SUPPLEMENTARY INFORMATION

Calix[4]arenes Comprised of Aniline Units

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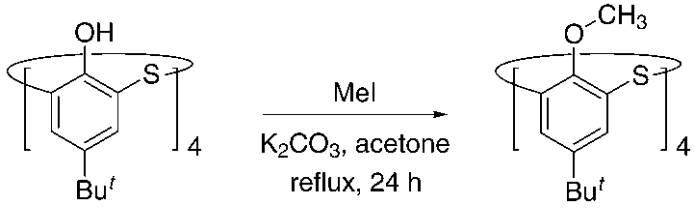
1.1 SO_2 Route

1.1.1 Tetra-*p*-*tert*-butyl-tetramethoxythiacalix[4]arene (**10**)

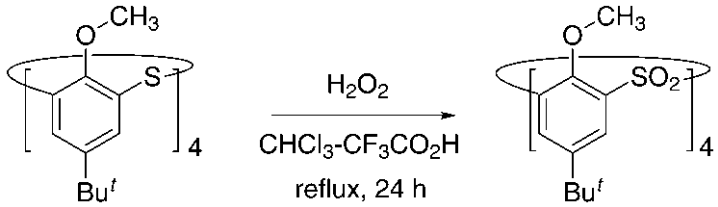


2 **10**

Procedure. To a suspension of **2** (5.0 g, 6.9 mmol) in dry acetone (100 ml), K_2CO_3 (19.1 g 138 mmol) and CH_3I (8.6 ml, 138 mmol) were added. After the reaction mixture was refluxed for 1 day, 2 M HCl (200 ml) was added in ice bath to terminate the reaction. The mixture was extracted with $CHCl_3$ (300 ml × 3), then the extract was evaporated to dryness to obtain crude product **10**. Recrystallization from CH_2Cl_2–*n*-hexane afforded essentially pure sample of **10** (4.81 g, 90%y).

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-tetramethoxy-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (10): mp 315.0~315.5 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ 1.24 (s, 36H, C(CH_3)$_3$), 3.45 (s, 12H, OCH_3), 7.44 (s, 8H, ArH); FTIR (KBr): 2963 (CH), 1269 (COC), 1009 (COC); FAB MS *m/z* 776 (M^+). Anal. Calcd for $C_{44}H_{56}O_4S_4$: C, 68.00; H, 7.26; S, 16.50. Found: C, 67.71; H, 7.12; S, 16.75.

1.1.2 Tetra-*p*-*tert*-butyl-tetramethoxysulfonylcalix[4]arene (**11**)

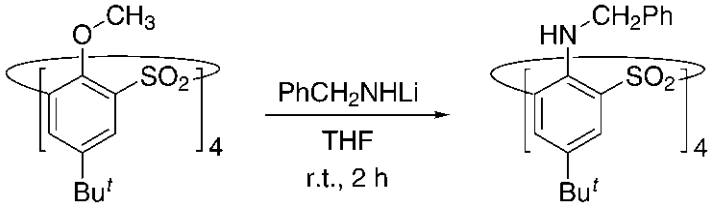


10 **11**

Procedure. The solution of **10** (4.75 g, 6.11 mmol) in $CHCl_3$ (80 ml) was added by CF_3COOH (15 ml) and 30% H_2O_2 aq. (50 ml) and then refluxed for 24 h. After cooling, the reaction was terminated by addition of Na_2SO_3 (15 g) in small portions. The mixture was extracted with $CHCl_3$ (150 ml × 3), then the extract was evaporated to dryness to give crude product (5.11 g). Recrystallization from CH_2Cl_2–*n*-hexane gave essentially pure sample of **11** (4.66 g, 86 %y).

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-tetramethoxy-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-2,2,8,8,14,14,20,20-octaoxide (11): mp >360 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ 1.33 (s, 36H, C(CH_3)$_3$), 4.01 (s, 12H, OCH_3), 8.28 (s, 8H, ArH); FTIR (KBr): 2959 (CH), 1323 (SO_2), 1225 (COC), 1138 (SO_2), 1086 (COC); FAB MS *m/z* 905 (M^+ + 1). Anal. Calcd for $C_{44}H_{56}O_{12}S_4$: C, 58.38; H, 6.24; S, 14.17. Found: C, 58.66; H, 6.30; S, 14.32.

1.1.3 Tetrakis(*N*-benzylamino)-tetra-*p*-*tert*-butylsulfonylcalix[4]arene (**12**)

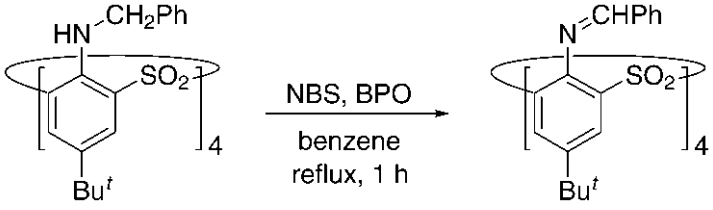


11 **12**

Procedure. A mixture of dry THF (75 ml) and dry benzylamine (11.00 ml, 99.4 mmol) was cooled to –78 °C, kept being stirred under N_2 atmosphere, then slowly added by 1.24 M *n*-butyllithium in *n*-hexane (56.30 ml, 88.4 mmol) dropwise. After addition was completed, the mixture was further kept stirred at 0 °C for 1 h. The solution was transferred to an dropping funnel and added to a mixture of **11** (5.01 g, 5.52 mmol) and 75 ml of dry THF being stirred at 0 °C under N_2. After dropping was completed, the reaction mixture was further stirred for 2 h at room temperature. The reaction was terminated by addition of saturated NH_4Cl aq. (20 ml). After acidifying the solution with 2 M HCl (50 ml), the mixture was extracted with $CHCl_3$ (200 ml × 3). The extract was further washed with distilled water (200 ml × 2) and evaporated to dryness to give yellowish crude product (7.02 g). After being triturated with acetone (100 ml), the solid residue was recrystallized from $CHCl_3$–EtOH to give essentially pure sample of **12** (4.66 g, 70%y). The conformation of **12** was assigned to be 1,3-alternate by X-ray crystallography (see section 2.1).

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-tetramethoxy-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-2,2,8,8,14,14,20,20-octaoxide (1,3-alternate 12): mp >360 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ 0.88 (s, 36H, $C(CH_3)_3$), 2.49 (t, 4H, J = 7.1Hz, $ArNHCH_2Ar$), 4.41 (d, 8H, J = 7.1Hz, $ArNHCH_2Ar$), 7.27-7.35 (m, 12H, $ArNHCH_2ArH$), 7.56-7.57 (m, 8H, $ArNHCH_2ArH$), 8.35 (s, 8H, $ArHNHCH_2Ar$); FTIR (KBr): 3350 (NH), 2964 (CH), 1321 (SO_2), 1155 (SO_2); FAB MS *m/z* 1205 (M^+ + 1). Anal. Calcd for $C_{68}H_{76}N_4O_8S_4$: C, 67.74; H, 6.35; N, 4.65; S, 10.64. Found: C, 67.78; H, 6.35; N, 4.56; S, 10.75.

1.1.4 Tetrakis(*N*-benzylidenamino)-tetra-*p*-*tert*-butylsulfonylcalix[4]arene (**13**)

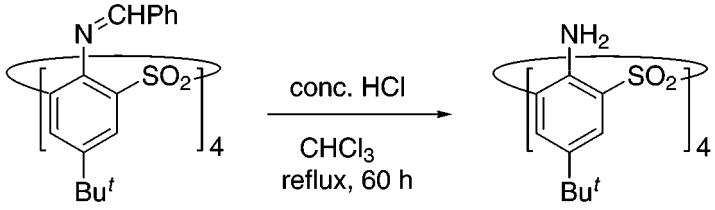


12 **13**

Procedure. A flask containing 1,3-alternate **12** (224.1 mg, 0.19 mmol) and *N*-bromosuccinimide (NBS, 206.3 mg, 1.16 mmol) was purged by N_2, then added by dry benzene (15 ml) and dibenzoyl peroxide (BPO, 22.3 mg, 0.09 mmol). The reaction mixture was refluxed for 1 h, added by 5 wt% $NaHSO_3$ (5 ml) to terminate the reaction, and extracted with $CHCl_3$ (50 ml × 3). The extract was evaporated to dryness to obtain crude product (289.4 mg),

which was recrystallized from CH_2Cl_2–*n*-hexane to give pure sample of **13** (199.7 mg, 90 %y).
5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-Tetrakis(*N*-benzylidenamino)-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-2,2,8,8,14,14,20,20-octaoxide (13): mp >360 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.86 (s, 36H, $C(CH_3)_3$), 7.45 (dd, 8H, *J* = 7.3, 1.5Hz, ArH), 7.52 (t, 8H, *J* = 7.3Hz, ArH), 7.62 (tt, 4H, *J* =7 .3, 1.5Hz, ArH), 7.92 (s, 8H, ArH), 8.27 (s, 4H, ArNCHAr); FTIR (KBr): 2964 (CH), 1636 (NC) 1315 (SO_2), 1132 (SO_2); FAB MS *m/z* 1197 (M^+ + 1). Anal. Calcd. for $C_{68}H_{68}N_4O_8S_4$: C, 68.20; H, 5.72; N, 4.68; S, 10.71. Found: C, 68.20; H, 5.78; N, 4.55; S, 10.83.

