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Polysulfonylamines. CVI.† 1,4,7,10,13,16-Hexaoxacyclooctadecane–Dimethyl Sulfoxide–Bis(4-fluorophenylsulfonyl)amine (1/2/2)

KARNA WIJAYA, OLIVER MOERS, ARMAND BLASCHETTE* AND PETER G. JONES*

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36. anchem.nat.tu-bs.de

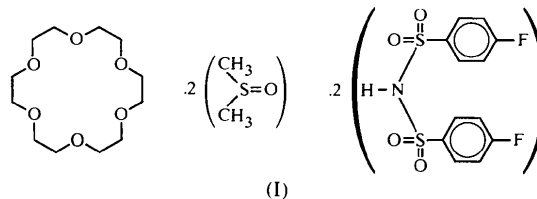## Abstract

In the centrosymmetric formula unit of the title complex, $C_{12}H_{24}O_6.2C_2H_6OS.2C_{12}H_9F_2NO_4S_2$, each dimethyl sulfoxide molecule is bonded to 18-crown-6 *via* a set of C—H···O interactions involving two H atoms of one methyl group. The sulfoxide O atoms accept a nearly linear N—H···O hydrogen bond from the disulfonylamine NH functions [N···O 2.651 (2) Å]. The macrocycle has approximately D_{3d} symmetry, and the disulfonylamine molecules feature a folded pseudo-C_s symmetric conformation.

Comment

In earlier work we have described the crystal structures of two binary complexes between monofunc-

tional di(organosulfonyl)amines, $(RSO_2)_2NH$ (R = Me or 2-naphthyl), and the potentially hexafunctional acceptor species 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6). These complexes involved N—H···O hydrogen bonds (Blaschette *et al.*, 1994; Henschel, Näveke *et al.*, 1995). In a number of similar cases, however, the isolation of binary adducts was found to be inherently impeded by the donor–acceptor disparity of the components; co-crystallizations led preferentially to polynary complexes, in which polar solvent molecules such as water or lower aliphatic alcohols were inserted as ambifunctional hydrogen-bonding links (complementarity mediators) between the NH donor and the hexaether ring (Henschel *et al.*, 1996, and references therein). The title compound, (I), was prepared intentionally. It is the first example of a ternary complex in which dimethyl sulfoxide acts as a link between a disulfonylamine and 18-crown-6, and in which the mediator is bonded to the polyether ring exclusively *via* C—H···O interactions. A search of the Cambridge Structural Database (Allen & Kennard, 1993) located no structural information for any other 18-crown-6 complex containing an uncharged sulfoxide molecule as the guest species. The X-ray structure of the related binary complex $2[(4-F-C_6H_4SO_2)_2NH].OSMe_2$, (II), has been determined in our laboratory (Blaschette *et al.*, 1993).

(I)

The centrosymmetric formula unit of the title complex is shown in Fig. 1. A traditional N—H···O hydrogen bond links the NH acids to the dimethyl sulfoxide molecules. The latter are situated one above and one below the plane of the ether O atoms; one methyl group of each sulfoxide species is bonded to the crown ether through a set of C—H···O interactions (Fig. 2). Selected intramolecular geometric data and hydrogen bond geometries are listed in Tables 1 and 2, respectively.

In the present structure, the disulfonylamine molecules adopt a folded conformation approximating to C_s symmetry (*vide* torsion angles in Table 1). The essentially planar phenyl rings are stacked, forming an interplanar angle of 12.86 (11)°. A similar conformation was observed for the analogous ternary complex 18-crown-6.2H_2O.2[(4-F-C_6H_4SO_2)_2NH] (Henschel, Blaschette & Jones, 1995), in contrast to complex (II) and to the pure disulfonylamine component (*loc. cit.*), where the molecule features an extended geometry with pseudo-C_2 symmetry. The internal bond lengths and angles of the amine component of (I) are similar to those in the refer-
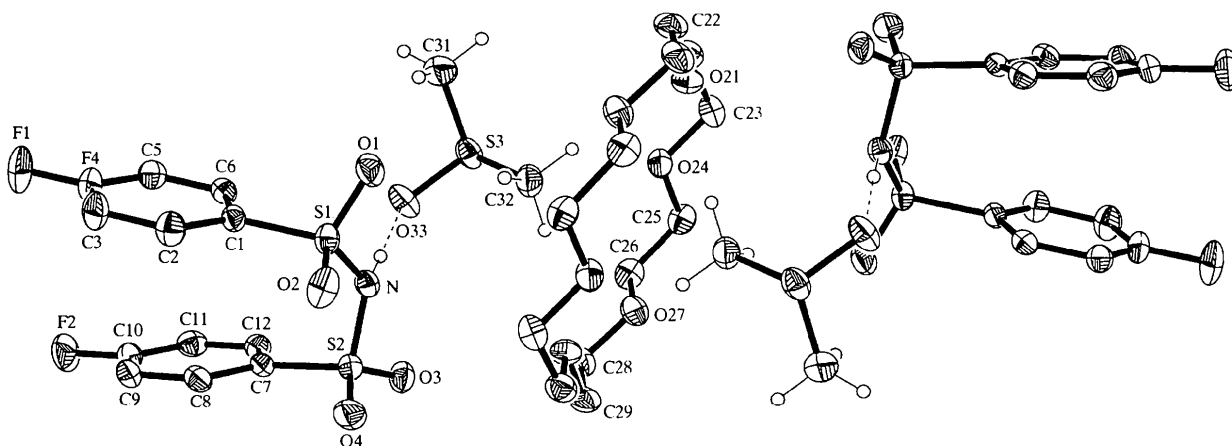
† Part CV: Näveke *et al.* (1998).

