Acta Cryst. (1995). C**51**, 1935–1937

N,N'-Ditosyl-*p*-phenylenediamine Bis(dimethyl sulfoxide), $C_{20}H_{20}N_2O_4S_2.2C_2H_6OS$

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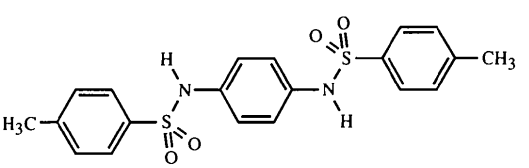
(*Received* 1 *December* 1994; *accepted* 6 *April* 1995)

Abstract

The title compound belongs to a group of inclusion compounds containing *N,N'*-ditosyl-*p*-phenylenediamine [IUPAC name: *N,N'*-*p*-phenylenebis(4-methylbenzenesulfonamide)] as the host molecule. Two dimethyl sulfoxide molecules are connected to one *N,N'*-ditosyl-*p*-phenylenediamine molecule through S=O···H—N hydrogen bonds. The solvent molecules are embedded in channels running along the *a* axis of the triclinic crystals.

Comment

N,N'-Ditosyl-*p*-phenylenediamine, (I), forms various inclusion compounds (Näther, 1994; Nagel, 1993). In general, from solutions containing hydrogen-bond acceptors such as dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide or pyridine, 2:1 adducts such as the one presented here crystallize (Fig. 1). The inclusion compounds with one molar equivalent of acetone, cyclopentanone, cyclopent-2-en-1-one, tetrahydrofuran, 2,5-dihydrofuran or dioxolane are isomorphous. They exhibit weak contacts between the O atoms of the solvent molecules and H atoms of the tolyl rings. Clathrates with one equivalent of benzene or furan represent a second type of isomorphous inclusion compound. The crystal structures of all the above compounds, as well as of the solvent-free host molecule, have been determined (Näther, 1994; Nagel, 1993). Here, the hydrogen-bonded adduct with dimethyl sulfoxide, a solvent known as a strong hydrogen-bond acceptor (Van der Sluis & Kroon, 1989) is presented.



(I)

The compound crystallizes in space group $P\bar{1}$ with one molecule of *N,N'*-ditosyl-*p*-phenylenediamine and two DMSO molecules in the unit cell. The asymmetric unit contains one solvent molecule in a general position and half a molecular of the host on a crystallographic centre of inversion. The structural data for the hydrogen-bonded aggregate (Table 2) are within the standard range of values. The *N,N'*-ditosyl-*p*-phenylenediamine molecule is able to rotate about the C1—N1, N1—S1 and S1—C10 bonds. The S atom is twisted out of the *p*-phenylenediamine plane by ω1(S1—N1—C1—C2) = 69.7 (2)° and the N atom is out of the tosyl plane by ω2(N1—S1—C10—C15) = 69.6 (1)°. The conformation of the sulfonamide fragment is characterized by ω3(C10—S1—N1—C1) = 67.3 (1)°, which is within the preferred range (Bindal, Golab & Katzenellenbogen, 1990; Kàlmàn, Czugler & Argay, 1981). The crystal packing diagram (Fig. 2) shows the solvent molecules embedded in channels running down the *a* axis, each channel containing two stacks of DMSO molecules. The solvent molecules in adjacent stacks are correlated through centres of inversion.

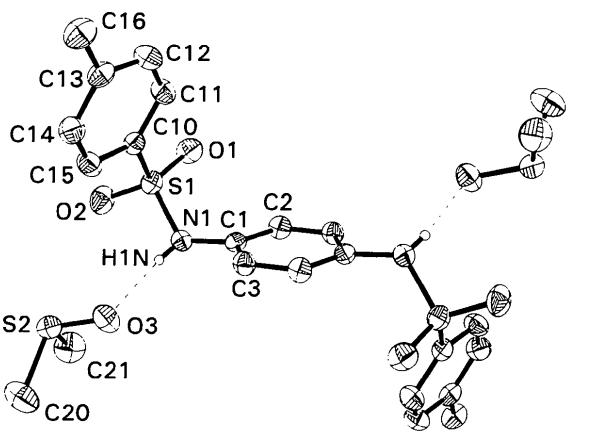


Fig. 1. View of the adduct showing 50% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme for the asymmetric unit.