1.1.5 Tetraamino-tetra-*p*-*tert*-butylsulfonylcalix[4]arene (**8**)

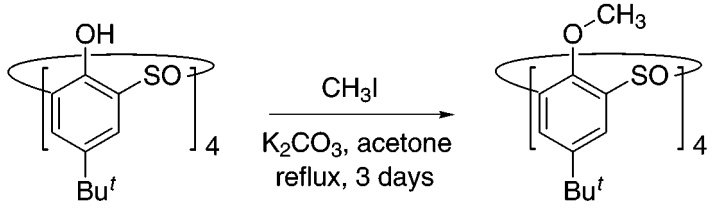


13 **8**

Procedure. A mixture of **13** (494.4 mg, 0.41 mmol), $CHCl_3$ (20 ml), and conc. HCl (20 ml) were refluxed for 60 h. After cooling, the reaction mixture was extracted with $CHCl_3$ (100 ml × 3). The extract was evaporated to dryness to give crude product (410.0 mg), which was further recrystallized from CH_2Cl_2–*n*-hexane to give pure sample of **8** (273.0 mg, 78%y) as white powder.
5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-tetraamino-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-2,2,8,8,14,14,20,20-octaoxide (8): mp >360 °C; ^{1}H NMR (500 MHz; DMSO-d_6) δ 1.24 (s, 36H, $C(CH_3)_3$), 5.65 (s, 8H, NH), 7.99 (s, 8H, ArH); FTIR (KBr): 3468 (NH), 3389 (NH), 2964 (CH), 1313 (SO_2), 1151 (SO_2); FAB MS *m/z* 845 (M^+ + 1). Anal. Calcd. for $C_{40}H_{52}N_4O_8S_4$: C, 56.85; H, 6.20; N, 6.63; S, 15.18. Found: C, 56.87; H, 6.18; N, 6.58; S, 15.41.

1.2 SO Route

1.2.1 Tetra-*p*-*tert*-butyl-tetramethoxy-sulfinylcalix[4]arene (**14**)



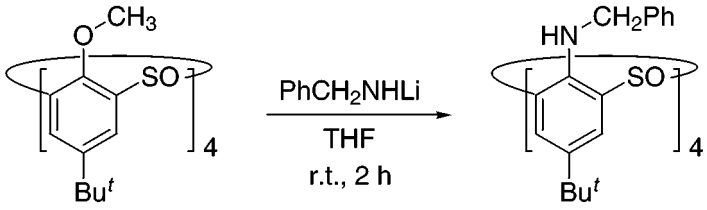
3 **14**

Procedure. A solution of **3** (6.09 g, 7.76 mmol) in anhydrous acetone (140 cm^3) was added K_2CO_3 (17.39 g, 125.8 mmol) and CH_3I (9.0 cm^3, 144.4 mmol) under N_2 atmosphere, then refluxed for 3 days. After cooling to ambient temperature, the reaction mixture was added by 2

M HCl (100 ml) in an ice-water bath and extracted with $CHCl_3$ (300 $cm^3 \times 4$). The extract was evaporated to dryness to give crude product. Recrystallization from CH_2Cl_2–*n*-hexane mixture afforded essentially pure sample of **14** (5.66 g, 87 %y).

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-tetramethoxy-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-2,8,14,20-tetraoxide (14): mp 308.5~309.0 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ 1.32 (s, 36H, $C(CH_3)_3$), 3.92 (s, 12H, OCH_3), 7.68 (d, 4H, *J* = 2.4, ArH), 8.13 (d, 4H, *J* = 2.4, ArH); FTIR (KBr): 2964 (CH), 1269 (COC), 1055 (SO) 991 (COC); FAB MS *m/z* 840 (M^+). Anal. Calcd for $C_{44}H_{56}O_8S_4$: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.64; H, 6.68; S, 15.50.

1.2.2 Tetrakis(*N*-benzylamino)-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (**15**)

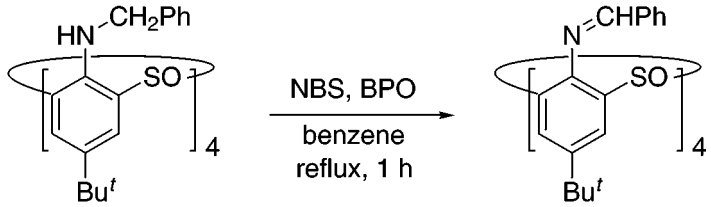


14 **15**

Procedure. Benzylamine (12.0 ml, 0.11 mol) in 90 ml dry THF was stirred and added by an *n*-hexane solution (56.3 ml) of 1.57 M *n*-butyl lithium (0.10 mol) dropwise under N_2 atmosphere at –78 °C. After addition was completed, the mixture was further stirred at 0 °C for 1 h to afford pink lithium benzylamide solution. The solution was transferred to a dropping funnel and added slowly and dropwise to a suspension of **14** (5.28 g, 6.28 mmol) in dry THF (70 ml) being stirred under N_2 atmosphere at 0 °C. The dark-red reaction mixture was further stirred at an ambient temperature for 2 h. The reaction was terminated by addition of saturated NH_4Cl aq. (20 ml). After acidifying by addition of 2 M HCl (80 ml), the mixture was extracted by $CHCl_3$ (200 ml × 3), then the organic layer was evaporated to dryness and washed with MeOH (100 ml) to give crude product. Recrystallization from CH_2Cl_2–MeOH solution afforded white powder of **15** (4.56 g, 64 %y). The conformation of **15** was unambiguously assigned to be 1,3-alternate by oxidation of the bridging sulfinyl groups to give the product having same spectroscopic properties as 1,3-alternate **12** does (see section 1.3).

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-tetrakis(*N*-benzylamino)-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-2,8,14,20-tetraoxide (1,3-alternate 15): mp 310.5 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ 0.90 (s, 36H, $C(CH_3)_3$), 3.34 (dd, 4H, *J* = 11.1, 2.9 Hz, ArNHC$\underline{H}_2$Ar), 4.17 (t, 4H, *J* = 11.1, ArN$\underline{H}$CH$_2$Ar), 4.27 (dd, 4H, *J* = 11.1, 2.9Hz, ArNHC$\underline{H}_2$Ar), 7.30 (tt, 4H, *J* = 7.4, 1.8 Hz, ArH), 7.37 (t, 8H, *J* = 7.4 Hz, ArH), 7.59 (d, 8H, *J* = 7.4 Hz, ArH), 7.60 (d, 4H, *J* = 2.4Hz, ArH), 792 (d, 4H, *J* = 2.4Hz, ArH); FTIR (KBr): 3354 (NH), 2963 (CH), 1045 (SO); FAB MS *m/z* 1141 ($M^+ + 1$). Anal. Calcd for $C_{68}H_{76}N_4O_4S_4$: C, 71.54; H, 6.71; N, 4.91; S, 11.24. Found: C, 71.30; H, 6.75; N, 4.79; S, 11.18.

1.2.3 Tetrakis(*N*-benzilideneamino)-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (**16**)

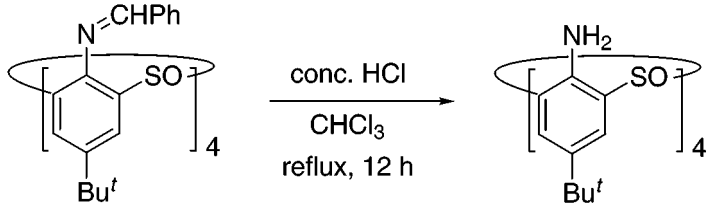


15 **16**

Procedure. A flask containing powders of 1,3-alternate **15** (4.39 g, 3.85 mmol) and NBS (4.23 g, 23.8 mmol) was purged by N_2, added by dry benzene (250 ml) and BPO (411 mg, 1.7 mmol), and then refluxed for 1 h. After cooling, the reaction mixture was added by 5% $NaHSO_3$ solution (30 ml) to terminate the reaction and extracted by $CHCl_3$ (200 ml × 3). After the extract was evaporated to dryness, the residue was washed with MeOH (100 ml), then dried in vacuo to give 3.99 g of crude product. Recrystallization from CH_2Cl_2–MeOH gave essentially pure sample of **16** (3.69 g, 85%).