Fig. 1. Structure of the title complex in the crystal. Ellipsoids represent 30% probability levels. Only H atoms of the dimethyl sulfoxide and NH groups are shown, and their radii are arbitrary.

ence structures and will not be discussed. The geometric parameters of the Me_2SO molecule (included in Table 1) are also normal, as compared with the corresponding data reported for (II) at 178 K and for solid Me_2SO at 278 K (Thomas *et al.*, 1966).

The approximately linear N—H···O hydrogen bond that connects the NH acid to the sulfoxide is significantly shorter [N···O 2.651 (2) Å] than the N—H···O bonds in (II), where the sulfoxide O atom acts as a difunctional acceptor (N···O 2.75 and 2.80 Å, angles subtended at the H atoms 177 and 175°). It is noteworthy that the angle S3—O33···H01 of 122.9 (7)° is consistent with the anticipated acceptor directionality of an S=O function.

The macrocycle in (I) has approximate D_{3d} symmetry. The C—O [average 1.419 (2) Å] and C—C distances [average 1.493 (3) Å] are normal, as are the C—O—C [average 111.83 (14)°] and O—C—C angles [average 109.1 (2)°]. The torsion angles of the ring are listed in Table 1. Alternate O atoms [O21, O27 and O24^i; symmetry code: (i) $1 - x, 2 - y, -z$] deviate from the best plane through all six O atoms by 0.2438 (8), 0.2315 (7) and 0.2303 (7) Å, respectively; C32 is 1.950 (2) Å from this plane, with the S3—C32 bond making an angle of 32.6° with the normal to the plane.

As shown in Fig. 2 and quantified in Table 2, only two of the methyl H atoms located at C32 are bonded to the crown ether, the third (H32B) pointing away from the ring plane. The bonding H atoms interact at *ca* 2.5 Å with a pair of centrosymmetrically related O atoms (O21 and O21^i); each of these O atoms thus accepts two hydrogen bonds, one approximately linear and the other markedly bent. Both H atoms in question show a second contact at *ca* 2.75 Å to the other O atoms within the asymmetric unit (O27 and O24). Although one of the corresponding C—H···O angles is very small, both sequences might be viewed as forming the second branches of three-centre hydro-
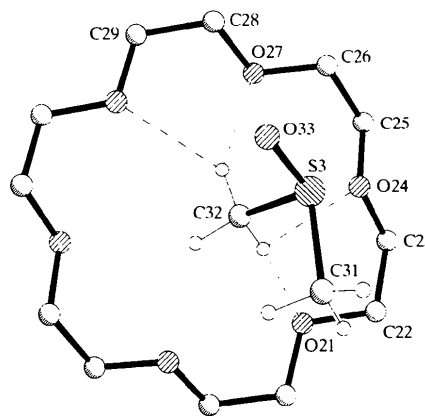

Fig. 2. Details of the interaction of one dimethyl sulfoxide molecule with the 18-crown-6 ring. Dashed lines indicate probable hydrogen-bonding interactions (see text and Table 2). Radii are arbitrary, and all H atoms except those on dimethyl sulfoxide are omitted.

gen bonds. Apart from geometric details, the C—H···O connectivity in (I) is very similar to that observed in binary complexes of 18-crown-6 with, for example, dimethyl ethynedicarboxylate (Goldberg, 1975), methyl 2-naphthalenesulfonate (Chênevert *et al.*, 1993), dicyanomethane (Kaufmann *et al.*, 1977) or dichloromethane (Jones *et al.*, 1994). In contrast, in the 1:2 (host:guest) complex between 18-crown-6 and dimethyl sulfone, one methyl group of each Me_2SO_2 molecule yields three C—H···O contacts to alternate ether O atoms (Bandy *et al.*, 1981).

