Monoclinic
$P2_1/n$
$a = 7.5611\ (2)$ Å
$b = 8.1393\ (1)$ Å
$c = 18.9671\ (4)$ Å
$\beta = 94.798\ (1)^\circ$
$V = 1163.18\ (4)$ Å^3
$Z = 4$
$D_x = 1.304$ Mg m^{-3}
D_m not measured
Cell parameters from 4959 reflections
$\theta = 2.16$–28.33°
$\mu = 0.252$ mm^{-1}
$T = 293\ (2)$ K
Slab
$0.48 \times 0.34 \times 0.16$ mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.89$, $T_{\max} = 0.96$
7772 measured reflections
2845 independent reflections
2157 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.034$
$\theta_{\max} = 28.27^\circ$
$h = -10 \rightarrow 9$
$k = -10 \rightarrow 7$
$l = -25 \rightarrow 24$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.121$
$S = 1.043$
2845 reflections
147 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.1025P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C12	1.734 (2)	O1—C14	1.432 (2)
S1—C1	1.740 (2)	C1—C13	1.513 (2)
O1—C8	1.366 (2)		
C12—S1—C1	92.1 (1)	C1—C2—C3	114.1 (2)
C8—O1—C14	117.0 (1)	C12—C3—C2	111.8 (1)
C2—C1—S1	111.5 (1)		

All the H atoms were fixed geometrically and allowed to ride on the atoms to which they are attached.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1318). Services for accessing these data are described at the back of the journal.

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10,11-Dibromo-3,6-ditosyl-3,6-diazabicyclo[6.4.0]dodeca-1(8),9,11-triene

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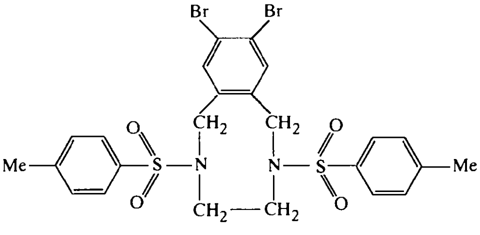
Abstract

The molecules of the title compound, $C_{24}H_{24}Br_2N_2O_4S_2$, crystallize in the tetragonal system, space group $P4_12_12$. The compound possesses a crystallographic twofold axis. The dihedral angle between the tosyl

rings is 12.9 (1)°. The eight-membered ring is close to the half-chair conformation. The crystal structure is stabilized by intermolecular C—H· · ·O interactions.

Comment

The title compound, (I), is a precursor in the synthesis of phthalocyanines (Ağar *et al.*, 1995). For many years, phthalocyanines have continuously attracted great interest in various research fields such as chemical sensors, electrochromism, batteries, photodynamic therapy, semiconductive materials, liquid crystals and nonlinear optics (Moser & Thomas, 1983; Leznoff & Lever, 1989–1993).



(I)

Fig. 1 shows the displacement ellipsoid plot of (I) with the numbering scheme. The geometry at the S atoms is distorted from the tetrahedral configuration, with the largest deviations in the O—S—O angles [O1—S1—O2 = 120.4 (3)°] and the O1—S1—N1 and O2—S1—N1 angles [106.6 (3) and 106.4 (2)°, respectively]. The C—N distances in the eight-membered ring are N1—C1 = 1.461 (6) and N1—C2 = 1.465 (6) Å. The S—N bond distance [S1—N1 = 1.623 (4) Å] contrasts with the previously observed range of 1.63–1.69 Å (Kálmán *et al.*, 1981). This shortening is due to the electronic withdrawing character of the phenylsulfonyl group (Govindasamy *et al.*, 1997). The S—C and mean S—O distances are 1.763 (5) and 1.429 (4) Å, respectively.

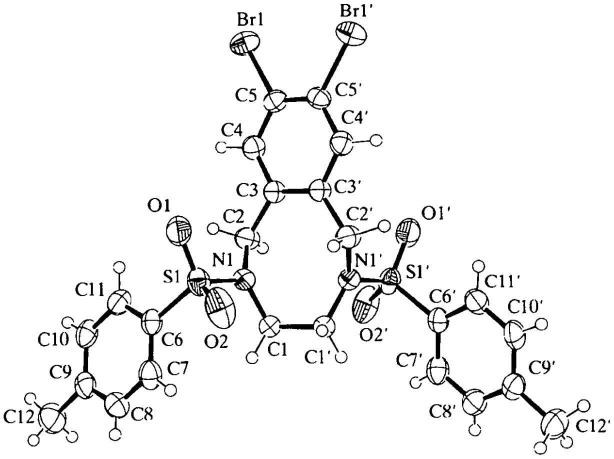


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as circles of an arbitrary radius.