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-*N*-benzilideneamino-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-2,8,14,20-tetraoxide (16): mp >360 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ 0.86 (s, 36H, C(CH_3)$_3$), 7.46 (t, 8H, *J* = 13.6Hz, ArH), 7.46 (d, 8H, *J* = 13.6, ArH), 7.55-7.59 (m, 12H, ArH), 8.42 (s, 4H, ArNCHAr); FTIR (KBr): 2955 (CH), 1631 (NC), 1047 (SO); FAB MS *m/z* 1133 (M^+ + 1). Anal. Calcd for $C_{68}H_{68}N_4O_4S_4$: C, 72.05; H, 6.05; N, 4.94; S, 11.32. Found: C, 71.68; H, 6.10; N, 4.84; S, 11.10.

1.2.4 Tetraamino-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (**7**)

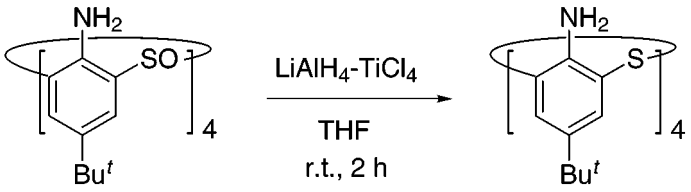


16 **7**

Procedure. The mixture of **16** (3.07 g, 2.71 mmol), $CHCl_3$ (200 ml), and conc. HCl (100 ml) was refluxed for 12 h. After cooling, the mixture was extracted with $CHCl_3$ (300 ml × 3), then the extract was evaporated to dryness. The solid residue was washed with MeOH (100 ml) and dried in vacuo to afford crude product. Recrystallization from CH_2Cl_2–MeOH gave essentially pure sample of **7** (1.80 g, 85%y).

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-tetraamino-2,8,14,20-tetrathiapenta-cyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-2,8,14,20-tetraoxide (7): mp >360 °C; ^{1}H NMR (500 MHz; DMSO-d_6, 110 °C) δ 1.17 (s, 36H, C(CH_3)$_3$), 5.36 (s, 8H, NH_2), 7.56 (s, 8H, ArH); FTIR (KBr): 3452 (NH), 3371 (NH), 2959 (CH), 1030 (SO); FAB MS *m/z* 781 (M^+ + 1). Anal. Calcd for $C_{40}H_{52}N_4O_4S_4$: C, 61.50; H, 6.71; N, 7.17; S, 16.42. Found: C, 61.43; H, 6.61; N, 7.11; S, 16.69.

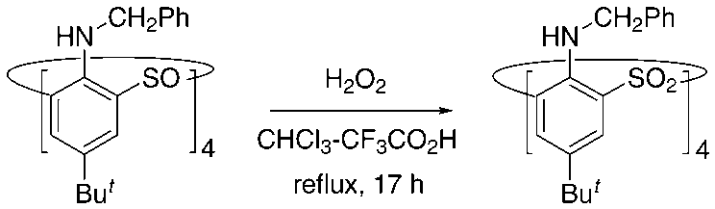
1.2.5 Tetraamino-tetra-*p*-*tert*-butylthiacalix[4]arene (**6**)



7 **6**

Procedure. A flask containing **7** (1.58 g, 2.02 mmol) was purged by N_2, added by dry THF (160 ml) and $LiAlH_4$ (1.23 g, 32.41 mmol), and cooled down to –78 °C. To the mixture being stirred, $TiCl_4$ (1.7 ml, 15.47 mmol) was added dropwise, allowed to be stirred for 15 min then further at an ambient temperature for 2 h. The black suspension was added by saturated NH_4Cl aq. (30 ml) in an ice-water bath to terminate the reaction, added by 2 M HCl (20 ml), extracted with $CHCl_3$ (150 ml × 3). After the extract was evaporated to dryness, the solid residue was triturated with MeOH (80 ml), and dried in vacuo to give crude product (1.04 g). Recrystallization from CH_2Cl_2–MeOH afforded essentially pure sample of **6** (940 mg, 65%y).
5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26,27,28-tetraamino-2,8,14,20-tetrathiapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (6): mp >360 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.12 (s, 36H, $C(CH_3)_3$), 4.88 (br, 8H, NH_2), 7.35 (s, 8H, ArH); FTIR (KBr): 3464 (NH), 3362 (NH), 2961 (CH); FAB MS *m/z* 717 (M^+ + 1). Anal. Calcd for $C_{40}H_{52}N_4S_4$: C, 66.99; H, 7.31; N, 7.81; S, 17.89. Found: C, 66.67; H, 7.21; N, 7.69; S, 17.72.

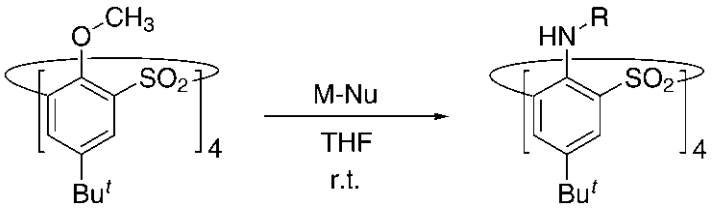
1.3 Oxidation of tetrakis(*N*-benzylamino)-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (15) to tetrakis(*N*-benzylamino)-tetra-*p*-*tert*-butylsulfonylcalix[4]arene (12)



15 **12**

Procedure. To a $CHCl_3$ solution (20 ml) of **15** (86.5 mg, 0.076 mmol), CF_3COOH (1.0 ml) and 30% H_2O_2 (5 ml) were added. After the mixture was refluxed for 17 h, Na_2SO_3 (450 mg) was added in small portions to terminate the reaction. The mixture was extracted with $CHCl_3$ (50 ml × 3), then the extract was evaporated to dryness. The solid residue was subjected to column chromatography (12 g silica gel, 3:1 $CHCl_3$:*n*-hexane) followed by evaporation to give a pure sample of **12** (80.0 mg, 87.3%), the conformation of which was assigned to be 1,3-alternate by comparison to 1,3-alternate **12** obtained by SO_2 route.

1.4 Chelation-assisted nucleophilic aromatic substitution reaction of Tetra-*p*-*tert*-butyl-tetramethoxysulfonylcalix[4]arene (11) by use of other nucleophiles



11

17: R = *n*-Bu
18: R = *i*-Pr
12: R = $PhCH_2$

Procedure. The same as described in section 1.1.3. The yields of the S_NAr reaction using metal amides including benzyl amide are summarized in Table S1.

Table S1 The yields of the product by S_NAr reaction

M-Nu	Product	%Yield	Notes
n-BuNHLi	**17**	62	Total yield of the three conformers in the ratio; partial cone : 1,2-alternate : [cone or 1,3-alternate][a] = 16 : 3 : 4.
i-PrNHLi	**18**	66	Total yield of the possible four conformers.
$PhCH_2NHLi$	**12**	70	Isolated yield of 1,3-alternate conformer. See section 1.1.3.
n-BuNHMgBr	–	–	Complex mixture of partially substituted products was obtained.

[a] Could not be assigned by ^1H NMR.

2. X-RAY CRYSTALLOGRAPHY

2.1 Tetrakis(*N*-benzylamino)-tetra-*p*-*tert*-butylsulfonylcalix[4]arene (12)

2.1.1 Preparation.

Single crystals of **12** suitable for X-ray analysis were obtained by slow liquid diffusion of MeOH into $CHCl_3$ solution of **12**.

