| | | | |
|---|---|---|---|
| C3—O4 | 1.459 (3) | C3A—O4A | 1.456 (3) |
| C3—C12 | 1.512 (3) | C3A—C12A | 1.517 (3) |
| C3—C18 | 1.520 (3) | C3A—C18A | 1.522 (3) |
| O4—N5 | 1.436 (2) | O4A—N5A | 1.438 (2) |
| N5—C1—N2 | 114.5 (2) | N5A—C1A—N2A | 114.6 (2) |
| N5—C1—C6 | 121.8 (2) | N5A—C1A—C6A | 121.7 (2) |
| N2—C1—C6 | 123.7 (2) | N2A—C1A—C6A | 123.7 (2) |
| C1—N2—C3 | 107.6 (2) | C1A—N2A—C3A | 106.4 (2) |
| C1—N2—H2N | 122.3 (19) | C1A—N2A—H2NA | 118.2 (15) |
| C3—N2—H2N | 121.3 (19) | C3A—N2A—H2NA | 117.9 (16) |
| O4—C3—N2 | 100.1 (2) | O4A—C3A—N2A | 100.4 (2) |
| O4—C3—C12 | 107.1 (2) | O4A—C3A—C12A | 107.3 (2) |
| N2—C3—C12 | 114.5 (2) | N2A—C3A—C12A | 113.9 (2) |
| O4—C3—C18 | 110.2 (2) | O4A—C3A—C18A | 109.6 (2) |
| N2—C3—C18 | 112.3 (2) | N2A—C3A—C18A | 112.8 (2) |
| C12—C3—C18 | 111.9 (2) | C12A—C3A—C18A | 112.1 (2) |
| N5—O4—C3 | 109.3 (2) | N5A—O4A—C3A | 109.1 (2) |
| C1—N5—O4 | 105.5 (2) | C1A—N5A—O4A | 105.2 (2) |
| N5—C1—C6—C7 | −32.2 (4) | N5A—C1A—C6A—C7A | −25.0 (4) |

Table 2. *Hydrogen-bonding geometry ($\mathring{A}$, °)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N2—H2N···N5$^i$ | 0.89 (3) | 2.44 (3) | 3.287 (3) | 160 (3) |
| N2A—H2NA···N5A$^{ii}$ | 0.92 (3) | 2.45 (3) | 3.303 (3) | 155 (2) |

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x, y − 1, z$.

The asymmetric unit contained two molecules of (III) related approximately by a centre of symmetry and differing in the orientation of the phenyl ring at C1. However, inspection of the *hkl* intensities did not allow a transformation to a smaller unit cell. Refined C—H distances are in the range 0.92 (3)–1.07 (4) Å.

Data collection: *KM4B8* (Gałdecki *et al.*, 1997a). Cell refinement: *KM4B8*. Data reduction: *DATAPROC* (Gałdecki *et al.*, 1997b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1322). Services for accessing these data are described at the back of the journal.

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# 2-Tosylaminobenzaldehyde†

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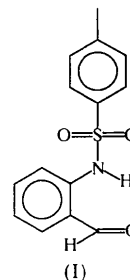
## Abstract

The title molecule, $C_{14}H_{13}NO_3S$, is not planar; the angle between the two aromatic rings is 81.85 (6)°. The conformation of the molecule in the solid state is determined by an intramolecular N—H···O hydrogen bond. This interaction modifies the electrophilic character of the C atom in the carboxaldehyde group, rendering it more suitable for a nucleophilic attack.

## Comment

The preparation of the title compound, (I), is the first step in the synthesis of dianionic Schiff bases (Bailey *et al.*, 1974; Bailey & McKenzie, 1980) that could act as polydentate ligands through both N and O atoms.



(I)

The crystal structures of the ligands *N,N'*-bis(2-tosylaminobenzylidene)-1,3-diaminopropane (Mahía *et al.*, 1999) and 2-isopropylidene-1-(*p*-toluenesulfonyl)-hydrazide (Ojala *et al.*, 1998), and of the mononuclear

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† Alternative name: *N*-(*o*-formylphenyl)-4-toluenesulfonamide.

copper(II) and nickel(II) complexes with bis[4-methyl-N-(2-pyridin-2-ylethyl)benzenesulfonamide] (Durán et al., 1997), have been described in the literature. Moreover, bis{N-[(2-pyrrolyl)methylidene]-N'-(tosyl-1,2-benzenediaminato)}zinc(II) (Romero et al., 1997) and bis[2-(p-toluenesulfonylamino)(2'-pyridyl)anilinato]-cobalt(II) (García-Vázquez et al., 1998), which contain the same p-toluenesulfonylamine group as the title compound, have been previously reported.

