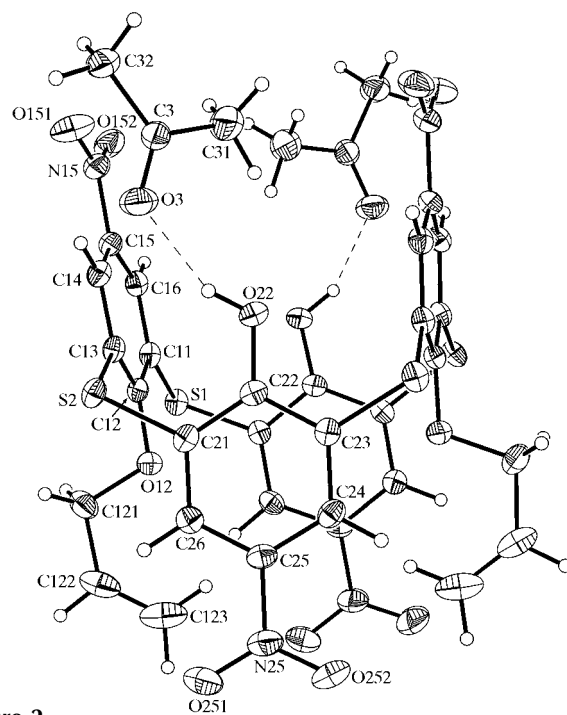


Figure 2

A perspective view of (3b1), showing the atom numbering. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. Non-labelled atoms are generated by the symmetry code $(-x + \frac{3}{2}, -y + \frac{3}{2}, z)$.

diether (Simaan *et al.*, 2003), a favourable packing was assumed as the reason for the 1,3-alternate conformation. In the case of (3b1), two intermolecular hydrogen bonds between calixarene molecules and solvent molecules are found in the crystal structure (Table 2); in the case of (3b2), there is one hydrogen bond to an adjacent molecule (Table 3). However, it seems likely that the reason for the adoption of this conformation is also related to the molecule itself.

Therefore, molecular mechanics calculations using the MMFF94 force field (Halgren, 1990) have been performed to assess the energy differences of the cone and 1,3-alternate conformations of the *syn*-1,3-diethers of 'classical' and of thiacalix[4]arenes. The results of these conformational analyses are summarized in Table 5.

The calculations suggest a different conformational behaviour for the two classes of compounds. In agreement with the experimental observations, the calix[4]arene derivatives prefer the cone conformation, which is stabilized over the 1,3-alternate form by hydrogen bonding [(IVa)–(IVc)]. In contrast, the *syn*-1,3-diethers of thiacalixarenes are predicted to exist predominantly in the 1,3-alternate arrangement [(IIIa)–(IIIc)]. This results mainly from unfavourable bonding contributions to the steric energy of the cone form, which are, however, in part compensated by favourable non-bonding terms due to hydrogen bonding for (IIIb) and (IIIc). For (IIIa), the 1,3-alternate conformer is also favoured by the non-bonding term, which may arise from the compensation of the dipole moments in this form.

Since it may be hypothesized that the distorted pinched cone conformation found in the crystal structure of (3a) is the result of packing forces due to π - π interactions, we have

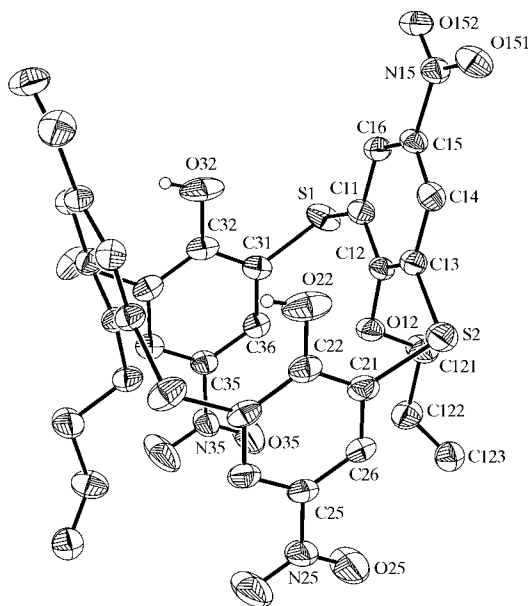


Figure 3

A perspective view of (3b2), showing the atom numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms bonded to C atoms have been omitted for clarity. Only one of the disordered atoms is shown. Non-labelled atoms are generated by the symmetry code (x , $-y + \frac{3}{2}$, z).

optimized this structure with the help of the MMFF94 force field. The resulting energy-minimized conformer is very similar to the crystal structure (the r.m.s. deviation of the calixarene C atoms is 0.18 Å), indicating that this pinched cone form is indeed an energy minimum. However, its energy is 5.5 kcal mol⁻¹ above the global minimum (which corresponds to the 1,3-alternate arrangement), suggesting that the packing forces contribute to the stabilization of this conformation in the crystal structure.

