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18-Isopropyl-15-(4-nitrophenyl)-5,8,11-trioxa-2,14-dithiabicyclo[14.4.1]henicosa-1(20),16,18-trien-21-one

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.006 Å
R factor = 0.055
wR factor = 0.167
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.

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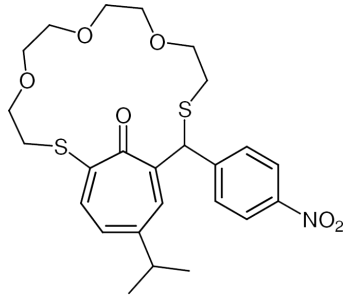
In the title 7-17 fused ring compound, $C_{25}H_{31}NO_6S_2$, the tropone ring is deformed to be a flattened boat conformation, with dihedral angles of 7.7 (3) and 16.9 (5)°. The best plane of the tropone ring intersects the crown S_2O_3 plane at an angle of 58.5 (1)°.

Comment

Mercurophilic dithiacrown derivatives having a troponoid pendant (Mori *et al.*, 1996, 1997; Kubo *et al.*, 1998) were recently prepared since these molecules are excellent carriers of the mercury(II) ion. Particularly noteworthy is, based on their reversible complexation behaviors with mercury(II) salts, the exclusive and selective transport of the mercury(II) ion among various metal ions through a liquid membrane.

As a matter of efficiency in the transport of the mercury(II) ion, the dithiacrown derivatives condensed with a tropone system showed a dependence on the cavity size of the crown ethers (Mori *et al.*, 1996). This was confirmed by the X-ray analyses (Kubo *et al.*, 1995, 1996, 2000*a*,*b*; Kato *et al.*, 1995; Mori *et al.*, 1998). In order to reveal the detailed structure of troponoid dithiacrown ether derivatives, the title compound, (I), has been investigated by X-ray analysis.



(I)

In (I), the tropone ring (O1 and C1–C7) makes angles of 58.5 (1), 59.6 (1) and 60.0 (2)° with the crown ether ring (defined by S1–S2 and O2–O4), the benzene ring (C20–C25), and the isopropyl group (C8–C10), respectively. The conformation of the ethereal moiety is: C11(*g*)S1(*g*)C12(*g*)C13(*t*)O2(*g*)C14(*g*)C15(*t*)O3(*t*)C16(*g*)C17(*t*)O4(*t*)C18(*g*)C19(*t*)S2, where *t* and *g* denote *trans* and *gauche* forms, respectively.

The tropone ring adopts a flattened boat conformation. The angle between the least-squares plane defined by C2/C3/C6/C7 and the plane defined by C3/C4/C5/C6 is 7.7 (3)°. The flattened boat form of the tropone ring was also observed in related compounds. In (I), the angle between the C1/C2/C7 and C2/C3/C6/C7 planes is 16.9 (5)°, which is smaller than that [20.8 (4)°] of 5,8,11-trioxa-2,14-dithiabicyclo[13.4.1]icosa-

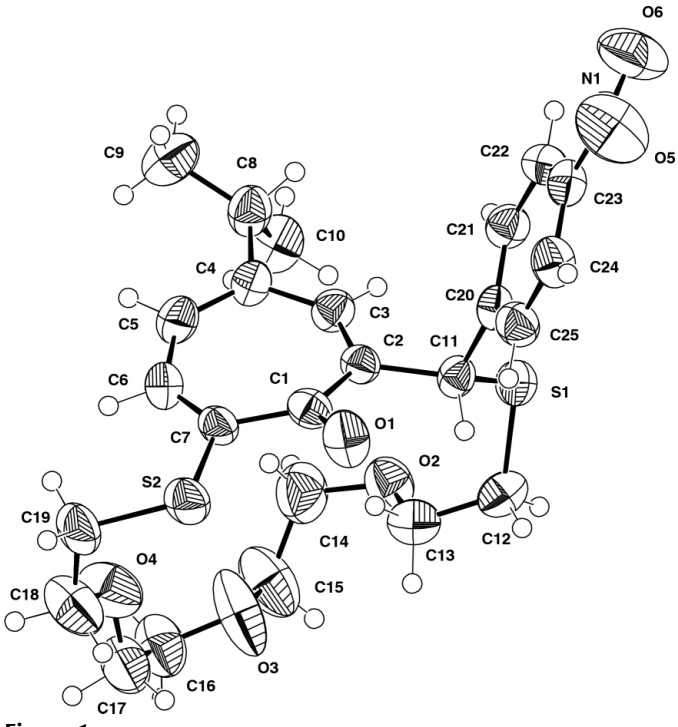


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.