The two aromatic rings of the molecule are essentially planar, with mean deviations of 0.005 Å for C2–C7 and 0.003 Å for C8–C13. The rings planes form an interplanar angle of 81.85 (6)°.

The S1—O1 and S1—O2 distances are similar [1.4316 (14) and 1.4236 (14) Å, respectively] and are consistent with S=O double bonding; similarly, the C14—O3 distance of 1.206 (3) Å is consistent with C=O double bonding. The geometry around C14 is trigonal planar, as confirmed by the C13—C14—O3 bond angle of 126.8 (2) Å. The C13, C14, H14A and O3 atoms form a perfect plane that is inclined at an angle of 3.54 (6)° to the ring C8–C13.

The conformation adopted by the title compound in the solid state is conditioned by a strong intramolecular N—H···O interaction [H1A···O3 1.97 (2) Å]. The resulting six-membered ring N1—C8—C13—C14—O3···H1A is planar (Fig. 1), with a mean deviation of 0.013 Å. This plane forms an angle of 2.68 (11)° with the C8–C13 ring.
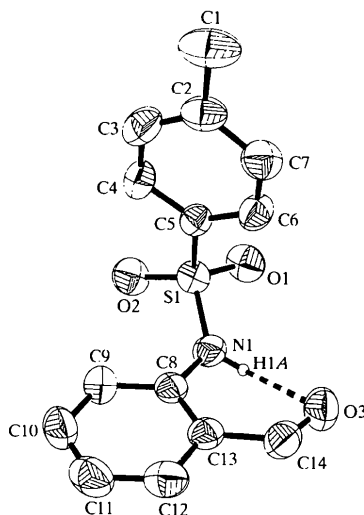


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms (except for that involved in the intramolecular hydrogen bond) have been omitted for clarity.

The C8—N1—S1 angle [125.03 (13)°] is distinctly larger than the expected value for an $sp^3$-hybridized N atom. We consider that this intramolecular hydrogen bond confers increased electrophilic character on the C atom of the carboxaldehyde group.

Finally, there are no significant structural changes between this molecule and N,N'-bis(2-tosylamino-benzylidene)-1,3-diaminopropane, obtained by reaction of the title compound with 1,3-diaminopropane (Mahía et al., 1999): the angle between the two aromatic rings for the aldehyde increases on condensation from 81.85 (6) to 82.8 (1)°; the C8—N1—S1—C5 torsion angle is similar in both the aldehyde and the Schiff base [59.86 (17) and 61.0 (2)°, respectively]; and there is no significant increase of the C8—N1—S1 angle in the condensed form [125.03 (1) to 126.15 (14)°].

## Experimental

The title compound was prepared by a method similar to that of Chernova et al. (1971), and was crystallized from chloroform solution by slow evaporation at room temperature. Elemental analysis for $C_{14}H_{13}NO_3S$ (%): calculated (found) C 61.1 (61.0), H 4.7 (4.9), N 5.1 (5.1), S 11.6 (11.7). Mass spectrometry (HL⁺): calculated (found) 276.3 (276.1, 100%). ¹H NMR (CDCl₃, p.p.m.): 10.7 (s, 1H), 9.7 (s, 1H), 7.7–7.0 (m, 8H), 2.3–2.2 (s, 3H). ¹³C NMR (CDCl₃, p.p.m.): 195.54, 144.68, 140.28, 136.68, 136.61, 136.27, 130.21 (2C), 127.67 (2C), 123.43, 122.24, 118.07, 21.97. IR spectroscopy (KBr, cm⁻¹): ν(N=H) 3136 (s), ν(C=N) 1671 (s), ν(C—N) 1336 (s), $\nu_{as}(SO_2)$ 1294 (s), $\nu_s(SO_2)$ 1155 (s).