The ring formed by atoms C3–C5 and their symmetry equivalents is planar, with a maximum deviation from the plane for C3 of −0.007 (3) Å. The ring formed by atoms C6–C11 is also planar, with maximum deviations from the plane of this eight-membered ring for C1, N1, C2, C3 of 0.010 (1), −0.539 (1), 0.378 (1) and 0.155 (1) Å, respectively. By also considering the deviations of the symmetry equivalents of these atoms, it can be seen that the structure is close to half-chair. The puckering parameters (Cremer & Pople, 1975) are q_2 = 0.754 (2), q_3 = 0.223 (2), Q_T = 0.960 (2) Å, φ = 135.0 (3)° and θ = 73.6 (2)°. The crystal packing has two intermolecular hydrogen bonds, as detailed in Table 2. In addition, the structure displays C—H· · ·O-type intramolecular interactions, which can be considered as weak hydrogen bonds.

Experimental

N,*N*′-Bis(*p*-tolylsulfonyl)ethylenediamine (7.36 g, 20 mmol) was dissolved in dry *N*,*N*-dimethylformamide (160 ml) containing well ground anhydrous K_2CO_3 (8.28 g, 60 mmol) and stirred at 300 K for 1 h. A solution of 1,2-bis(bromomethyl)-4,5-dibromobenzene (12.6 g, 30 mmol) in dry *N*,*N*-dimethylformamide (160 ml) was added dropwise over a period of 16–20 h. The mixture was then stirred at 300 K for 36 h and an ice–water mixture (500 g) was added. The resulting solid was collected by filtration, washed with water to remove excess base and the residue washed with water followed by cold ethanol. The yellow–white residue was dissolved in $CHCl_3$, dried with $MgSO_4$ and filtered. The filtrate was evaporated to dryness and the subsequent yellow–white residue was purified by column chromatography. The product, (I), was recrystallized from $CHCl_3$ by cooling. Elemental analysis: $C_{24}H_{24}Br_2N_2O_4S_2$ requires C 45.85, H 3.8, N 4.45%; found C 45.80, H 3.86, N 4.41%.

Crystal data

$C_{24}H_{24}Br_2N_2O_4S_2$
M_r = 628.39
Tetragonal
$P4_12_12$
a = 10.4475 (1) Å
c = 22.8183 (2) Å
V = 2490.62 (4) Å^3
Z = 4
D_x = 1.676 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 7264 reflections
θ = 2.64–33.20°
μ = 3.46 mm^{-1}
T = 293 (2) K
Prismatic
0.38 × 0.20 × 0.20 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical using *SADABS* (Sheldrick, 1996)
T_{min} = 0.325, T_{max} = 0.501

2635 reflections with $I > 2\sigma(I)$
R_{int} = 0.068
θ_{max} = 33.18°
$h = -14 \rightarrow 16$
$k = -16 \rightarrow 14$
$l = -26 \rightarrow 34$

22 912 measured reflections
2791 independent reflections (plus 1930 Friedel-related reflections)
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.141$
$S = 1.010$
4721 reflections
191 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 3.5783P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0001 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.003 (8)

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

Br1—C5	1.892 (4)	S1—O1	1.427 (4)
N1—C1	1.461 (6)	S1—O2	1.432 (4)
N1—C2	1.465 (6)	S1—C6	1.763 (5)
N1—S1	1.623 (4)		
O1—S1—O2	120.4 (3)	O2—S1—N1	106.4 (2)
O1—S1—N1	106.6 (3)	C8—C9—C12	121.6 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*B*···O2^{i}	1.01 (6)	2.56 (5)	3.367 (6)	136 (4)
C10—H10···O1^{ii}	0.93 (1)	2.57 (6)	3.382 (7)	147 (5)

Symmetry codes: (i) $-\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{4} + z$; (ii) $y - 1, x, -z$.

Though data were collected to a 2θ maximum of 66.4°, only reflections having 2θ less than 55° were used for structure solution and refinement. The crystal structure in the tetragonal system can be solved in either of the enantiomorphous space groups $P4_32_12$ or $P4_12_12$. The crystal was initially solved in $P4_32_12$, but the *R* values and the Flack (1983) parameter indicated $P4_12_12$. These results led us to use $P4_12_12$. Only methyl-group H atoms were located geometrically; the other H atoms were located from a difference Fourier map and refined isotropically. The C—H bond lengths range from 0.87 (6) to 1.02 (4) Å, while U_{iso} values range from 0.03 (1) to 0.09 (2) Å^2.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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C—H···O interactions in acenaphthene-5,6-dicarboxylic anhydride

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Abstract

The title substance, $C_{14}H_8O_3$, crystallized in the centrosymmetric space group *C*2/*c* with a half-molecule in the asymmetric unit (the molecule lies on a twofold axis). The three leading C—H···O interactions have H···O distances 2.47 (2), 2.84 (2) and 2.91 (2) Å, and C···O distances 3.338 (2), 3.445 (2) and 3.606 (2) Å, respectively. These interactions link each molecule directly to six neighbors, leading to a three-dimensional network of C—H···O interactions. Structural comparisons are made with naphthalene-1,2-dicarboxylic anhydride and naphthalene-1,4,5,8-tetracarboxylic 1,8:4,5-dianhydride.

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