2.1.2 Crystallographic data.

Empirical Formula	$C_{68}H_{76}N_4O_8S_4$
Formula Weight	1205.61
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.02 X 0.03 X 0.03 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	10737 (0.0 - 54.8°)
Lattice Parameters	a = 12.2362(5)Å α = 97.939(2)°
	b = 13.789(2)Å β = 101.5790(6)°
	c = 19.941(1)Å γ = 99.4768(7)°
	V = 3199.7(4) Å^3
Space Group	$P\bar{1}$ (#2)
Z value	2
D_{calc}	1.251 g/cm^3
F_{000}	1280.00
μ(MoKα)	2.06 cm^{-1}

2.1.3 Intensity Measurements

Diffractometer	Rigaku/MSC Mercury CCD
Radiation	MoKα (λ = 0.71069Å) graphite monochromated
Temperature	-73.0°C
Voltage, Current	50 kV, 40 mA
Collimator Size	5.0 mm
Detector Aperture	70 mm x 70 mm
Data Images	480 exposures at 20.0 seconds
ω oscillation Range (χ = 45°, ϕ = 0°)	-80.0 - 100.0°
ω oscillation Range (χ = 45°, ϕ = 90°)	-30.0 - 30.0°
Detector Position	35.00 mm
Pixel Size	0.137 mm
Detector Swing Angle	10.00°
$2\theta_{max}$	55.8°
No. of Reflections Measured	Total: 24660, Unique: 13780 (R_{int} = 0.021)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9790 - 1.0000)

2.1.4 Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares

Function Minimized	$\Sigma\, w\, (\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 5.00\sigma(I)$)	6854
No. Variables	791
Reflection/Parameter Ratio	8.66
Residuals: *R*; *Rw*	0.061 ; 0.066
Residuals: *R1*	0.061
No. of Reflections to calc *R1*	6854
Goodness of Fit Indicator	2.25
Max Shift/Error in Final Cycle	3.038
Maximum peak in Final Diff. Map	0.26 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.17 $e^-/Å^3$

2.1.5 Special Comments for Structure Refinement

Two *tert*-butyl groups, which were found disorderly, were finally divided in the three parts by the successive procedure of refinements and D-Fourier syntheses. These carbons were refined isotropically in the same occupancy. Only amine hydrogens, clearly found from D-map, were refined isotropically. The other hydrogens except for the disordered *tert*-butyl hydrogens were calculated, which were fixed in the refinement.

2.1.6 Results

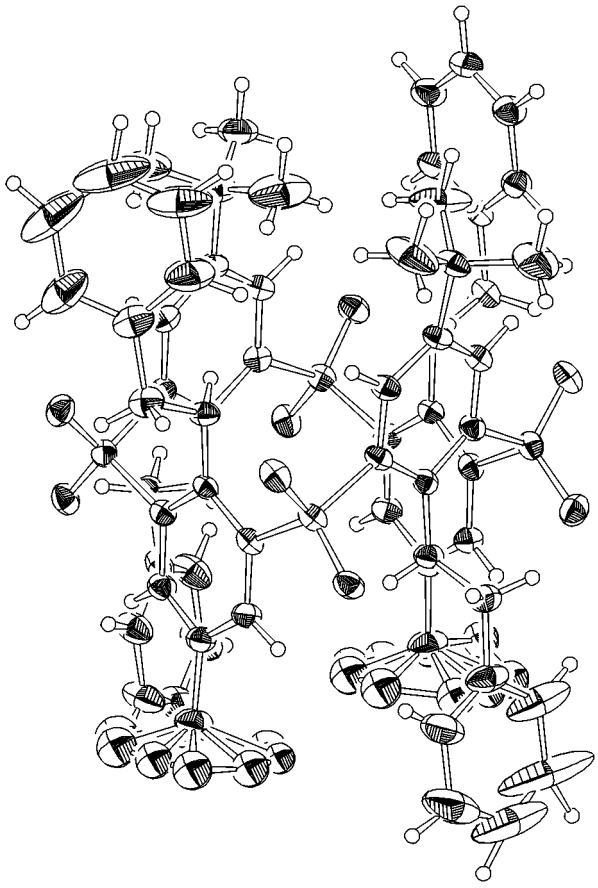


Figure S1. Ortep drawing for compoud **12**.

Table S2. Atomic coordinates, B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
S(2)	0.12622(10)	0.04455(9)	0.59275(6)	3.23(3)	1.0000
S(1)	-0.05579(10)	0.36894(9)	0.69066(6)	3.36(3)	1.0000
S(3)	0.49889(10)	0.18225(9)	0.81889(6)	3.34(3)	1.0000
S(4)	0.31473(10)	0.50347(9)	0.91870(6)	3.33(3)	1.0000
O(1)	-0.0563(3)	0.4655(3)	0.6719(2)	4.36(9)	1.0000
O(2)	-0.1629(3)	0.3023(3)	0.6828(2)	4.12(8)	1.0000
O(3)	0.0242(3)	-0.0293(2)	0.5810(2)	3.89(8)	1.0000
O(4)	0.1997(3)	0.0324(3)	0.5461(2)	3.87(8)	1.0000
O(5)	0.5796(3)	0.1745(2)	0.7762(2)	4.03(8)	1.0000
O(6)	0.5265(3)	0.1566(2)	0.8868(2)	4.29(8)	1.0000
O(7)	0.3361(3)	0.4860(3)	0.9893(2)	4.23(8)	1.0000
O(8)	0.3276(3)	0.6055(2)	0.9079(2)	4.03(8)	1.0000
N(1)	-0.0349(3)	0.1411(3)	0.6697(2)	3.22(9)	1.0000
N(2)	0.3755(4)	0.1565(3)	0.6623(2)	3.46(9)	1.0000
N(3)	0.3563(3)	0.2868(3)	0.9112(2)	3.51(9)	1.0000
N(4)	0.1797(3)	0.5020(3)	0.7667(2)	3.44(9)	1.0000
C(1)	0.0280(3)	0.2051(3)	0.6359(2)	2.77(9)	1.0000
C(2)	0.0283(4)	0.3087(3)	0.6411(2)	3.08(10)	1.0000
C(3)	0.0891(4)	0.3674(4)	0.6048(2)	3.6(1)	1.0000
C(4)	0.1514(4)	0.3278(4)	0.5603(2)	3.8(1)	1.0000
C(5)	0.1555(4)	0.2277(4)	0.5569(2)	3.5(1)	1.0000
C(6)	0.0971(4)	0.1679(3)	0.5940(2)	3.15(10)	1.0000
C(7)	0.2030(4)	0.0511(3)	0.6800(2)	3.14(10)	1.0000
C(8)	0.1451(4)	-0.0002(3)	0.7218(2)	3.4(1)	1.0000
C(9)	0.1950(4)	-0.0004(3)	0.7909(2)	3.3(1)	1.0000
C(10)	0.3043(4)	0.0548(3)	0.8167(2)	3.4(1)	1.0000
C(11)	0.3634(4)	0.1080(3)	0.7755(2)	3.07(10)	1.0000
C(12)	0.3152(4)	0.1059(3)	0.7049(2)	2.77(9)	1.0000
C(13)	0.4119(3)	0.3450(3)	0.8704(2)	2.80(9)	1.0000
C(14)	0.4051(4)	0.4464(3)	0.8718(2)	3.12(10)	1.0000
C(15)	0.4682(4)	0.5072(3)	0.8374(3)	3.5(1)	1.0000
C(16)	0.5392(4)	0.4708(4)	0.7988(3)	3.7(1)	1.0000
C(17)	0.5403(4)	0.3701(4)	0.7922(3)	3.6(1)	1.0000
C(18)	0.4796(4)	0.3084(3)	0.8277(2)	3.18(10)	1.0000
C(19)	0.1258(4)	0.4416(3)	0.8075(2)	2.90(9)	1.0000
C(20)	0.1735(4)	0.4390(3)	0.8772(2)	3.03(10)	1.0000
C(21)	0.1106(4)	0.3919(4)	0.9187(2)	3.4(1)	1.0000
C(22)	-0.0025(4)	0.3432(4)	0.8932(2)	3.5(1)	1.0000
C(23)	-0.0459(4)	0.3369(4)	0.8225(2)	3.5(1)	1.0000
C(24)	0.0153(4)	0.3831(3)	0.7803(2)	3.14(10)	1.0000
C(25)	-0.1461(4)	0.0848(4)	0.6241(2)	3.6(1)	1.0000
C(26)	-0.2015(4)	0.0113(4)	0.6624(2)	3.5(1)	1.0000
C(27)	-0.1898(4)	-0.0875(4)	0.6537(3)	4.5(1)	1.0000
C(28)	-0.2399(5)	-0.1523(4)	0.6905(3)	5.1(1)	1.0000
C(29)	-0.3034(5)	-0.1205(4)	0.7362(3)	4.7(1)	1.0000
C(30)	-0.3144(5)	-0.0224(4)	0.7453(3)	4.6(1)	1.0000
C(31)	-0.2653(4)	0.0430(4)	0.7084(3)	4.0(1)	1.0000
C(32)	0.4422(4)	0.0933(4)	0.6260(3)	4.1(1)	1.0000
C(33)	0.4875(4)	0.1477(4)	0.5738(3)	4.0(1)	1.0000
C(34)	0.5772(5)	0.2279(5)	0.5951(3)	5.2(1)	1.0000
C(35)	0.6186(5)	0.2809(5)	0.5483(3)	6.3(2)	1.0000
C(36)	0.5703(6)	0.2503(6)	0.4779(3)	6.4(2)	1.0000
C(37)	0.4824(6)	0.1691(6)	0.4556(3)	6.8(2)	1.0000
C(38)	0.4411(5)	0.1176(5)	0.5034(3)	5.6(2)	1.0000
C(39)	0.4291(5)	0.2928(4)	0.9824(3)	4.5(1)	1.0000
C(40)	0.3803(6)	0.2120(4)	1.0170(3)	5.3(1)	1.0000
C(41)	0.4425(8)	0.1427(6)	1.0377(4)	9.2(3)	1.0000