Experimental

To a suspension of 18-crown-6 (0.20 g, 0.75 mmol) in anhydrous nitromethane (5 ml) were added successively a solution of $(4\text{-F-C}_6H_4SO_2)_2NH$ (0.50 g, 1.5 mmol) in the same solvent (15 ml) and the appropriate amount of pure dimethyl sulfoxide (0.10 ml, *ca* 1.5 mmol). The resulting clear solution

was slowly reduced in volume by evaporating the solvent *in vacuo* at room temperature. Crystals suitable for X-ray analysis were separated in a yield of 64% (0.52 g), m.p. 343–353 K [for comparison, m.p. of pure dimethyl sulfoxide 291.6 K (Thomas *et al.*, 1966), m.p. of pure 18-crown-6 312 K (Dunitz & Seiler, 1974) and m.p. of (4-F-$C_6H_4SO_2$)$_2$NH 455–456 K (Dykhanov, 1959*a*,*b*)]. ^{1}H NMR (CD$_3$CN, 200 MHz): δ 2.57 (*s*, 12H, Me$_2$SO), 3.51 (*s*, 24H, 18-crown-6), 7.21–7.29 and 7.82–7.89 (8H and 8H, aromatic H); δ(NH) not detected. Elemental analysis: found C 44.13, H 5.03, N 2.57%; $C_{40}H_{54}F_4N_2O_{16}S_6$ requires C 44.19, H 5.01, N 2.58%.

Crystal data

$C_{12}H_{24}O_6.2C_2H_6OS.-$
2$C_{12}H_9F_2NO_4S_2$
$M_r = 1087.21$
Triclinic
$P\bar{1}$
$a = 9.466\,(3)$ Å
$b = 9.564\,(3)$ Å
$c = 14.842\,(6)$ Å
$\alpha = 77.46\,(3)°$
$\beta = 71.93\,(3)°$
$\gamma = 73.94\,(3)°$
$V = 1214.8\,(7)$ Å^3
$Z = 1$
$D_x = 1.486$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 47 reflections
$\theta = 10.0–11.5°$
$\mu = 0.366$ mm^{-1}
$T = 143\,(2)$ K
Block
$0.6 \times 0.6 \times 0.5$ mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
4221 measured reflections
4055 independent reflections
3752 reflections with
$I > 2\sigma(I)$
$R_{int} = 0.033$

$\theta_{max} = 25.04°$
$h = -10 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.084$
$S = 1.061$
4055 reflections
314 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.6534P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0152 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N—S1	1.6449 (16)	S3—C32	1.776 (2)
N—S2	1.6589 (16)	S3—C31	1.784 (2)
S3—O33	1.5186 (14)		
S1—N—S2	126.90 (10)	O33—S3—C32	106.79 (9)
S1—N—H01	114 (2)	O33—S3—C31	105.22 (10)
S2—N—H01	114 (2)	C32—S3—C31	98.69 (11)
S2—N—S1—O1	171.74 (11)	C25—O24—C23—C22	−174.65 (15)
S2—N—S1—O2	43.00 (13)	C23—O24—C25—C26	175.20 (15)
S2—N—S1—C1	−73.88 (13)	O24—C25—C26—O27	−76.31 (19)

N—S1—C1—C2	135.93 (15)	C28—O27—C26—C25	175.47 (15)
S1—N—S2—O3	−174.57 (10)	C26—O27—C28—C29	−177.23 (15)
S1—N—S2—O4	−45.01 (13)	O27—C28—C29—O21^i	67.1 (2)
S1—N—S2—C7	71.78 (13)	C28—C29—O21^i—C22^i	174.55 (15)
N—S2—C7—C8	−90.05 (16)	C29—O21^i—C22^i—C23^i	174.62 (15)
O21—C22—C23—O24	65.92 (19)		

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N—H01$\cdots$O33	0.84 (2)	1.81 (2)	2.651 (2)	177 (2)
C32—H32$C\cdots$O21	0.98	2.47	3.439 (3)	173
C32—H32$A\cdots$O21^i	0.98	2.48	3.338 (3)	146
C32—H32$C\cdots$O24	0.98	2.73	3.287 (3)	117
C32—H32$A\cdots$O27	0.98	2.75	3.598 (3)	145

