C4a—C4b—C5	121.9 (2)	C4a—C10a—C10	120.3 (2)
C4a—C4b—C8a	119.8 (2)	C13—C12—S	107.45 (13)
C4b—C8a—C9	119.47 (15)	C14—C13—C12	111.3 (2)
C10—C9—C8a	120.1 (2)		

Compound (4)

Crystal data

$C_{18}H_{18}S$
$M_r = 266.38$
Monoclinic
$P2_1/c$
$a = 9.010$ (4) Å
$b = 23.124$ (8) Å
$c = 6.888$ (3) Å
$\beta = 97.81$ (3)°
$V = 1421.8$ (10) Å^3
$Z = 4$
$D_x = 1.244$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20
  reflections
$\theta = 4–8°$
$\mu = 0.211$ mm^{-1}
$T = 193$ (2) K
Plate
$0.3 \times 0.2 \times 0.2$ mm
Colourless

Data collection

Rigaku AFC-7S diffractom-
  eter
$\omega/2\theta$ scans
Absorption correction: none
2851 measured reflections
2851 independent reflections
2273 reflections with
  $I > 2\sigma(I)$

$\theta_{max} = 26.51°$
$h = -11 \rightarrow 11$
$k = -28 \rightarrow 28$
$l = 0 \rightarrow 8$
20 standard reflections
  every 100 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.166$
$S = 1.964$
2839 reflections
227 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0016P)^2 + 0.1P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.077$
$\Delta\rho_{max} = 0.362$ e Å^{-3}
$\Delta\rho_{min} = -0.631$ e Å^{-3}
Extinction correction:
  SHELXL93
Extinction coefficient:
  0.0016 (14)
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 4. *Selected geometric parameters (Å, °) for (4)*

S—C9	1.766 (3)	C8a—C9	1.459 (4)
S—C12	1.803 (3)	C9—C10	1.357 (4)
C4—C4a	1.410 (3)	C10—C10a	1.430 (4)
C4a—C4b	1.449 (4)	C12—C13	1.527 (4)
C4a—C10a	1.416 (4)	C13—C14	1.525 (4)
C4b—C5	1.418 (4)	C14—C15	1.521 (4)
C4b—C8a	1.430 (3)		
C9—S—C12	104.51 (13)	C10—C9—S	123.6 (2)
C4—C4a—C4b	123.1 (2)	C8a—C9—S	115.7 (2)
C4b—C4a—C10a	118.8 (2)	C9—C10—C10a	121.5 (2)
C4a—C4b—C5	122.5 (2)	C4a—C10a—C10	120.3 (2)
C4a—C4b—C8a	120.2 (2)	C13—C12—S	107.5 (2)
C4b—C8a—C9	118.4 (2)	C14—C13—C12	111.7 (2)
C10—C9—C8a	120.7 (2)	C15—C14—C13	112.1 (3)

Observed intensities were corrected for Lorentz and polar-ization effects and extinction. All non-H atoms were refined anisotropically. H atoms with isotropic U values were placed in calculated positions and refined using a riding model for (1), (2) and (4). In compound (3), additional H-atom coordinates and isotropic U values were refined.

For all compounds, data collection: *MSC/AFC Diffrac-tometer Control Software* (Molecular Structure Corpora-tion, 1992); cell refinement: *MSC/AFC Diffractometer Con-trol Software*; data reduction: *TEXSAN* (Molecular Struc-ture Corporation, 1993); program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC*; software used to prepare material for publica-tion: *SHELXL93*.

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5,8-Bis(4-methoxy-2,3,6-trimethylbenzene-sulfonyl)-1,4-dioxa-5,8-diazocane

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Abstract

The molecular shape of the title compound, $C_{24}H_{34}N_2$-O_8S_2, in the crystalline state is characterized by internal twofold symmetry, with the eight-membered ring adopt-ing a crown conformation.