C(42)	0.397(2)	0.0673(9)	1.0702(6)	13.8(5)	1.0000
C(43)	0.289(2)	0.066(1)	1.0808(5)	13.5(4)	1.0000
C(44)	0.226(1)	0.1331(8)	1.0611(5)	11.6(4)	1.0000
C(45)	0.2718(8)	0.2038(6)	1.0283(4)	8.2(2)	1.0000
C(46)	0.1492(5)	0.6038(4)	0.7749(3)	4.3(1)	1.0000
C(47)	0.2097(7)	0.6720(4)	0.7353(4)	6.3(2)	1.0000
C(48)	0.156(1)	0.6806(6)	0.6705(5)	10.6(3)	1.0000
C(49)	0.204(2)	0.7467(8)	0.6357(9)	20.9(9)	1.0000
C(50)	0.296(2)	0.805(1)	0.661(1)	17.8(8)	1.0000
C(51)	0.3660(10)	0.8035(7)	0.7309(10)	14.1(5)	1.0000
C(52)	0.3148(7)	0.7319(6)	0.7679(6)	10.0(3)	1.0000
C(53)	0.2166(6)	0.3940(4)	0.5191(3)	5.7(2)	1.0000
C(54)	0.1287(5)	-0.0529(4)	0.8376(3)	4.5(1)	1.0000
C(55)	0.6153(5)	0.5401(4)	0.7648(3)	5.5(2)	1.0000
C(56)	-0.0788(4)	0.3024(4)	0.9394(3)	4.4(1)	1.0000
C(531)	0.182(2)	0.496(1)	0.515(1)	4.2(4)	0.3333
C(532)	0.331(2)	0.359(2)	0.512(1)	6.2(5)	0.3333
C(533)	0.209(2)	0.337(1)	0.4455(9)	4.7(3)	0.3333
C(534)	0.280(2)	0.343(2)	0.474(1)	7.2(5)	0.3333
C(535)	0.134(2)	0.354(1)	0.4371(10)	5.8(4)	0.3333
C(536)	0.324(2)	0.469(2)	0.579(1)	7.3(5)	0.3333
C(537)	0.347(2)	0.409(2)	0.556(1)	6.5(5)	0.3333
C(538)	0.233(2)	0.504(2)	0.545(1)	6.6(5)	0.3333
C(539)	0.141(2)	0.474(2)	0.491(1)	6.2(6)	0.3333
C(541)	0.2074(7)	-0.0824(6)	0.8962(3)	8.5(2)	1.0000
C(542)	0.0470(5)	-0.1475(5)	0.7973(3)	6.0(2)	1.0000
C(543)	0.0603(9)	0.0197(6)	0.8655(5)	11.3(3)	1.0000
C(551)	0.586(2)	0.636(2)	0.760(1)	6.1(4)	0.3333
C(552)	0.741(2)	0.563(2)	0.818(1)	7.2(5)	0.3333
C(553)	0.626(1)	0.481(1)	0.6914(8)	3.6(3)	0.3333
C(554)	0.535(2)	0.614(2)	0.726(1)	4.2(3)	0.3333
C(555)	0.708(2)	0.613(2)	0.826(1)	6.0(5)	0.3333
C(556)	0.674(2)	0.485(1)	0.7155(9)	3.7(3)	0.3333
C(557)	0.668(2)	0.644(2)	0.815(1)	6.9(6)	0.3333
C(558)	0.540(2)	0.575(2)	0.703(1)	7.9(7)	0.3333
C(559)	0.723(3)	0.497(2)	0.756(2)	9.0(8)	0.3333
C(561)	-0.1217(8)	0.1928(5)	0.9169(4)	9.3(3)	1.0000
C(562)	-0.1826(7)	0.3526(6)	0.9313(4)	8.6(3)	1.0000
C(563)	-0.0217(6)	0.3302(8)	1.0155(4)	9.5(3)	1.0000
H(1)	0.0874	0.4378	0.6103	4.4081	1.0000
H(2)	0.2001	0.1987	0.5286	4.2779	1.0000
H(3)	0.0683	-0.0364	0.7023	4.0266	1.0000
H(4)	0.3406	0.0550	0.8644	4.0730	1.0000
H(5)	0.4600	0.5758	0.8404	4.2624	1.0000
H(6)	0.5854	0.3413	0.7638	4.4303	1.0000
H(7)	0.1469	0.3905	0.9658	4.3180	1.0000
H(8)	-0.1206	0.2966	0.8007	3.8758	1.0000
H(9)	-0.1476	-0.1126	0.6217	5.5688	1.0000
H(10)	-0.2338	-0.2211	0.6843	6.0157	1.0000
H(11)	-0.3378	-0.1655	0.7620	5.6850	1.0000
H(12)	-0.3594	0.0016	0.7775	5.2124	1.0000
H(13)	-0.2714	0.1118	0.7160	4.8028	1.0000
H(14)	0.6142	0.2467	0.6435	6.0217	1.0000
H(15)	0.6844	0.3352	0.5653	7.9634	1.0000
H(16)	0.5977	0.2848	0.4445	7.3404	1.0000
H(17)	0.4484	0.1489	0.4063	7.8319	1.0000
H(18)	0.3805	0.0618	0.4864	6.7091	1.0000
H(19)	0.5196	0.1405	1.0271	10.7413	1.0000
H(20)	0.4194	0.0143	1.0897	15.2408	1.0000
H(21)	0.2356	0.0245	1.1006	14.0663	1.0000

H(22)	0.1438	0.1323	1.0651	14.4494	1.0000
H(23)	0.2235	0.2494	1.0099	9.9533	1.0000
H(24)	0.0804	0.6357	0.6471	12.7270	1.0000
H(28)	0.3529	0.7253	0.8163	12.3930	1.0000
H(29)	-0.1945	0.1295	0.6118	4.4401	1.0000
H(30)	-0.1323	0.0492	0.5831	4.4401	1.0000
H(31)	0.5037	0.0815	0.6590	4.9793	1.0000
H(32)	0.3939	0.0320	0.6029	4.9793	1.0000
H(33)	0.5040	0.2858	0.9787	5.3173	1.0000
H(34)	0.4329	0.3562	1.0097	5.3173	1.0000
H(35)	0.0697	0.5962	0.7572	5.1047	1.0000
H(36)	0.1693	0.6337	0.8222	5.1047	1.0000
H(37)	-0.057(8)	0.173(7)	0.710(5)	10(1)	1.0000
H(38)	0.38(1)	0.183(9)	0.661(7)	17(1)	1.0000
H(39)	0.315(8)	0.232(7)	0.895(5)	13(1)	1.0000
H(40)	0.252(9)	0.516(9)	0.776(6)	16(1)	1.0000
H(41)	0.1634	-0.1121	0.9253	10.5023	1.0000
H(42)	0.2487	-0.1268	0.8786	10.5023	1.0000
H(43)	0.2580	-0.0232	0.9234	10.5023	1.0000
H(44)	0.0065	-0.1773	0.8273	7.0495	1.0000
H(45)	-0.0045	-0.1309	0.7602	7.0495	1.0000
H(46)	0.0893	-0.1923	0.7789	7.0495	1.0000
H(47)	0.1116	0.0788	0.8914	13.9940	1.0000
H(48)	0.0107	0.0362	0.8277	13.9940	1.0000
H(49)	0.0182	-0.0100	0.8948	13.9940	1.0000
H(50)	-0.1703	0.1696	0.9454	11.2948	1.0000
H(51)	-0.1621	0.1791	0.8698	11.2948	1.0000
H(52)	-0.0586	0.1599	0.9218	11.2948	1.0000
H(53)	-0.1577	0.4224	0.9452	10.2692	1.0000
H(54)	-0.2233	0.3370	0.8843	10.2692	1.0000
H(55)	-0.2301	0.3278	0.9601	10.2692	1.0000
H(56)	0.0424	0.2995	1.0242	11.4516	1.0000
H(57)	0.0006	0.4000	1.0280	11.4516	1.0000
H(58)	-0.0744	0.3060	1.0418	11.4516	1.0000
H(59)	0.2016	0.7793	0.5910	12.1466	1.0000
H(60)	0.3729	0.8480	0.6584	10.8671	1.0000
H(61)	0.4471	0.8504	0.7734	13.3677	1.0000