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

H atoms attached to N were refined freely, methyl H atoms were refined as rigid groups allowed to rotate but not tip (all starting positions from difference syntheses), and all other H atoms were riding.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.
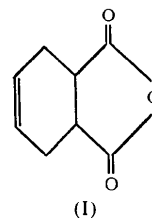
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(I)

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L'Anhydride cis-1,2,3,6-Tétrahydro-phtalique

Arij Ben Fredj, Sadok Ben Redjeb, Fatma Ben Amor, Ahmed Driss

Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisie. E-mail: sonia.zghal@cck.rnu.tn

Abstract

The crystal structure of cis-1,2,3,6-tetrahydrophthalic anhydride, $C_8H_8O_3$, has been determined by X-ray diffraction. This bicyclic compound crystallizes in space group $P2_1/a$, with two independent molecules per asymmetric unit. The folded conformation found for the two molecules is in close agreement with the results obtained for other cyclic anhydrides having a similar molecular arrangement. The same feature is observed in the anhydride ring structure. The differences between the two independent molecules in the unit cell were interpreted as the result of packing effects, caused by intermolecular nucleophile–electrophile (Nu–El) interactions.

Commentaire

Les anhydrides et les hydrocarbures cycliques ont fait l'objet, ces dernières années, de plusieurs travaux de recherche structurale, en particulier par diffraction des rayons X, par diffraction électronique en phase gazeuse et par diverses techniques de calcul semi-empirique (Coiro et al., 1985; Smith et al., 1974; Rudman, 1971; Geise & Romers, 1966; Van Den Enden et al., 1978; Spelbos et al., 1977; Favini et al., 1982). Dans ce sens, nous proposons dans cet article l'étude de la structure cristalline de l'anhydride cis-1,2,3,6-tétrahydrophtalique, (I). Ce dernier, partic-
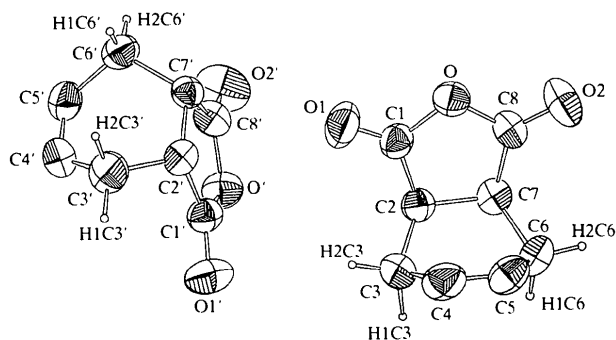
ulièrement connu par sa synthèse Diels–Alder, n'a en effet donné lieu qu'à un nombre restreint de travaux (Larter et al., 1977; Werner et al., 1973; Nageswara & Baldeschwieller, 1963; Remane et al., 1975). L'analyse structurale effectuée par diffraction des rayons X d'un monocristal de cet anhydride montre que sa maille cristalline comprend deux groupements formulaires indépendants, A et B, par unité asymétrique (Fig. 1).

Fig. 1. Vue perspective de $C_8H_8O_3$. Les ellipsoïdes ont 50% de probabilité.

Les géométries obtenues correspondantes confirment la configuration cis pour ce composé et indiquent que la conformation du noyau cyclohexénique est du type bateau, les carbones en α de la liaison C=C étant du même côté du plan moyen du noyau cyclohexénique. Il est à remarquer que ces géométries ont déjà été observées pour d'autres anhydrides cycliques ayant un arrangement moléculaire similaire à celui de l'anhydride étudié (Craig et al., 1976; Destro et al., 1971). Pour le cycle anhydride des groupements formulaires A et B, les longueurs trouvées des liaisons C—O, C=O et C—C, ainsi que les valeurs des angles de valence et des angles dièdres, sont comparables à celles obtenues pour l'anhydride succinique étudié par diffraction des rayons X (Ehrenberg, 1965; Biagini & Cannas, 1965) et par diffraction électronique en phase gazeuse (Brendhaugen et al., 1973).

Sa structure montre une similarité avec celles d'autres anhydrides cycliques analogues (Jones & Schrumpf, 1987; Filippini et al., 1972; Destro et al., 1969). Les conformations de A et B restent toutefois légèrement distinctes, l'angle dièdre formé par les plans appartenant au cyclohexène, c'est á dire, C3–C6, et C3, C2, C7 et C6, étant de 47,6 (1)° et de 46,9 (1)° respectivement pour A et B, et celui formé par les plans C3–C6 et le plan