In conclusion, the conformation of (thia)calix[4]arenes and their derivatives is determined by various competing factors. The thiacalix[4]arene skeleton obviously prefers the 1,3-alternate conformation. Thus, tetraethers are usually obtained as 1,3-alternate conformers from thiacalixarenes and as cone conformers from methylene-bridged calixarenes. A circular

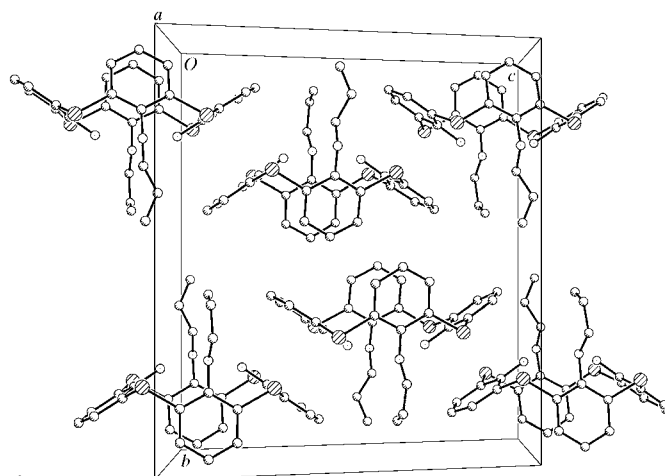


Figure 4

A packing diagram of (3a), viewed along the a axis; atoms of the minor disordered component have been omitted for clarity.

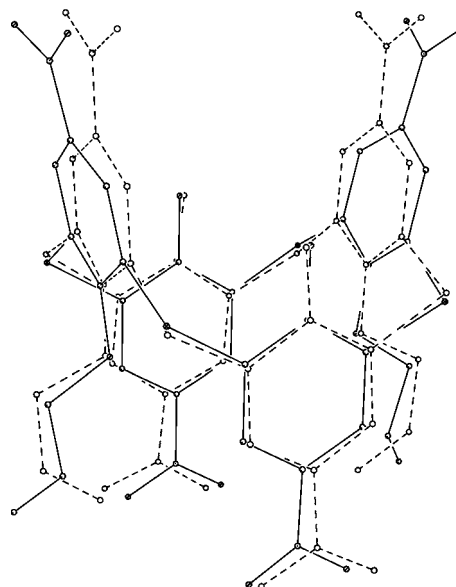


Figure 5

A least-squares fit of (3b1) and (3b2); only the S atoms are fitted (the r.m.s. deviation is 0.170 Å).

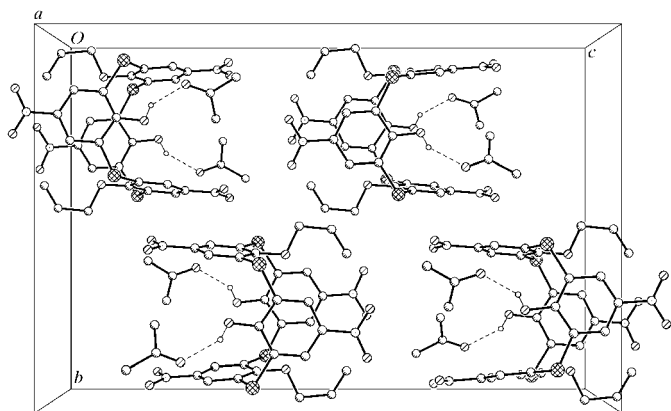


Figure 6
A packing diagram of (3b1), viewed along the *a* axis. Hydrogen bonds are indicated by dashed lines.