B_{eq} = 8/3 $\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S3. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0375(6)	0.0490(7)	0.0421(7)	0.0110(5)	0.0101(5)	0.0062(6)
S(2)	0.0420(7)	0.0434(7)	0.0363(6)	0.0051(5)	0.0124(5)	0.0028(5)
S(3)	0.0385(6)	0.0409(7)	0.0470(7)	0.0090(5)	0.0073(5)	0.0082(5)
S(4)	0.0353(6)	0.0441(7)	0.0437(7)	0.0016(5)	0.0128(5)	-0.0021(5)
O(1)	0.061(2)	0.052(2)	0.059(2)	0.022(2)	0.016(2)	0.015(2)
O(2)	0.033(2)	0.062(2)	0.055(2)	0.003(2)	0.008(2)	-0.002(2)
O(3)	0.045(2)	0.046(2)	0.050(2)	0.000(2)	0.011(2)	-0.001(2)
O(4)	0.047(2)	0.063(2)	0.039(2)	0.015(2)	0.015(1)	0.003(2)
O(5)	0.041(2)	0.053(2)	0.061(2)	0.014(2)	0.017(2)	0.003(2)
O(6)	0.057(2)	0.054(2)	0.048(2)	0.012(2)	-0.002(2)	0.013(2)
O(7)	0.047(2)	0.071(2)	0.040(2)	0.008(2)	0.011(2)	0.002(2)
O(8)	0.044(2)	0.039(2)	0.066(2)	0.001(1)	0.016(2)	-0.001(2)
N(1)	0.038(2)	0.047(2)	0.035(2)	0.002(2)	0.012(2)	0.006(2)
N(2)	0.043(2)	0.047(3)	0.047(2)	0.009(2)	0.021(2)	0.014(2)
N(3)	0.047(2)	0.045(2)	0.037(2)	-0.003(2)	0.009(2)	0.011(2)
N(4)	0.046(2)	0.040(2)	0.050(2)	0.006(2)	0.021(2)	0.011(2)

C(1)	0.033(2)	0.040(2)	0.029(2)	0.001(2)	0.008(2)	0.004(2)
C(2)	0.034(2)	0.047(3)	0.035(2)	0.007(2)	0.007(2)	0.005(2)
C(3)	0.048(3)	0.043(3)	0.045(3)	0.007(2)	0.014(2)	0.011(2)
C(4)	0.048(3)	0.054(3)	0.043(3)	0.008(2)	0.016(2)	0.013(2)
C(5)	0.048(3)	0.050(3)	0.038(3)	0.007(2)	0.018(2)	0.006(2)
C(6)	0.044(3)	0.041(3)	0.033(2)	0.007(2)	0.009(2)	0.005(2)
C(7)	0.045(3)	0.039(3)	0.036(2)	0.007(2)	0.011(2)	0.004(2)
C(8)	0.043(3)	0.042(3)	0.044(3)	0.001(2)	0.015(2)	0.006(2)
C(9)	0.050(3)	0.034(2)	0.041(2)	0.005(2)	0.015(2)	0.003(2)
C(10)	0.052(3)	0.041(3)	0.039(3)	0.010(2)	0.011(2)	0.011(2)
C(11)	0.038(2)	0.035(2)	0.044(3)	0.007(2)	0.010(2)	0.007(2)
C(12)	0.040(2)	0.032(2)	0.037(2)	0.010(2)	0.015(2)	0.006(2)
C(13)	0.027(2)	0.040(2)	0.035(2)	-0.001(2)	0.003(2)	0.003(2)
C(14)	0.033(2)	0.044(3)	0.040(2)	0.003(2)	0.011(2)	0.000(2)
C(15)	0.046(3)	0.036(3)	0.057(3)	0.007(2)	0.023(2)	0.008(2)
C(16)	0.046(3)	0.042(3)	0.055(3)	0.007(2)	0.021(2)	0.012(2)
C(17)	0.043(3)	0.046(3)	0.053(3)	0.009(2)	0.021(2)	0.009(2)
C(18)	0.037(2)	0.041(3)	0.040(2)	0.004(2)	0.008(2)	0.006(2)
C(19)	0.034(2)	0.036(2)	0.042(2)	0.009(2)	0.015(2)	0.003(2)
C(20)	0.035(2)	0.036(2)	0.042(3)	0.002(2)	0.015(2)	0.000(2)
C(21)	0.041(3)	0.048(3)	0.039(2)	0.002(2)	0.015(2)	0.006(2)
C(22)	0.042(3)	0.047(3)	0.045(3)	0.003(2)	0.019(2)	0.009(2)
C(23)	0.036(2)	0.048(3)	0.050(3)	0.004(2)	0.013(2)	0.008(2)
C(24)	0.038(2)	0.045(3)	0.039(2)	0.009(2)	0.013(2)	0.008(2)
C(25)	0.036(2)	0.053(3)	0.045(3)	0.003(2)	0.011(2)	0.002(2)
C(26)	0.033(2)	0.048(3)	0.048(3)	0.000(2)	0.009(2)	0.003(2)
C(27)	0.051(3)	0.047(3)	0.073(4)	-0.001(2)	0.028(3)	0.003(3)
C(28)	0.063(4)	0.044(3)	0.087(4)	0.004(3)	0.027(3)	0.008(3)
C(29)	0.053(3)	0.062(4)	0.072(4)	0.005(3)	0.028(3)	0.025(3)
C(30)	0.062(3)	0.059(3)	0.061(3)	0.013(3)	0.031(3)	0.013(3)
C(31)	0.049(3)	0.049(3)	0.057(3)	0.008(2)	0.018(2)	0.010(2)
C(32)	0.044(3)	0.061(3)	0.057(3)	0.016(2)	0.021(2)	0.012(3)
C(33)	0.036(3)	0.068(3)	0.049(3)	0.008(2)	0.017(2)	0.010(3)
C(34)	0.055(3)	0.090(4)	0.050(3)	-0.002(3)	0.015(3)	0.014(3)
C(35)	0.063(4)	0.101(5)	0.069(4)	-0.017(4)	0.024(3)	0.017(4)
C(36)	0.072(4)	0.120(6)	0.067(4)	0.014(4)	0.037(4)	0.041(4)
C(37)	0.071(4)	0.141(7)	0.043(3)	0.003(4)	0.023(3)	0.014(4)
C(38)	0.057(3)	0.098(5)	0.052(3)	-0.002(3)	0.021(3)	0.000(3)
C(39)	0.068(4)	0.059(3)	0.037(3)	0.002(3)	0.006(2)	0.008(2)
C(40)	0.099(5)	0.060(4)	0.034(3)	0.002(3)	0.009(3)	0.007(3)
C(41)	0.170(9)	0.093(6)	0.076(5)	0.029(6)	-0.008(5)	0.038(5)
C(42)	0.31(2)	0.091(7)	0.089(8)	0.02(1)	-0.04(1)	0.046(6)
C(43)	0.32(2)	0.099(8)	0.050(5)	-0.06(1)	0.014(9)	0.025(5)
C(44)	0.20(1)	0.133(9)	0.110(7)	-0.024(8)	0.076(8)	0.054(7)
C(45)	0.137(7)	0.096(6)	0.101(6)	0.016(5)	0.068(5)	0.041(5)
C(46)	0.063(3)	0.044(3)	0.067(3)	0.013(3)	0.031(3)	0.013(2)
C(47)	0.114(6)	0.043(3)	0.114(6)	0.030(4)	0.079(5)	0.027(4)
C(48)	0.28(1)	0.064(5)	0.096(6)	0.048(6)	0.099(7)	0.035(4)
C(49)	0.61(4)	0.073(7)	0.23(2)	0.10(1)	0.32(2)	0.077(10)
C(50)	0.41(3)	0.11(1)	0.32(2)	0.15(2)	0.32(2)	0.14(1)
C(51)	0.139(9)	0.061(6)	0.39(2)	0.024(6)	0.17(1)	0.04(1)
C(52)	0.088(6)	0.065(5)	0.26(1)	0.020(4)	0.096(7)	0.053(6)
C(53)	0.094(5)	0.061(4)	0.081(4)	0.020(3)	0.053(4)	0.029(3)
C(54)	0.069(4)	0.051(3)	0.054(3)	0.004(3)	0.030(3)	0.013(3)
C(55)	0.072(4)	0.049(3)	0.102(5)	0.011(3)	0.054(4)	0.017(3)
C(56)	0.046(3)	0.067(4)	0.053(3)	-0.002(3)	0.022(2)	0.012(3)
C(541)	0.109(6)	0.136(7)	0.067(4)	-0.029(5)	0.008(4)	0.057(5)
C(542)	0.075(4)	0.072(4)	0.084(4)	-0.005(3)	0.028(3)	0.033(4)
C(543)	0.22(1)	0.088(6)	0.187(9)	0.044(6)	0.170(9)	0.037(6)
C(561)	0.180(8)	0.058(4)	0.137(7)	-0.014(5)	0.119(7)	0.009(4)

C(562)	0.097(6)	0.131(7)	0.128(7)	0.026(5)	0.080(5)	0.036(5)
C(563)	0.082(5)	0.203(9)	0.067(4)	-0.030(5)	0.028(4)	0.041(5)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

2.2 Tetraamino-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (7)

2.2.1 Preparation

Single crystals of **7** suitable for X-ray analysis were obtained by slow liquid diffusion of MeOH into $CHCl_3$ solution of **7**.