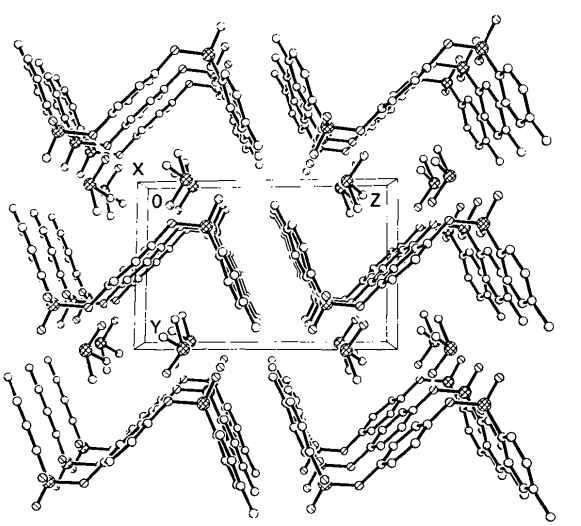


Fig. 2. Packing viewed along the *a* axis with all H atoms omitted for clarity.

Experimental

N,N′-Ditosyl-*p*-phenylenediamine can be obtained by the method of Stetter & Roos (1954). Isothermal diffusion of water in a solution of *N,N′*-ditosyl-*p*-phenylenediamine in dimethyl sulfoxide yields clear colourless crystals of the title compound, which can be stored are room temperature without significant loss of solvent.

Crystal data

$C_{20}H_{20}N_2O_4S_2.2C_2H_6OS$
$M_r = 572.76$
Triclinic
$P\bar{1}$
$a = 6.846\ (1)$ Å
$b = 8.076\ (1)$ Å
$c = 12.741\ (2)$ Å
$\alpha = 89.99\ (1)°$
$\beta = 83.09\ (1)°$
$\gamma = 82.77\ (1)°$
$V = 693.7\ (2)$ Å^3
$Z = 1$
$D_x = 1.371$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 80 reflections
$\theta = 16$–$22°$
$\mu = 0.383$ mm^{-1}
$T = 200\ (2)$ K
Prism
0.5 × 0.3 × 0.2 mm
Colourless