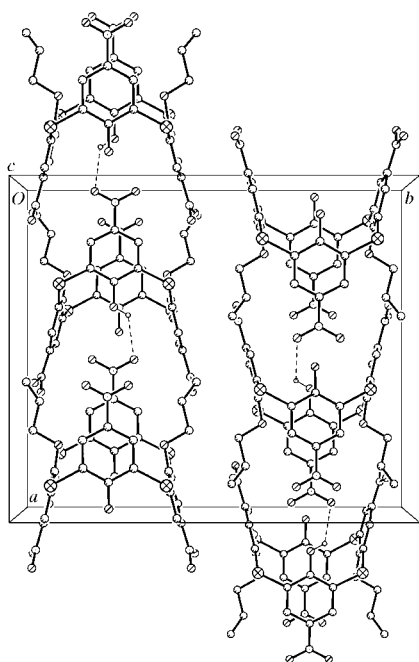


Figure 7
A packing diagram of (3b2), viewed along the *c* axis; atoms of the minor disordered component have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.

array of intramolecular hydrogen bonds between hydroxy groups explains the preference for the cone conformation of the tetrahydroxy compounds in both cases. The competition between intramolecular hydrogen bonds (stabilizing the cone conformation) and compensation of dipole moments (in the 1,3-alternate conformation) explains why (3a) is found in the cone conformation and (3b) in the 1,3-alternate conformation. 1,3-Diethers of calix[4]arenes, however, are (nearly) always found in the cone conformation.

Experimental

Compounds (3a) and (3b) were obtained under standard conditions, refluxing thiacalix[4]arene [(1), *R* = H] or tetranitrothiacalix[4]arene [(1), *R* = NO₂] with an excess of allyl bromide and sodium carbonate

in acetone and acetonitrile, respectively. Details of the syntheses will be published elsewhere (Böhmer & Kasyan, 2006)

Compound (3a)

Crystal data

C₃₀H₂₄O₄S₄
M_r = 576.73
 Monoclinic, *P*₂₁/*c*
a = 9.2591 (8) Å
b = 18.5282 (13) Å
c = 16.7729 (17) Å
 β = 104.297 (7)°
V = 2788.3 (4) Å³

Z = 4
D_x = 1.374 Mg m⁻³
 Mo *K*α radiation
 μ = 0.38 mm⁻¹
T = 173 (2) K
 Rod, colourless
 0.36 × 0.12 × 0.10 mm

Data collection

Stoe IPDS-II two-circle diffractometer
 ω scans
 Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)
T_{min} = 0.877, *T_{max}* = 0.963

39745 measured reflections
 6073 independent reflections
 4194 reflections with *I* > 2σ(*I*)
R_{int} = 0.096
 θ_{max} = 27.1°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.048
wR(*F*²) = 0.124
S = 1.00
 6073 reflections
 361 parameters

H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(*F_o*²) + (0.0693*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.38 e Å⁻³
 Δρ_{min} = -0.33 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °) for (3a).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O22—H22...O32	0.83 (3)	2.17 (3)	2.904 (2)	146 (3)
O42—H42...O32	0.82 (3)	2.23 (3)	2.939 (2)	146 (3)

Compound (3b1)

Crystal data

C₃₀H₂₀N₄O₁₂S₄·2C₃H₆O
M_r = 872.90
 Orthorhombic, *Pccn*
a = 8.8760 (3) Å
b = 17.3100 (5) Å
c = 26.0798 (10) Å
V = 4007.0 (2) Å³

Z = 4
D_x = 1.447 Mg m⁻³
 Mo *K*α radiation
 μ = 0.31 mm⁻¹
T = 173 (2) K
 Plate, colourless
 0.42 × 0.37 × 0.19 mm

Data collection

Stoe IPDS-II two-circle diffractometer
 ω scans
 Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)
T_{min} = 0.881, *T_{max}* = 0.944

56923 measured reflections
 4617 independent reflections
 4227 reflections with *I* > 2σ(*I*)
R_{int} = 0.067
 θ_{max} = 27.7°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.034
wR(*F*²) = 0.084
S = 1.06
 4617 reflections
 267 parameters

w = 1/[σ²(*F_o*²) + (0.0372*P*)² + 2.018*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.31 e Å⁻³
 Δρ_{min} = -0.20 e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0023 (3)

H atoms treated by a mixture of independent and constrained refinement

Table 2

Hydrogen-bond geometry (Å, °) for (3b1).

D—H...A	D—H	H...A	D...A	D—H...A
O22—H22...O3	0.87 (2)	1.94 (2)	2.7558 (16)	155 (2)

Compound (3b2)
Crystal data

C ₃₀ H ₂₀ N ₄ O ₁₂ S ₄	Z = 4
M _r = 756.74	D _x = 1.568 Mg m ⁻³
Orthorhombic, <i>Pnma</i>	Mo Kα radiation
a = 17.2475 (17) Å	μ = 0.37 mm ⁻¹
b = 20.4150 (19) Å	T = 173 (2) K
c = 9.1020 (10) Å	Plate, colourless
V = 3204.9 (6) Å ³	0.39 × 0.12 × 0.04 mm

