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Polysulfonylamines. CI. 1,4,7,10-Tetraoxacyclododecane–Di(benzenesulfonyl)amine (1/2)[†]

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Abstract

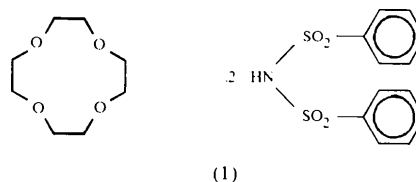
In the centrosymmetric formula unit of the title complex, C₈H₁₆O₄·2C₁₂H₁₁NO₄S₂, the disulfonylamine molecules are linked to 12-crown-4 via a slightly bent N—H···O hydrogen bond [N···O 2.771 (2) Å]. The macrocycle adopts the [66] conformation and the (PhSO₂)₂NH molecules have an open pseudo-C₂ symmetric conformation with the phenyl groups lying on opposite sides of the S–N–S plane.

Comment

Hydrogen-bond-mediated crystalline complexes between uncharged molecules and coronands, especially

[†] Part C: Moers *et al.* (1998).

1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), have attracted much attention since the first representatives were reported in 1971 (Pedersen, 1971). It was alleged in a review article that 'guests containing monodentate acidic OH groups...do not associate directly with 18-crown-6'; instead, ternary complexes having water molecules inserted between the substrate and the hexafunctional 18-crown-6 ring were reported to be formed preferentially (Goldberg, 1989; for updated references *cf.* Henschel, Blaschette & Jones, 1995). In contrast to these findings and using di(organo-sulfonyl)amines, (RSO₂)₂NH, as substrates, we were able to demonstrate that binary hydrogen-bonded complexes of 18-crown-6 with mono-acidic guests can indeed be isolated despite the donor–acceptor disparity of their molecular components. Thus, N—H···O-bonded adducts of 18-crown-6 with di(methanesulfonyl)amine (3:2) and bis(2-naphthalenesulfonyl)amine (1:2) were obtained by co-crystallization from anhydrous methanol or 2-propanol, respectively, and structurally characterized by low-temperature X-ray diffraction (Blaschette *et al.*, 1994; Henschel, Nèveke *et al.*, 1995). As an extension of this work, we now present the first example, (1), of a binary complex in which a disulfonylamine is directly attached to the smaller coronand 1,4,7,10-tetraoxacyclododecane (12-crown-4).



The centrosymmetric formula unit of the title complex is shown in Fig. 1; selected intramolecular geometric data are listed in Table 1. A slightly bent N—H···O hydrogen bond, in which the N···O distance is *ca* 0.17 Å shorter than the sum of the van der Waals radii (2.94 Å; Emsley, 1991), links the N—H acids to the crown ether [N—H01 0.80 (2), H01···O34 1.98 (2), N···O34 2.771 (2) Å and N—H01···O34 170 (2)°]. Together with the analogous adducts 12-crown-4.2D, where D = Ph₃SiOH (Babaian *et al.*, 1990) or (EtSO₂)₂CH₂ (Michalides *et al.*, 1995), compound (1) forms a series of binary complexes displaying O—H···O, C—H···O or N—H···O interactions.

The macrocycle in (1) adopts the C_v-symmetric [66] conformation that also occurs in pure crystalline 12-crown-4 (Groth, 1978), in the aforementioned molecular 1:2 complexes and in a number of other structures [for systematic conformational analyses of the coronand in its complexes *cf.* Raithby *et al.* (1997) and Hay *et al.* (1995)]. The C—O [average 1.431 (2) Å] and C—C distances [average 1.499 (3) Å] are normal, as are the C—O—C angles [average 114.59 (14)°], the O—C—C angles [average 110.2 (2)°] and the 'bite' of the

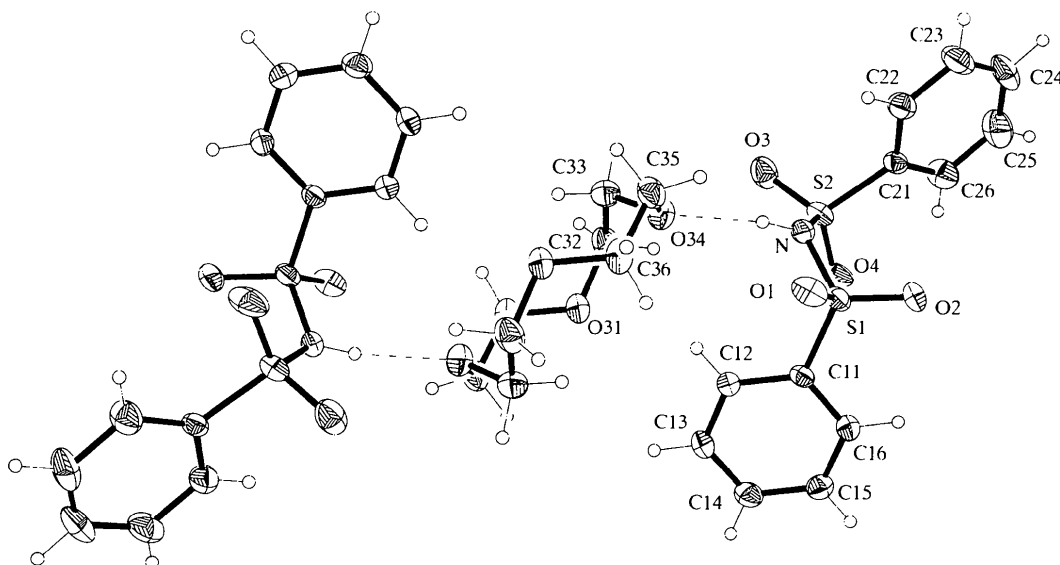


Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary.

coronand [average distance between adjacent O atoms: 2.975(2) Å]. The torsion angles of the crown are included in Table 1.