Comment

For the last decade, the field of macrocyclic chemistry has generated intense interest among scientists because of its wide range of applications (Alexander, 1995; Dietrich, Viout & Lehn, 1993). In our continued effort to synthesize novel macrocycles, in particular those related to oxa-macrocycles, which potentially exhibit degenerate properties when complexed with metals, we isolated, from the reaction between bis[N-(4-methoxy-2,3,6-benzenesulfonyl)]diaminoethan-1,2-diol and bis-(tosyl)ethan-1,2-diol in the presence of caesium carbonate in anhydrous DMF, the 1:1 adduct, (1), instead of the 2:2 adduct, (2). NMR and mass spectroscopic analysis of the product did not fully discriminate between (1) and (2). In the mass spectrum, although the main peak was observed at 543.5 m.u. (M^+ + H), a low-intensity peak was also recorded at 1086.5 m.u. ($2M^+$ + H). A single-crystal structure determination was therefore undertaken and has confirmed the exclusive formation of the 1:1 adduct, (1).
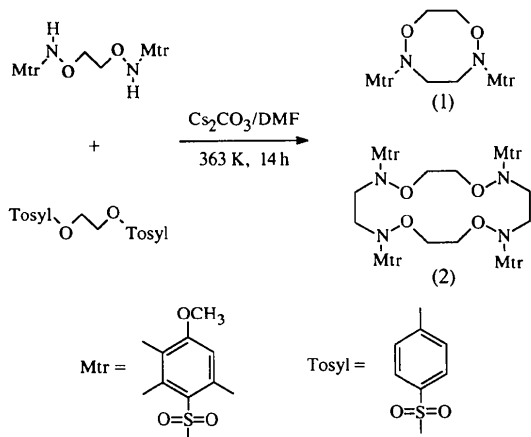
The molecular structure of (1) with the labelling scheme is depicted in Fig. 1. The molecule possesses approximate C_2 point symmetry, with the twofold axis running through the midpoints of the bonds C3—C4 and
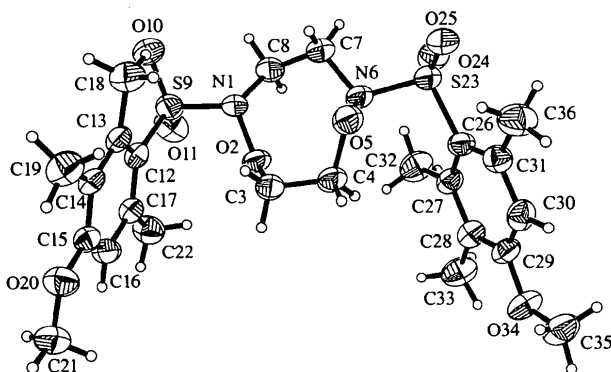
C7—C8. Only the phenyl-ring substituent atoms C19, O20, C21, C22 and their pseudo-symmetric equivalents C33, O34, C35, C36 fail to satisfy the internal rotation symmetry. The best plane through the eight-membered ring (r.m.s. deviation 0.342 Å) makes an angle of 74.1 (1)° with the best plane through ring C12–C17 (r.m.s. deviation 0.009 Å), and of 55.9 (1)° with the best plane through ring C26–C31 (r.m.s. deviation 0.014 Å).

The atoms of the eight-membered ring are displaced alternately above and below the best plane through the eight atoms. This crown conformation is energetically the most favourable, with the C3—C4 and C7—C8 bonds having *gauche* conformations [torsion angles O2—C3—C4—O5 61.9 (5) and N6—C7—C8—N1 64.7 (5)°] and the sulfonyl groups placed equatorially. According to the Cremer & Pople (1975) treatment, the eight-membered ring (numbered in sequence N1, O2...) can be described by the puckering coordinates $q(2)$, $q(3)$, $q(4)$, $\varphi(2)$ and $\varphi(3)$, which are 0.477 (4), 0.020 (4) and −0.843 (4) Å and 230.3 (5) and 122 (11)°, respectively. Both N atoms are sp^3 hybridized, with the sum of the angles around the N atom being 326 (N1) and 329° (N6).

The crystal packing shows the stacking of the aromatic rings and short intermolecular contacts (2.450 Å) between atoms O10 and H21C of molecules related by an inversion centre.

Experimental

Diaminoethane-1,2-diol dihydrochloride, prepared as previously described (Shirayev, Moiseev & Kong Thoo Lin, 1997) (0.25 g, 0.0015 mol) was dissolved in anhydrous pyridine (15 ml). To this solution was added 4-methoxy-2,3,6-trimethyl-benzenesulfonyl chloride (0.79 g, 0.0032 mol). After 2 h the solvent was removed and the solid residue was dissolved in chloroform and washed with bicarbonate solution. Evaporation of the solvent gave a solid which was recrystallized from acetonitrile to give bis(N-Mtr)diaminoethan-1,2-diol as colourless crystals (42%). To a solution of the ethan-1,2-diol (15.5 g, 0.25 mol) and triethylamine (71 ml, 0.5 mol) in dichloromethane (400 ml) was added tosyl chloride (95 g, 0.5 mol). After 5 h, at room temperature a precipitate formed. It was filtered off and the filtrate was washed with bicarbonate solution. After drying and evaporation of the dichloromethane layer, the crude product was recrystallized from ethanol to afford pure bis(tosyl)ethan-1,2-diol as colourless crystals (66%). A mixture of bis(N-Mtr)diaminoethan-1,2-diol (0.25 g, 0.00048 mol), bis(tosyl)ethan-1,2-diol (0.179 g, 0.00048 mmol) and Cs_2CO_3 (0.358 g, 0.0011 mmol) in anhydrous DMF (30 ml) was heated at 363 K for 14 h in a pressure bottle. The residue left after removal of solvent was dissolved in water and extracted three times with chloroform. After drying and evaporation of the solvent, the crude product was recrystallized from ethanol/acetonitrile to give (1) as colourless crystals (24%, m.p. 481–483 K). FAB MS (VGZAB–E NOBA matrix): m/z = 543.5 (M^+ + H). ^{1}H NMR (CDCl$_3$, 90 MHz, Jeol EX90, δ p.p.m.): 2.08 (3H singlet, CH$_3$), 2.53 (3H singlet, CH$_3$), 2.62

Fig. 1. View of (1) with labelling showing 50% probability displacement ellipsoids (*SHELXTL/PC*; Sheldrick 1990). H atoms are shown as small circles of arbitrary radii.

