

***N,N'*-Bis(2-tosylaminobenzylidene)-
benzene-1,2-diamine**José Mahía,^{a*} Miguel A. Maestro,^a Miguel Vázquez,^b
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Received 8 November 1999

Accepted 17 January 2000

The conformation of the title compound, $C_{34}H_{30}N_4O_4S_2$, is strongly influenced by intramolecular $N-H \cdots N$ hydrogen-bond interactions and by the rigidity endowed by the presence of a phenyl group between the imine N atoms. The molecule is not planar, with very short distances between the imine N atoms [$N \cdots N$ 2.753 (3) Å] and the amine N atoms [$N \cdots N$ 5.148 (4) Å]. Consequently, important changes in its conformation will be required if it is to act as a tetradentate ligand *via* its four N atoms.

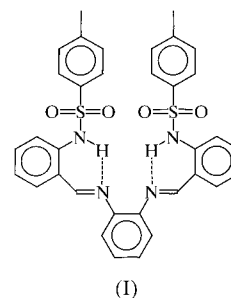
Comment

In recent years, chemists have been interested in obtaining new tetradentate Schiff bases, in particular dianionic N_4 ligands, because they can act as ligands in bioinorganic chemistry processes. The emphasis on these species is undoubtedly related to the existence of naturally occurring metal complexes, such as metalloporphyrins, vitamin B_{12} , *etc.*, which act as effective catalysts in many biological processes (Zhang *et al.*, 1990; Irie *et al.*, 1990).

In our research into metal catalysts containing N_4 tetradentate Schiff base ligands, our group has synthesized and reported some non planar N_4 Schiff bases: *N,N'*-bis-(2-tosylaminobenzylidene)-1,3-propanediamine (PTS; Mahía, Maestro, Vázquez, Bermejo, Sanmartín & Maneiro, 1999) and *N,N'*-bis(2-tosylaminobenzylidene)-1,2-ethanediamine (ETS; Mahía *et al.*, 2000). We have now determined the crystal structure of the title compound, (I). We have used 1,2-diaminobenzene in an attempt to obtain a new N_4 tetradentate Schiff base derived from 2-tosylaminobenzaldehyde (Chernova *et al.*, 1971; Mahía, Maestro, Vázquez, Bermejo, González & Maneiro, 1999). This new Schiff base will result in a molecule with greater planarity and steric interference than in the other Schiff bases prepared by us.

In compound (I), the $N2-C14$ and $N3-C21$ distances of 1.283 (3) and 1.264 (3) Å, respectively, are consistent with

$C=N$ double bonding. Similarly, the $S1-O1$, $S1-O2$, $S2-O3$ and $S2-O4$ distances [1.435 (2), 1.427 (2), 1.426 (2) and 1.430 (2) Å, respectively] are consistent with $S=O$ double bonding.



The conformation of (I) in the solid state is strongly influenced by two strong $N-H \cdots N$ interactions (Fig. 1 and Table 2). Due to these hydrogen bonds, the atoms H1A, N1, C8, C13, C14 and N2, and H4A, N4, C27, C22, C21 and N3 form two planar six-membered rings, with plane deviations of 0.028 and 0.043 Å, respectively. There are also two weak intermolecular $C-H \cdots O$ interactions in the compound (Table 2).

The presence of the two tosyl groups prevents the molecule from being planar. The angle between the least-squares planes of the $C8-C13$ and $C22-C27$ aromatic rings is $62.47 (9)^\circ$ and the values of the torsion angles $C21-N3-C20-C15$ and $C14-N2-C15-C20$ are $112.0 (2)$ and $135.6 (2)^\circ$, respectively. However, the $C5-S1-N1$ and $C28-S2-N4$ bond angles [$107.4 (1)$ and $106.9 (1)^\circ$, respectively] and the $C8-N1-S1-C5$ and $C27-N4-S2-C28$ torsion angles [$-71.8 (3)$ and $-75.5 (2)^\circ$, respectively], indicate that both tosyl groups adopt a similar conformation in the molecule.

There are several structural differences between compound (I) and the other Schiff bases, ETS and PTS, obtained from 2-tosylaminobenzaldehyde and previously reported by our group. The rigidity introduced by the phenyl group between the imine N atoms forces the four N atoms in (I) into greater proximity than in either ETS or PTS. Thus, the distances between the imine N atoms $N2 \cdots N3$ [2.753 (3) in (I), 2.930 (4) in ETS and 4.413 (3) Å in PTS] and between the amine N atoms $N1 \cdots N4$ [5.148 (4) in (I), 5.865 (3) in ETS and 7.724 (3) Å in PTS] are shorter in (I) than in the other molecules. Consequently, the distance between the S atoms is shorter in (I) [6.544 (2) Å] than in the other derivatives [7.673 (1) in ETS and 9.007 (1) Å in PTS]. The extra rigidity introduced by the phenyl bridge in (I) also causes a change in the disposition of the tosyl groups with respect to that shown in the other molecules. In ETS and PTS, the tosyl groups appear in opposite positions, probably to minimize the steric hindrance, but this spatial disposition is not possible in (I) due to the greater proximity between the tosyl groups.

It is noteworthy that while the aromatic rings of the two tosyl groups are practically perpendicular to each other in PTS, forming an angle of $82.5 (1)^\circ$, these aromatic rings adopt a semi-parallel conformation in ETS [$17.1 (2)^\circ$] and (I) [$17.5 (2)^\circ$].

