Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,3-Alternate thiacalix[4]bisazacrown chloroform disolvate

Xiong Li, Shu-Ling Gong,* Yu-Fang Liu, Qin Zheng and Yuan-Yin Chen

Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

Correspondence e-mail: gongsl@chem.whu.edu.cn

Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.057
wR factor = 0.177
Data-to-parameter ratio = 16.5

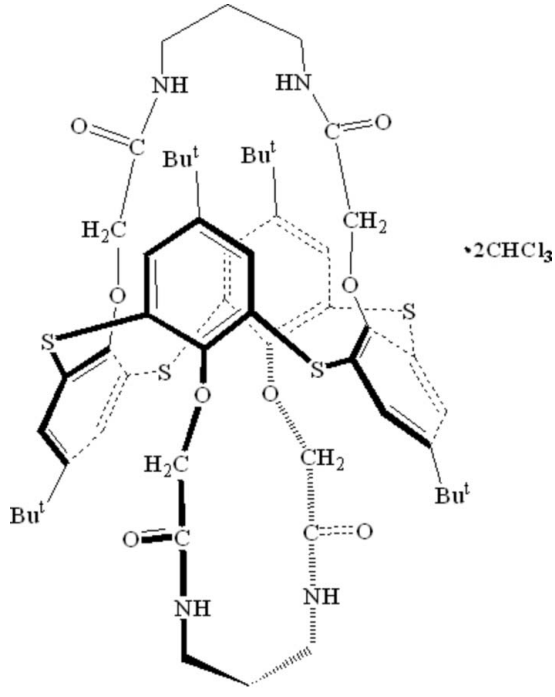
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 6 February 2007
Accepted 22 March 2007

In the title compound [systematic name: 5,11,17,23-*tert*-butyl-25,27:26,28-bis(2,8-dioxo-3,7-diazanonane-1,9-diyldioxy)-2,8,-14,20-tetrathiacalix[4]arene chloroform disolvate], $C_{54}H_{68}N_4O_8S_4\cdot 2CHCl_3$, the thiacalixarene molecule, locked in the 1,3-alternate conformation by two amide bridges, possesses twofold rotation symmetry with an cage-like cavity.

Comment

The title compound, a doubly amide-bridged thiacalix[4]arene, representing one of the first examples of cage-like molecules in thiacalixarene chemistry (Lhotak & Pojarova, 2006), has been prepared by a direct aminolysis reaction of thiacalix[4]arene tetraacetate with an excess of 1,3-diaminopropane. Similar structures of classical calix[4]arene analogues, which were obtained by a multistep synthesis starting with the corresponding diesters, have already been reported (Bitter *et al.*, 1999).



(I)

All four N—H bonds of both amide bridges are oriented into the cavity of thiacalix[4]arene and the amide groups form intramolecular hydrogen bonds to the ether O atoms (Table 1). The compound represents a well preorganized cavity with potential applications for the encapsulation of suitable guest molecules by possible hydrogen-bonding interactions.

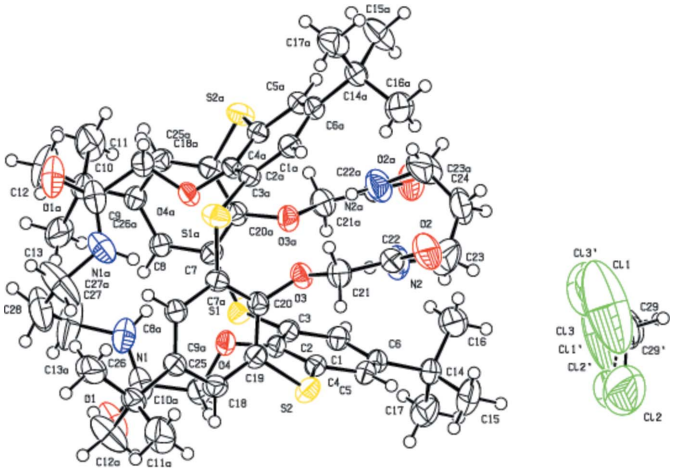


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The suffix a corresponds to symmetry code ($2 - x$, y, $\frac{1}{2} - z$). The chloroform molecule is disordered over two sites, both of which are shown.

Experimental

The title compound has been prepared by a direct aminolysis reaction of thiacalix[4]arene tetraacetate with an excess of 1,3-diaminopropane; a solution of thiacalix[4]arene tetraacetate (0.5 mmol) and 1,3-diaminopropane (50 mmol) in tetrahydrofuran (25 ml) was refluxed for 24 h. The reaction mixture was separated by column chromatography on silica gel with acetone as eluant. Single crystals of (I) were grown from a chloroform–acetone (1:1 *v*/*v*) solution.

Crystal data

$C_{54}H_{68}N_4O_8S_4\cdot 2CHCl_3$
$M_r = 1268.10$
Monoclinic, $C2/c$
$a = 21.8177$ (15) Å
$b = 16.5383$ (11) Å
$c = 17.7990$ (12) Å
$\beta = 105.171$ (1)°
$V = 6198.5$ (7) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.47$ mm^{-1}
$T = 297$ (2) K
0.47 × 0.43 × 0.31 mm

Data collection

Bruker SMART APEX II 4K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.811$, $T_{max} = 0.869$
18287 measured reflections
6416 independent reflections
5336 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.178$
$S = 1.11$
6416 reflections
390 parameters
65 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O4	0.86	2.24	2.650 (3)	110
N2—H2···O3	0.86	2.19	2.620 (3)	111
C16—H16A···O2^{i}	0.96	2.50	3.435 (4)	165
C29—H29···O1^{ii}	0.98	2.36	3.287 (16)	157

Symmetry codes: (i) $x, -y+1, z-\frac{1}{2}$; (ii) $x, y-1, z$.

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry (C—H = 0.96 Å) with U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—C bond. Other H atoms were placed in geometrically idealized positions (N—H = 0.86 and C—H = 0.93–0.98 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(N,C). The chloroform molecule is disordered over two sites with occupancy factors of 0.550 (8) and 0.450 (8). For the C—Cl bonds, a distance restraint of 1.74 (1) Å was used.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

The authors are greatly indebted to the National Natural Science Foundation of China for financial support of this work (No. 20272044).

References

Bitter, I., Grun, A., Balazs, B., Toth, G., Horvath, G. & Toke, L. (1999). *Synth. Commun.* **29**, 3905–3917.
Bruker (1997). *SMART*, *SAINT* and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Lhotak, P. & Pojarova, M. (2006). *J. Org. Chem.* **71**, 5404–5406.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.