2.2.2 Crystallographic data

Empirical Formula	$C_{40}H_{52}N_4O_4S_4$
Formula Weight	781.12
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.15 X 0.15 X 0.20 mm
Crystal System	tetragonal
Lattice Type	I-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	5649 (0.0 - 56.4°)
Lattice Parameters	a = 15.4664(5)Å, c = 18.4847(6)Å V = 4421.7(2) Å^3
Space Group	$I4_1/a$ (#88)
Z value	4
D_{calc}	1.173 g/cm^3
F_{000}	1664.00
μ (MoKα)	2.56 cm^{-1}

2.2.3 Intensity Measurements

Diffractometer	Rigaku/MSC Mercury CCD
Radiation	MoKα (λ = 0.71069Å) graphite monochromated
Temperature	-123.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	5.0 mm
Detector Aperture	70 mm x 70 mm
Data Images	900 exposures at 30.0 seconds
ω oscillation Range (χ = 45°, ϕ = 0°)	-75.0 - 105.0°
ω oscillation Range (χ = 45°, ϕ = 90°)	-75.0 - 105.0°
Detector Position	40.00 mm
Pixel Size	0.137 mm
Detector Swing Angle	15.00°
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 15298, Unique: 2596 (R_{int} = 0.023)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8096 - 1.0000)

2.2.4 Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\, w\, (\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 5.00\sigma(I)$)	1402
No. Variables	138
Reflection/Parameter Ratio	10.16
Residuals: *R*; *Rw*	0.043 ; 0.050
Residuals: *R1*	0.043
No. of Reflections to calc *R1*	1402
Goodness of Fit Indicator	1.22
Max Shift/Error in Final Cycle	3.932
Maximum peak in Final Diff. Map	0.53 e^-/Å^3
Minimum peak in Final Diff. Map	-0.33 e^-/Å^3

2.2.5 Special Comments for Structure Refinement

Methyl carbons on *tert*-butyl groups, which were found disorderly, were refined in the 0.7:0.3 ratio of occupancy anisotropically for the major carbons and isotropically for minor ones. Hydrogen except for the disordered *tert*-butyl groups were found from D-map. Hydrogens for the major *tert*-butyl groups were calculated. Only amino hydrogens were refined isotropically and the other hydrogens were fixed in the refinement.

2.2.6 Results

Table S4. Atomic coordinates, B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
S(1)	-0.14748(5)	0.04063(5)	0.13044(4)	1.74(2)	1.0000
O(1)	-0.1395(2)	-0.0253(1)	0.0715(1)	2.32(5)	1.0000
N(1)	0.0278(2)	0.0794(2)	0.0530(2)	2.38(6)	1.0000
C(1)	0.0314(2)	0.0744(2)	0.1265(2)	1.68(6)	1.0000
C(2)	0.1084(2)	0.0848(2)	0.1656(2)	1.71(6)	1.0000
C(3)	0.1116(2)	0.0754(2)	0.2401(2)	2.20(7)	1.0000
C(4)	0.0382(2)	0.0582(3)	0.2811(2)	2.73(8)	1.0000
C(5)	-0.0393(2)	0.0499(2)	0.2436(2)	2.20(7)	1.0000
C(6)	-0.0432(2)	0.0580(2)	0.1683(2)	1.70(6)	1.0000
C(7)	0.0447(3)	0.0488(4)	0.3632(2)	5.2(1)	1.0000
C(8)	0.1102(5)	-0.0211(8)	0.3813(4)	6.5(2)	0.7000
C(8')	-0.011(2)	-0.046(2)	0.380(2)	9.2(7)	0.3000
C(9)	0.0888(7)	0.1364(8)	0.3926(3)	8.6(3)	0.7000
C(9')	-0.009(2)	0.119(2)	0.397(2)	8.5(7)	0.3000
C(10)	-0.0385(4)	0.0392(9)	0.3995(3)	7.8(3)	0.7000
C(10')	0.123(1)	0.034(1)	0.395(1)	4.4(4)	0.3000
H(1)	0.073(3)	0.078(3)	0.029(2)	3.0(9)	1.0000
H(2)	-0.018(3)	0.066(3)	0.032(2)	3.2(9)	1.0000
H(3)	0.1688	0.0832	0.2662	2.3442	1.0000
H(4)	-0.0959	0.0417	0.2730	2.3442	1.0000
H(5)	0.1719	0.0055	0.3623	1.9535	1.0000
H(6)	0.1189	-0.0121	0.4349	13.9193	1.0000
H(7)	0.0991	-0.0675	0.3670	13.9193	1.0000
H(8)	0.1405	0.1498	0.3683	16.4549	1.0000
H(9)	0.0493	0.1858	0.3859	16.4549	1.0000

H(10)	0.0976	0.1255	0.4471	1.9535	1.0000
H(11)	-0.0298	0.0494	0.4494	16.7950	1.0000
H(12)	-0.0757	0.0854	0.3823	1.9535	1.0000
H(13)	-0.0622	-0.0125	0.3892	16.7950	1.0000

B_{eq} = 8/3 $\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

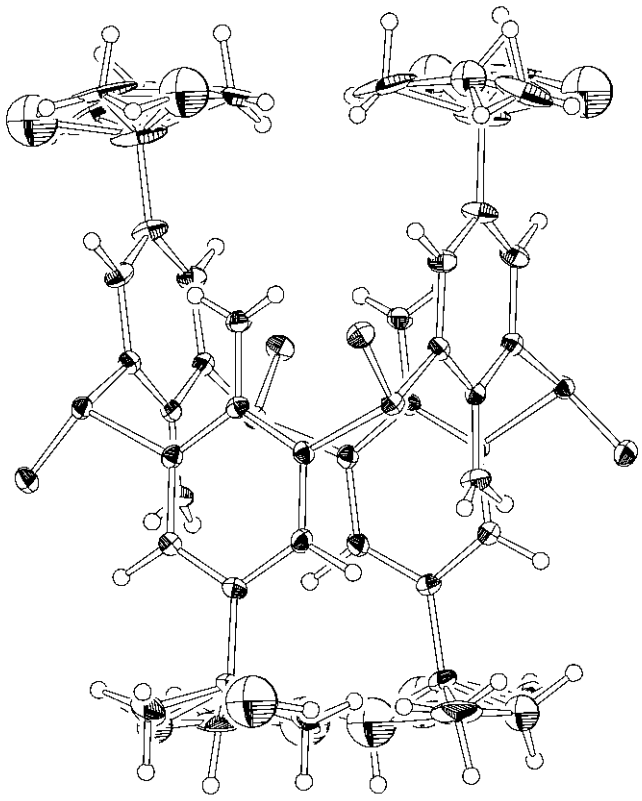


Figure S2. Ortep drawing of molecule **6**.

Table S5. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0224(4)	0.0208(4)	0.0229(4)	-0.0021(3)	0.0018(3)	0.0008(3)
O(1)	0.035(1)	0.023(1)	0.030(1)	-0.002(1)	0.002(1)	-0.006(1)
N(1)	0.023(2)	0.047(2)	0.020(1)	-0.006(1)	0.001(1)	-0.004(1)
C(1)	0.025(1)	0.018(1)	0.021(1)	0.000(1)	0.001(1)	-0.002(1)
C(2)	0.022(2)	0.019(2)	0.024(2)	0.002(1)	0.004(1)	0.002(1)
C(3)	0.025(2)	0.035(2)	0.023(2)	0.006(1)	-0.001(1)	0.001(1)
C(4)	0.029(2)	0.054(3)	0.020(2)	0.009(2)	0.000(1)	0.010(2)
C(5)	0.024(2)	0.034(2)	0.025(2)	0.007(1)	0.006(1)	0.008(1)
C(6)	0.021(2)	0.020(2)	0.023(2)	0.002(1)	-0.001(1)	0.000(1)
C(7)	0.037(2)	0.141(5)	0.021(2)	0.021(3)	-0.001(2)	0.020(3)
C(8)	0.062(5)	0.139(9)	0.048(5)	0.030(6)	0.003(4)	0.058(6)
C(9)	0.098(7)	0.21(1)	0.021(3)	-0.016(7)	-0.014(4)	-0.037(5)
C(10)	0.028(3)	0.25(1)	0.017(3)	0.024(5)	0.001(3)	0.049(5)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

2.3 Tetraamino-tetra-*p*-*tert*-butylthiacalix[4]arene (6)

2.3.1 Preparation

Single crystals of **6** suitable for X-ray analysis were obtained by slow liquid diffusion of MeOH into $CHCl_3$ solution of **6**.