Data collection

Siemens *P*4 four-circle-diffractometer
ω scans
Absorption correction: none
2876 measured reflections
2876 independent reflections
2509 observed reflections $[I > 2\sigma(I)]$
$\theta_{max} = 26.55°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 16$
4 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0316$
$wR(F^2) = 0.0918$
$S = 1.067$
2876 reflections
182 parameters
$w=1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.2724P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.297$ e Å^{-3}
$\Delta\rho_{min} = -0.326$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.064 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for S2′; $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	U_{eq}/U_{iso}
S1	0.00135 (6)	−0.28073 (5)	−0.27868 (3)	0.02943 (13)
O1	0.2118 (2)	−0.3256 (2)	−0.28400 (9)	0.0392 (3)
O2	−0.0771 (2)	−0.12859 (15)	−0.32505 (10)	0.0415 (3)
N1	−0.0905 (2)	−0.2615 (2)	−0.15400 (10)	0.0296 (3)
C1	−0.0414 (2)	−0.3872 (2)	−0.07910 (11)	0.0268 (3)
C2	0.1494 (2)	−0.4127 (2)	−0.04897 (12)	0.0306 (3)
C3	−0.1892 (2)	−0.4741 (2)	−0.02995 (12)	0.0300 (3)
C10	−0.1002 (2)	−0.4473 (2)	−0.33244 (12)	0.0279 (3)
C11	0.0178 (2)	−0.5965 (2)	−0.36185 (14)	0.0359 (4)
C12	−0.0649 (3)	−0.7245 (2)	−0.40537 (14)	0.0383 (4)
C13	−0.2644 (2)	−0.7060 (2)	−0.42003 (12)	0.0329 (3)
C14	−0.3799 (2)	−0.5561 (2)	−0.38866 (14)	0.0371 (4)
C15	−0.3004 (2)	−0.4269 (2)	−0.34522 (13)	0.0354 (4)
C16	−0.3536 (3)	−0.8455 (2)	−0.46827 (15)	0.0432 (4)
S2 †	−0.56778 (7)	0.00810 (6)	−0.18955 (3)	0.03731 (15)
S2′ ‡	−0.5994 (10)	0.0514 (9)	−0.0973 (6)	0.0365 (14)
O3	−0.4933 (2)	−0.1402 (2)	−0.12677 (10)	0.0423 (3)
C20	−0.8054 (3)	0.0830 (3)	−0.1215 (2)	0.0555 (5)
C21	−0.4352 (3)	0.1735 (3)	−0.1526 (2)	0.0530 (5)

† Occupancy = 0.94.
‡ Occupancy = 0.06.

Table 2. *Selected geometric parameters* (Å, °)

S1—O1	1.434 (1)	C11—C12	1.386 (2)
S1—O2	1.434 (1)	C12—C13	1.390 (2)
S1—N1	1.637 (1)	C13—C14	1.391 (2)
S1—C10	1.764 (2)	C13—C16	1.511 (2)
N1—C1	1.430 (2)	C14—C15	1.381 (2)
C1—C3	1.391 (2)	S2—O3	1.509 (1)
C1—C2	1.396 (2)	S2—C20	1.782 (2)
C2—C3^i	1.387 (2)	S2—C21	1.800 (2)
C3—C2^i	1.387 (2)	S2′—C20	1.471 (7)
C10—C11	1.388 (2)	S2′—O3	1.648 (7)
C10—C15	1.389 (2)	S2′—C21	1.680 (7)
O1—S1—O2	120.04 (8)	C12—C11—C10	119.6 (2)
O1—S1—N1	108.18 (7)	C11—C12—C13	121.1 (2)
O2—S1—N1	104.20 (7)	C12—C13—C14	118.3 (2)
O1—S1—C10	108.27 (7)	C12—C13—C16	120.9 (2)
O2—S1—C10	108.38 (7)	C14—C13—C16	120.9 (2)
N1—S1—C10	107.09 (7)	C15—C14—C13	121.6 (2)
C1—N1—S1	121.6 (1)	C14—C15—C10	119.2 (2)
C3—C1—C2	120.1 (1)	O3—S2—C20	104.65 (9)
C3—C1—N1	119.5 (1)	O3—S2—C21	104.82 (9)
C2—C1—N1	120.2 (1)	C20—S2—C21	98.3 (1)
C3^i—C2—C1	119.1 (1)	C20—S2′—O3	113.5 (4)
C2^i—C3—C1	120.8 (1)	C20—S2′—C21	118.5 (5)
C11—C10—C15	120.3 (2)	O3—S2′—C21	104.3 (4)
C11—C10—S1	120.7 (1)	H1N—O3—S2	118.1 (6)
C15—C10—S1	119.0 (1)		
C10—S1—N1—C1	67.3 (1)	N1—S1—C10—C15	69.6 (1)
S1—N1—C1—C2	69.7 (2)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O3	0.80 (2)	2.00 (2)	2.789 (2)	174 (2)