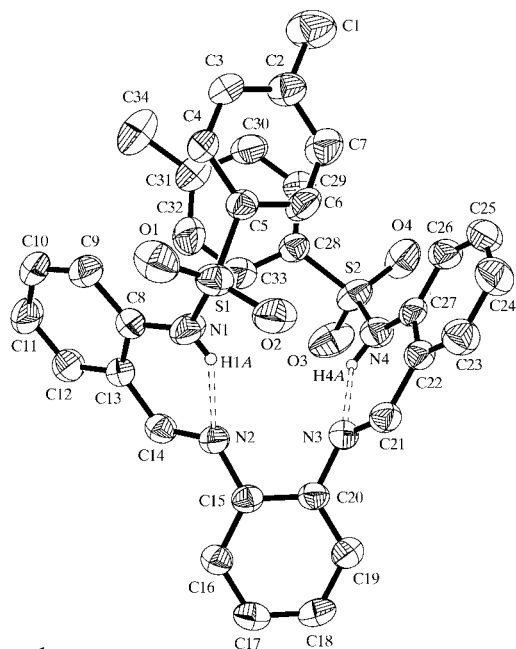


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms (except for those involved in the intramolecular hydrogen bonds) are omitted for clarity.

Experimental

The title Schiff base was synthesized by condensation of 2-tosylaminobenzaldehyde (Chernova *et al.*, 1971; Mahía, Maestro, Vázquez, Bermejo, González & Maneiro, 1999) and 1,2-diaminobenzene. To a solution of 2-tosylaminobenzaldehyde (5 g, 18.2 mmol) in chloroform (150 ml) was added 1,2-diaminobenzene (1 g, 9.1 mmol). The mixture was heated to 338 K and stirred for 3 h. The resultant yellow solution was filtered and concentrated. Yellow crystals of (I) were formed after one night of slow evaporation at room temperature (yield 4.2 g, 73%; m.p. 455 K). Elemental analysis for $C_{34}H_{30}N_4O_4S_2$: calculated (found) C 65.6 (65.6), H 4.9 (4.9), N 9.0 (9.1), S 10.3 (10.4)%; mass spectroscopy (HL^+): calculated (found) 622.8 (623.3, 100%); 1H NMR ($CDCl_3$, p.p.m.): 13.15 (s, 2H), 8.61 (s, 2H), 7.81–6.78 (m, 20H), 2.17 (s, 6H); IR spectroscopy (KBr, cm^{-1}): $\nu(N-H)$ 3387 m, $\nu(C=N)$ 1614 s, $\nu(C-N)$ 1337 s, $\nu_{as}(SO_2)$ 1291 s, $\nu_s(SO_2)$ 1160 s.

Crystal data

$C_{34}H_{30}N_4O_4S_2$
 $M_r = 622.74$
 Monoclinic, $P2_1/c$
 $a = 9.704$ (2) Å
 $b = 19.102$ (4) Å
 $c = 17.407$ (4) Å
 $\beta = 103.85$ (2)°
 $V = 3132.7$ (12) Å³
 $Z = 4$
 $D_x = 1.320$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 80 reflections
 $\theta = 3-27^\circ$
 $\mu = 0.215$ mm⁻¹
 $T = 298$ (2) K
 Block, yellow
 $0.45 \times 0.30 \times 0.15$ mm

Table 1
Selected geometric parameters (Å, °).

S1...S2	6.5443 (17)	N2-N3	2.753 (3)
N1...N4	5.148 (4)		
N1-S1-C5	107.40 (12)	N4-S2-C28	106.93 (11)
C5-S1-N1-C8	-71.8 (3)	C14-N2-C15-C20	135.6 (2)
C28-S2-N4-C27	-75.5 (2)	C21-N3-C20-C15	112.0 (2)

Data collection

Siemens CCD area-detector diffractometer
 $R_{int} = 0.037$
 $\theta_{max} = 28.31^\circ$
 ω scans
 $h = -10 \rightarrow 12$
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
 $k = -21 \rightarrow 25$
 $l = -23 \rightarrow 23$
 $T_{min} = 0.910$, $T_{max} = 0.969$
 First 50 frames
 17 247 measured reflections
 every set of frames
 7742 independent reflections
 intensity decay: -0.10%
 4794 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.143$
 $S = 1.026$
 415 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 1.2358P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 H atoms treated by a mixture of independent and constrained refinement
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.251$ e Å⁻³
 $\Delta\rho_{min} = -0.366$ e Å⁻³
 7742 reflections

Table 2

Hydrogen-bonding geometry (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1A...N2	0.78 (3)	2.00 (3)	2.668 (3)	144 (2)
N4-H4A...N3	0.88 (3)	2.00 (3)	2.657 (3)	131 (3)
C23-H23A...O4 ⁱ	0.98 (3)	2.51 (3)	3.427 (3)	156 (2)
C29-H29A...O2 ⁱⁱ	0.97 (3)	2.51 (3)	3.233 (3)	131 (2)

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

The positions of all H atoms were calculated geometrically and a riding model was used in their refinement, except for those involved in the hydrogen bonds. H atoms involved in hydrogen bonds were found in an electron-density map and then freely refined.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

We thank the Xunta de Galicia (PGIDT99PXI20903B) for their financial support. The Universidade da Coruña also thanks the Xunta de Galicia (XUGA INFRA-97) for supporting the acquisition of the CCD diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1099). Services for accessing these data are described at the back of the journal.

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