1(19),15,17-trien-20-one (Kubo *et al.*, 2000*a*) and that [33.8 (6)°] of 5-oxa-2,8-dithiabicyclo[7.4.1]tetradeca-9,11,13-trien-14-one (Mori *et al.*, 1998). This result suggests that the smaller size of the crown ethers leads to increased deformation of the tropone ring.

Experimental

The title compound, (I), was obtained by condensation from NaH-mediated 3,6,9-trioxa-1,11-undecanedithiol and 4-isopropyl-2-(α-tosyloxy-4-nitrobenzyl)tropone (Mori *et al.*, 1992). Single crystals of (I) were obtained by recrystallization from $CHCl_3$.

Crystal data

$C_{25}H_{31}NO_6S_2$
M_r = 505.63
Monoclinic, $P2_1/c$
a = 11.663 (1) Å
b = 18.862 (2) Å
c = 11.363 (1) Å
β = 94.882 (6)°
V = 2490.6 (3) Å^3
Z = 4
D_x = 1.348 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
θ = 10.1–18.0°
μ = 0.26 mm^{-1}
T = 296 (2) K
Prism, yellow
0.3 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius FR590 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.982, T_{max} = 1.000
5321 measured reflections
5059 independent reflections
2259 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 26.3°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.167
S = 1.00
5059 reflections
307 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.8224P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S2—C7	1.756 (4)	C3—C4	1.417 (5)
O1—C1	1.236 (4)	C4—C5	1.369 (6)
C1—C2	1.469 (5)	C5—C6	1.410 (6)
C1—C7	1.476 (5)	C6—C7	1.359 (6)
C2—C3	1.352 (5)		
C3—C4—C8—C9	−156.8 (4)	O2—C14—C15—O3	89.5 (6)
C3—C4—C8—C10	73.6 (5)	C15—O3—C16—C17	−170.5 (5)
C12—S1—C11—C2	−83.5 (3)	C18—O4—C17—C16	177.9 (5)
C11—S1—C12—C13	66.4 (4)	O3—C16—C17—O4	67.5 (6)
C14—O2—C13—C12	−169.0 (4)	C17—O4—C18—C19	165.1 (4)
S1—C12—C13—O2	67.5 (4)	O4—C18—C19—S2	−64.9 (6)
C13—O2—C14—C15	−57.9 (6)	C7—S2—C19—C18	93.3 (4)
C16—O3—C15—C14	128.6 (5)	C2—C11—C20—C21	−74.2 (5)

All H atoms were located at ideal positions and constrained with U_{iso} held fixed to 1.2 times or 1.5 (H_2O) times U_{eq} of the parent atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL*97.

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *SIR*97. *J. Appl. Cryst.* **32**, 115–119.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
Hall, S. R. & du Boulay, D. (1995). *Xtal_GX*. University of Western Australia, Australia.
Kato, N., Kubo, K., Mori, A. & Takeshita, H. (1995). *Heterocycles*, **41**, 1901–1904.
Kubo, K., Kato, N., Mori, A. & Takeshita, H. (1995). *Chem. Lett.* pp. 629–630.
Kubo, K., Mori, A., Kato, N. & Takeshita, H. (1996). *Acta Cryst.* C**52**, 1656–1658.
Kubo, K., Mori, A., Kato, N. & Takeshita, H. (1998). *Heterocycles*, **49**, 385–392.
Kubo, K., Kato, N., Mori, A. & Takeshita, H. (2000*a*). *Heterocycles*, **53**, 535–538.
Kubo, K., Mori, A., Kato, N. & Takeshita, H. (2000*b*). *Acta Cryst.* C**56**, e396–e397.
Mori, A., Yin, B. Z. & Takeshita, H. (1992). *Chem. Express*, **7**, 313–316.
Mori, A., Kubo, K. & Takeshita, H. (1996). *Coord. Chem. Rev.* **148**, 71–96.
Mori, A., Kubo, K. & Takeshita, H. (1997). *Heterocycles*, **46**, 509–516.
Mori, A., Kubo, K., Kato, N., Takeshita, H., Shiono, M. & Achiwa, N. (1998). *Heterocycles*, **47**, 149–152.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.