(3H singlet, CH₃), 3.28 (2H singlet, CH₂), 3.71 (2H singlet, CH₂), 3.79 (3H singlet, OCH₃), 6.54 (1H singlet, aromatic proton).

Crystal data

$C_{24}H_{34}N_2O_8S_2$	Cu $K\alpha$ radiation
$M_r = 542.65$	$\lambda = 1.54178$ Å
Triclinic	Cell parameters from 20
$P\bar{1}$	reflections
$a = 9.079\,(1)$ Å	$\theta = 11–19°$
$b = 10.188\,(2)$ Å	$\mu = 2.282$ mm⁻¹
$c = 14.920\,(2)$ Å	$T = 289\,(2)$ K
$\alpha = 74.49\,(1)°$	Block
$\beta = 80.00\,(1)°$	$0.40 \times 0.35 \times 0.20$ mm
$\gamma = 83.13\,(1)°$	White
$V = 1305.7\,(3)$ Å³	
$Z = 2$	
$D_x = 1.380$ Mg m⁻³	
D_m not measured	

Data collection

Siemens P4-PC diffractometer	$R_{int} = 0.039$
	$\theta_{max} = 50.44°$
$2\theta/\omega$ scans	$h = -1 \rightarrow 8$
Absorption correction: none	$k = -9 \rightarrow 9$
3455 measured reflections	$l = -14 \rightarrow 14$
2684 independent reflections	3 standard reflections
2479 reflections with	every 97 reflections
$I > 2\sigma(I)$	intensity decay: 5%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.058$	$\Delta\rho_{max} = 0.33$ e Å⁻³
$wR(F^2) = 0.165$	$\Delta\rho_{min} = -0.35$ e Å⁻³
$S = 1.061$	Extinction correction:
2682 reflections	SHELXL93 (Sheldrick,
326 parameters	1993)
H atoms riding with $U(H) = 1.2U_{eq}(C)$	Extinction coefficient: 0.0012 (5)
$w = 1/[\sigma^2(F_o^2) + (0.0979P)^2 + 1.6198P]$ where $P = (F_o^2 + 2F_c^2)/3$	Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—O2	1.445 (4)	N6—S23	1.689 (4)
N1—C8	1.456 (5)	C7—C8	1.495 (6)
N1—S9	1.708 (4)	S9—O11	1.421 (3)
O2—C3	1.428 (5)	S9—O10	1.441 (3)
C3—C4	1.501 (6)	S9—C12	1.763 (4)
C4—O5	1.439 (5)	S23—O25	1.420 (4)
O5—N6	1.440 (4)	S23—O24	1.430 (4)
N6—C7	1.482 (6)	S23—C26	1.776 (4)
O2—N1—C8	108.0 (3)	O11—S9—O10	117.1 (2)
O2—N1—S9	105.7 (2)	O11—S9—N1	111.16 (19)
C8—N1—S9	112.6 (3)	O10—S9—N1	103.58 (18)
C3—O2—N1	110.3 (3)	O11—S9—C12	111.2 (2)
O2—C3—C4	112.7 (3)	O10—S9—C12	112.1 (2)
O5—C4—C3	112.5 (3)	N1—S9—C12	100.04 (18)
N6—O5—C4	110.6 (3)	O25—S23—O24	117.4 (2)
O5—N6—C7	109.0 (3)	O25—S23—N6	110.89 (19)
O5—N6—S23	106.2 (2)	O24—S23—N6	104.1 (2)
C7—N6—S23	113.4 (3)	O25—S23—C26	111.1 (2)
N6—C7—C8	112.5 (4)	O24—S23—C26	111.4 (2)
N1—C8—C7	112.6 (4)	N6—S23—C26	100.38 (18)

Rapid decomposition of the crystal led to premature termination of the data collection ($\theta_{max} = 50°$) and precluded measurement of ψ-scan data for empirical absorption.

Data collection and data reduction: *XSCANS* (Siemens, 1992). Program used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program used to refine structure and to prepare material for publication: *SHELXL93* (Sheldrick, 1993) and *SHELXTL/PC*. Program used to search for internal symmetry: *BUNYIP* in *Xtal3.4* (Hall, King & Stewart, 1995). Molecular graphics: *SHELXTL/PC*.

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Two Pairs of Stereoisomers of Dimethyl 2-(3,4,5-Trimethoxyphenyl)tetrahydrofuran-3,4-dicarboxylate

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Abstract

Two racemic pairs of stereoisomers of the title compound, $C_{17}H_{22}O_8$, were characterized by single-crystal