2.3.2 Crystallographic data

Empirical Formula	$C_{40}H_{52}N_4S_4$
Formula Weight	717.12
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.30 X 0.20 X 0.20 mm
Crystal System	tetragonal
Lattice Type	I-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	5340 (0.0 - 55.0°)
Lattice Parameters	a = 15.1754(6) Å, c = 18.5967(8) Å V = 4281.8(3) Å^3
Space Group	$I4_1/a$ (#88)
Z value	4
D_{calc}	1.112 g/cm^3
F_{000}	1536.00
μ (MoKα)	2.52 cm^{-1}

2.3.3 Intensity Measurements

Diffractometer	Rigaku/MSC Mercury CCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Temperature	-93.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	5.0 mm
Detector Aperture	70 mm x 70 mm
Data Images	900 exposures at 30.0 seconds
ω oscillation Range (χ = 45°, ϕ = 0°)	-77.0 - 103.0°
ω oscillation Range (χ = 45°, ϕ = 90°)	-77.0 - 103.0°
Detector Position	40.00 mm
Detector Swing Angle	13.00°
Pixel Size	0.137 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 18329, Unique: 2498 (R_{int} = 0.023)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8960 - 1.0000)

2.3.4 Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\, w\, (|Fo| - |Fc|)^2$
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0500

Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 5.00\sigma(I)$)	1341
No. Variables	129
Reflection/Parameter Ratio	10.40
Residuals: *R*; *Rw*	0.042 ; 0.045
Residuals: *R1*	0.042
No. of Reflections to calc R1	1341
Goodness of Fit Indicator	1.56
Max Shift/Error in Final Cycle	0.205
Maximum peak in Final Diff. Map	0.23 e^-/Å^3
Minimum peak in Final Diff. Map	-0.17 e^-/Å^3

2.3.5 Special Comments for Structure Refinement

Methyl carbons on *tert*-butyl groups, which were found disorderly, were refined in the 0.7:0.3 ratio of occupancy anisotropically for the major carbons and isotropically for minor ones. Hydrogen except for the disordered *tert*-butyl groups were found from D-map. Hydrogens for the major *tert*-butyl groups were calculated. Only amino hydrogens were refined isotropically and the other hydrogens were fixed in the refinement.

2.3.6 Results

Table S6. Atomic coordinates, B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
S(1)	0.86569(4)	0.02838(4)	0.12350(4)	2.80(1)	1.0000
N(1)	1.0433(2)	0.0751(2)	0.0556(1)	3.10(4)	1.0000
C(1)	1.0432(2)	0.0737(1)	0.1294(1)	2.31(4)	1.0000
C(2)	1.1200(1)	0.0898(1)	0.1698(1)	2.41(4)	1.0000
C(3)	1.1202(2)	0.0807(2)	0.2437(1)	2.93(5)	1.0000
C(4)	1.0455(2)	0.0567(2)	0.2822(1)	3.39(5)	1.0000
C(5)	0.9690(2)	0.0432(2)	0.2427(1)	3.11(5)	1.0000
C(6)	0.9667(1)	0.0518(1)	0.1682(1)	2.50(4)	1.0000
C(7)	1.0484(2)	0.0469(3)	0.3642(1)	5.83(7)	1.0000
C(8)	1.1145(4)	-0.0193(5)	0.3855(3)	7.2(2)	0.7000
C(8')	1.021(1)	-0.071(1)	0.3727(8)	8.0(4)	0.3000
C(9)	1.0901(4)	0.1365(5)	0.3961(3)	8.0(2)	0.7000
C(9')	1.1286(9)	0.047(1)	0.3986(8)	6.3(3)	0.3000
C(10)	0.9610(3)	0.0398(6)	0.3974(2)	6.9(2)	0.7000
C(10')	0.976(2)	0.090(2)	0.399(1)	11.6(8)	0.3000
H(1)	1.088(2)	0.095(2)	0.034(2)	4.5(7)	1.0000
H(2)	0.989(2)	0.071(2)	0.035(2)	5.7(7)	1.0000
H(3)	1.1679	0.0942	0.2660	2.1937	1.0000
H(4)	0.9158	0.0347	0.2697	4.3681	1.0000
H(5)	1.1182	-0.0309	0.4348	8.7884	1.0000
H(6)	1.0972	-0.0789	0.3632	8.7884	1.0000
H(7)	1.1717	-0.0091	0.3661	8.7884	1.0000
H(8)	1.0941	0.1351	0.4473	9.3457	1.0000
H(9)	1.1474	0.1475	0.3769	9.3457	1.0000
H(10)	1.0535	0.1872	0.3836	9.3457	1.0000
H(11)	0.9246	0.0878	0.3838	7.5186	1.0000
H(12)	0.9332	-0.0140	0.3798	7.5186	1.0000
H(13)	0.9650	0.0361	0.4477	7.5186	1.0000

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S7. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0347(3)	0.0291(3)	0.0427(3)	-0.0051(3)	-0.0066(3)	0.0078(3)
N(1)	0.039(1)	0.048(1)	0.0306(9)	-0.0043(9)	0.003(1)	-0.0022(10)
C(1)	0.0338(9)	0.0240(9)	0.0300(9)	0.0023(7)	0.0024(9)	0.0022(10)
C(2)	0.028(1)	0.029(1)	0.035(1)	0.0036(9)	0.0061(8)	0.0054(9)
C(3)	0.028(1)	0.049(1)	0.035(1)	0.004(1)	-0.0040(9)	0.006(1)
C(4)	0.032(1)	0.064(2)	0.033(1)	0.006(1)	-0.0004(9)	0.017(1)
C(5)	0.029(1)	0.051(1)	0.038(1)	0.002(1)	0.0025(9)	0.017(1)
C(6)	0.0306(10)	0.027(1)	0.038(1)	0.0004(8)	-0.0021(8)	0.0066(9)
C(7)	0.034(1)	0.153(3)	0.034(1)	0.013(2)	0.002(1)	0.030(2)
C(8)	0.075(4)	0.148(6)	0.051(3)	0.035(3)	0.000(3)	0.056(4)
C(9)	0.085(4)	0.184(6)	0.035(3)	-0.022(4)	-0.001(3)	-0.030(3)
C(10)	0.037(2)	0.207(8)	0.019(2)	-0.004(4)	-0.001(2)	0.030(3)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

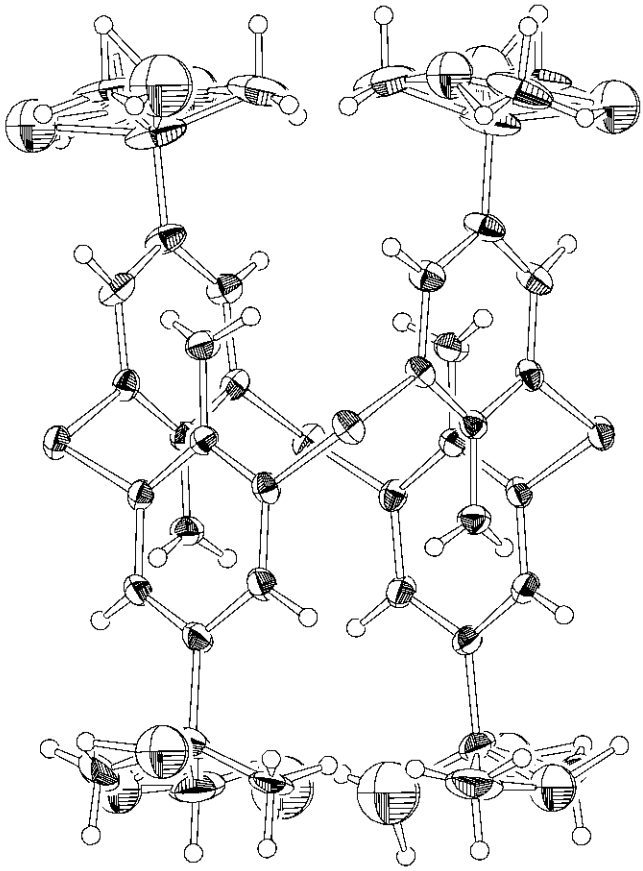


Figure S3. Ortep drawing of molecule **6**.