The observed solid-state conformations of the (CSO₂)₂N moiety in disulfonylamines and disulfonylamides vary between the C₂-symmetric (open or extended) and C_s-symmetric (folded or hairpin-like) archetypes, the C atoms lying on opposite sides of the S–N–S plane in the former and on the same side of this plane in the latter case (Bombicz *et al.*, 1996). In the present structure, the (PhSO₂)₂NH molecules display an extended conformation roughly approximating to C₂ symmetry (*cf.* torsion angles in Table 1). A similar geometry was found in the structure of the uncomplexed compound, where the molecules are linked into chains by an N—H···O hydrogen bond [N···O 2.854(6) Å; Cotton & Stokely, 1970].

Experimental

A solution of 12-crown-4 (0.18 g, 1.1 mmol) and (PhSO₂)₂NH (0.60 g, 2.0 mmol) in anhydrous nitromethane (10 ml) was stored for 3 d at 243 K in a closed flask. The crystals, which separated in a yield of 64% (0.49 g), were suitable for X-ray analysis. M.p. 363–398 K [for comparison, m.p. of pure 12-crown-4 *ca* 273 K (Groth, 1978) and m.p. of (PhSO₂)₂NH 429–430 K (DeChristopher *et al.*, 1974)]. ¹H NMR (CD₃CN, 200 MHz): 3.59 (s, 16H, 12-crown-4), 7.48–7.58 and 7.63–7.85 (12H and 8H, aromatic H); δ(NH) not detected. Elemental analysis for a sample analogously obtained in anhydrous methanol (crystals not suitable for X-ray study): found C 49.92, H 4.94, N 3.64, S 16.44%; C₃₂H₃₈N₂O₁₂S₄ requires C 49.86, H 4.97, N 3.63, S 16.64%.

Crystal data

C₈H₁₆O₄·2C₁₂H₁₁NO₄S₂

*M*_r = 770.88

Monoclinic

*P*2₁/*n*

a = 10.2947(10) Å

b = 16.368(2) Å

c = 10.3822(10) Å

β = 96.845(10)°

V = 1737.0(3) Å³

Z = 2

*D*_x = 1.474 Mg m⁻³

*D*_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 64 reflections

θ = 3.0–12.5°

μ = 0.340 mm⁻¹

T = 173(2) K

Irregular block

0.60 × 0.50 × 0.40 mm

Colourless

Data collection

Siemens *P4* diffractometer

ω scans

Absorption correction: none

3906 measured reflections

3050 independent reflections

2523 reflections with

I > 2σ(*I*)

*R*_{int} = 0.015

θ_{max} = 25°

h = -12 → 12

k = -19 → 3

l = -12 → 0

3 standard reflections

every 250 reflections

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.028

wR(*F*²) = 0.073

S = 1.037

3050 reflections

231 parameters

H atoms: see below

w = 1/[σ²(*F*_o²) + (0.039*P*)²

+ 0.4308*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.34 e Å⁻³

Δρ_{min} = -0.28 e Å⁻³

Extinction correction:

SHELXL93

Extinction coefficient:

0.0050(7)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

N—S1	1.6552 (15)	N—S2	1.6578 (15)
S1—N—S2	124.97 (10)	H01—N—S2	111 (1)
H01—N—S1	115 (1)		
S2—N—S1—O1	176.56 (10)		
S2—N—S1—O2	48.44 (12)		
S2—N—S1—C11	-68.21 (12)		
S1—N—S2—O3	160.72 (10)		
S1—N—S2—O4	31.44 (13)		
S1—N—S2—C21	-85.81 (11)		
N—S1—C11—C12	-55.43 (15)		
N—S2—C21—C22	-46.71 (16)		
O31—C32—C33—O34	73.49 (19)		
C32—C33—O34—C35	-153.49 (15)		
C33—O34—C35—C36	97.73 (18)		
O34—C35—C36—O31 ¹	-76.43 (19)		
C35—C36—O31 ¹ —C32 ¹	161.40 (15)		
C36—O31 ¹ —C32 ¹ —C33 ¹	-94.79 (18)		

Symmetry code: (i) 2 - x, 1 - y, 1 - z.

H atoms were initially placed in geometrically calculated positions, except for the amino H atom, which was found in a difference Fourier synthesis. During refinement, these H atoms were refined freely and constrained to ride on their parent C atoms, respectively. For all H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: XSCANS (Fait, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1226). Services for accessing these data are described at the back of the journal.

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2-Dicyanomethylene-5,6-dimethyl-1,2-dihydropyridine-3-carbonitrile†

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Abstract

The title compound, C₁₁H₈N₄, exists as the NH tautomer (a 1,2-dihydropyridine) in the solid state, although the bond-length differences in the ring are minimal (thus implying delocalized multiple bonding). Molecules are linked in pairs by N—H···N hydrogen bonds over inversion centres.

Comment

We have described several novel syntheses of 2(1H)-pyridinethiones (Elgemeie *et al.*, 1990; Elgemeie, Elzanate & Mansour, 1992; Elgemeie, Alnaimi & Alarab, 1992). These compounds, as well as a number of suitably functionalized pyridine derivatives, are considered important intermediates for the synthesis of various

† Zwitterionic name: (3-cyano-5,6-dimethyl-2-pyridinio)dicyano-methanide.