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

Data were corrected for Lorentz and polarization effects. All C, N, O and S atoms except S2′ were refined with anisotropic displacement parameters. All H atoms were located from the difference map, placed in idealized positions (except the H atom on N1) and refined with isotropic displacement parameters (in groups for methyl H atoms) using a riding model for H atoms bound to C atoms, with distances C—H(methyl) = 0.98 and C—H(aromatic) = 0.95 Å, respectively. Refinement using only one site for S2 leads to a peak of 1.7 e Å^{-3} in the difference map. From the position of this peak it is reasonable to assume that S2 is disordered. On refinement with two sites, S2 and S2′, in the dimethyl sulfoxide molecule, the best fit was obtained with occupation factors of 0.94 and 0.06, respectively.

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC XP* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93 *CIFTAB*.

The project has been supported by the A. Messer Foundation, the Deutsche Forschungsgemeinschaft, the State of Hesse and the Fonds der Chemischen Industrie.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: JZ1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1937–1940

(±)-(4aα,4bβ,10bβ,12aβ)-9-Bromo-2-methyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydronaphtho[2,1-*f*]isoquinoline Formed from the Acid-Catalyzed Cyclization of 5-[2-(4-Bromophenyl)-ethyl]-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline

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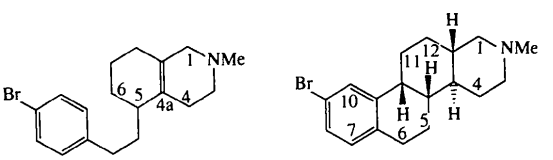
(*Received* 4 *October* 1994; *accepted* 7 *April* 1995)

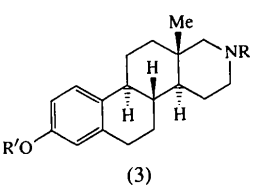
Abstract

The title compound, $C_{18}H_{24}BrN$, was produced by treating 5-[2-(4-bromophenyl)ethyl]-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline with 48% hydrobromic acid. Cyclization took place between position 2 of the aromatic ring and position 6 of the octahydroisoquinoline ring, following acid-catalyzed isomerization of the double bond.

Comment

The acid-catalyzed cyclization of 5-[2-(4-bromophenyl)-ethyl]-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline, (1), could potentially give a variety of cyclized products. NMR studies ruled out cyclization at position 4a of the octahydroisoquinoline ring system since there was no aliphatic quaternary signal present in the ^{13}C NMR spectrum. Further studies involving 2D-COSY and HETCOR spectral techniques suggested that the cyclized product was (±)-(4aα,4bβ,10bβ,12aβ)-9-bromo-2-methyl-1,2,3,4,4a,4*b*,5,6,10*b*,11,12,12a-dodecahydronaphtho[2,1-*f*]isoquinoline, (2), and this was confirmed by the X-ray crystallographic analysis described in this paper.





The tetracyclic structure (2) was formed as a result of cyclization between the 2 position of the aromatic ring and the 6 position of the octahydroisoquinoline ring system. This is made possible by an acid-catalyzed isomerization of the double bond from the $\Delta^{4a,8a}$ to the

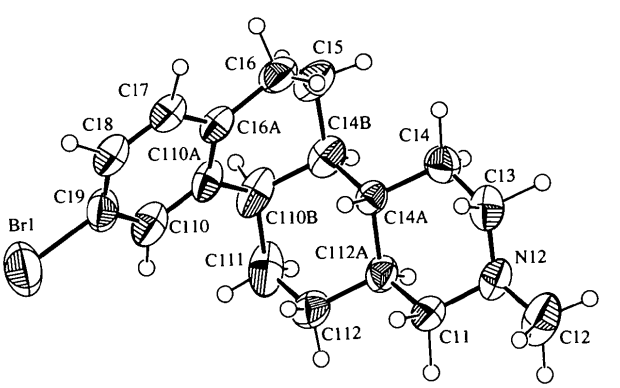


Fig. 1. A view of one of the independent molecules showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small circles of arbitrary radii.