Data collection

Stoe IPDS-II two-circle diffractometer	44126 measured reflections
ω scans	3127 independent reflections
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	2375 reflections with I > 2σ(I)
T _{min} = 0.892, T _{max} = 0.961	R _{int} = 0.098
	θ _{max} = 25.8°

Refinement

Refinement on F ²	w = 1/[σ ² (F _o ²) + (0.1315P) ² + 3.5315P]
R[F ² > 2σ(F ²)] = 0.093	where P = (F _o ² + 2F _c ²)/3
wR(F ²) = 0.257	(Δ/σ) _{max} < 0.001
S = 1.10	Δρ _{max} = 0.74 e Å ⁻³
3127 reflections	Δρ _{min} = -0.48 e Å ⁻³
239 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0092 (19)

Table 3

Hydrogen-bond geometry (Å, °) for (3b2).

D—H...A	D—H	H...A	D...A	D—H...A
O22—H22...O25 ⁱ	0.84	2.45	2.915 (8)	116
O22—H22...S2 ⁱⁱ	0.84	2.48	3.031 (3)	124
O32—H32...S1 ⁱⁱ	0.84	2.49	3.039 (3)	124

Symmetry codes: (i) x - 1/2, -y + 3/2, -z + 1/2; (ii) x, -y + 3/2, z.

Table 4

Dihedral angles (°) between the reference plane defined by the four S atoms and the mean planes through the aromatic rings for the three structures.

	p1	p2	p3	p4
(3a)	71.24 (5)	146.22 (5)	102.27 (5)	147.31 (5)
(3b1)	95.34 (3)	89.24 (3)	—	—
(3b2)	103.09 (11)	89.10 (17)	89.64 (15)	—

Notes: p1 is the plane through C11–C16; p2 is the plane through C21–C26; p3 is the plane through C31–C36; p4 is the plane through C41–C46. In (3b2), atoms C23 and C24 are symmetry equivalents of C21 and C26, and C33 and C34 are symmetry equivalents of C31 and C36.

For all three title compounds, H atoms were located in a difference electron-density map, and for (3a) and (3b1), the hydroxy H atoms were refined isotropically. All other H atoms were refined with fixed individual displacement parameters [*U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(methyl C,O)] using a riding model, with C–H distances

Table 5

 MMFF94 calculated energies (in kcal mol⁻¹) of the cone and 1,3-alternate (alt) conformers of (III) and (IV) (roman numbers are used to characterize the calculations).

		bond	non-bond	total	ΔE
(IIIa)	cone	54.6	98.3	152.9	3.6
	alt	50.0	99.3	149.3	
(IIIb)	cone	70.6	146.2	216.8	7.5
	alt	67.9	141.4	209.3	
(IIIc)	cone	77.5	143.4	220.9	1.2
	alt	74.0	145.7	219.7	
(IVa)	cone	45.0	79.5	124.5	-10.6
	alt	49.0	86.1	135.1	
(IVb)	cone	62.4	187.3	249.7	-5.3
	alt	62.6	192.4	255.0	
(IVc)	cone	69.2	126.4	195.6	-7.7
	alt	74.4	128.9	203.3	

 Notes: the descriptors *a*, *b* and *c* refer to *p*-substituents H, NO₂ and *t*-Bu; bond is the sum of bonding interactions; non-bond is the sum of non-bonding interactions; total is the sum of all the energy contributions; ΔE = total(cone) – total(alt)

ranging from 0.95 to 0.99 Å and, for (3b2), O–H = 0.84 Å. For (3a), one terminal atom of a propenyloxy chain is disordered over two positions with site-occupation factors of 0.556 (7) and 0.444 (7). Similarly, for (3b2), one terminal atom of a propenyloxy chain is disordered over two positions with site-occupation factors of 0.726 (15) and 0.274 (15); these two atoms were refined isotropically. The two hydroxy H atoms of (3b2) are disordered over two equally occupied positions. The conformational search of (III)/(IV) was performed with the Randomsearch module of the SYBYL program package (Tripos Associates, 1996). Starting structures were generated manually from the 1,3-alternate and cone conformers of a previously calculated *p*-*tert*-butylcalix[4]arene. All Ar–X bonds and the single bonds of the ether groups were chosen as rotatable. A maximum of 2000 cycles of random perturbation of the dihedral angles was allowed using an energy cutoff of 20 kcal mol⁻¹ above the actual minimum. A constant dielectric with ε = 1 was used. The resulting structures were minimized with the MMFF94 force field, which is included in the SYBYL program, until the r.m.s. energy gradient was less than 10⁻³ kcal mol⁻¹ Å⁻¹.

For all compounds, data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3005). Services for accessing these data are described at the back of the journal.

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