### Crystal data

| | |
|---|---|
| $C_{14}H_{13}NO_3S$ | Mo Kα radiation |
| $M_r = 275.31$ | $\lambda = 0.71073$ Å |
| Monoclinic | Cell parameters from 58 |
| $P2_1/c$ | reflections |
| $a = 13.8993 (7)$ Å | $\theta = 3-26°$ |
| $b = 8.2374 (4)$ Å | $\mu = 0.246$ mm⁻¹ |
| $c = 12.0633 (6)$ Å | $T = 298 (2)$ K |
| $\beta = 105.843 (1)°$ | Block |
| $V = 1328.71 (11)$ Å³ | $0.40 \times 0.35 \times 0.20$ mm |
| $Z = 4$ | Pale brown |
| $D_x = 1.376$ Mg m⁻³ | |
| $D_m$ not measured | |

### Data collection

| | |
|---|---|
| Siemens CCD diffractometer | 2471 reflections with |
| ω scans | $I > 2\sigma(I)$ |
| Absorption correction: | $R_{int} = 0.022$ |
| empirical (SADABS; | $\theta_{max} = 28.27°$ |
| Sheldrick, 1996) | $h = -18 \rightarrow 15$ |
| $T_{min} = 0.904$, $T_{max} = 0.952$ | $k = -10 \rightarrow 10$ |
| 7166 measured reflections | $l = -13 \rightarrow 16$ |
| 3267 independent reflections | |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0467P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | $+ 0.4657P]$ |
| $wR(F^2) = 0.113$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.015$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3267 reflections | $\Delta\rho_{max} = 0.24$ e Å⁻³ |
| 177 parameters | $\Delta\rho_{min} = -0.40$ e Å⁻³ |

H atoms treated by a mixture of independent and constrained refinement

Extinction correction: none Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| S1—O2 | 1.4236 (14) | O3—C14 | 1.206 (3) |
| S1—O1 | 1.4316 (14) | N1—C8 | 1.415 (2) |
| S1—N1 | 1.6353 (16) | C13—C14 | 1.466 (3) |
| S1—C5 | 1.7596 (17) | | |
| O2—S1—O1 | 119.51 (9) | O1—S1—C5 | 108.34 (8) |
| O2—S1—N1 | 109.33 (9) | N1—S1—C5 | 106.64 (8) |
| O1—S1—N1 | 104.13 (9) | C8—N1—S1 | 125.03 (13) |
| O2—S1—C5 | 108.18 (9) | O3—C14—C13 | 126.8 (2) |
| C5—S1—N1—C8 | 59.9 (2) | | |

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

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N1—H1A···O3 | 0.88 (2) | 1.97 (2) | 2.708 (2) | 141 (2) |

The positions of all H atoms were calculated geometrically and a riding model was used in their refinement, except for H1A which was involved in the intramolecular hydrogen bond and was found in a residual electronic density map and refined freely.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1360). Services for accessing these data are described at the back of the journal.

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# ent-Isocopal-12-ene-15,16-dialdehyde from Spongia officinalis

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## Abstract

The X-ray analysis of the natural product *ent*-isocopal-12-ene-15,16-dialdehyde, 1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-4b,8,8,10a-tetramethyl-1,2-phenanthrene-dicarboxaldehyde, $C_{20}H_{30}O_2$, is reported. The compound was isolated, together with other diterpenes of the spongian type, from the diethyl ether soluble fraction of *Spongia officinalis* [Cimino, Morrone & Sodano (1982). *Tetrahedron Lett.* **23**, 4139–4142] and characterized. In the asymmetric unit, there are two molecules showing high geometrical and conformational similarity. The C-20 diterpenoid presents a *trans*-fused tricyclic system with a 1,4-dialdehyde function, adjacent to the double bond of the cyclohexene ring. Short intramolecular contacts, especially between the axial and isooriented methyl groups, cause significant distortions in the ring skeleton similar to that observed in other correlated structures. The profile of the molecule is rather bent (radius of curvature about 13 Å) in the direction perpendicular to the averaged molecular plane. Similar bending has been observed in the correlated scalaradial and 12-deacetoxyscalaradial structures and helps to improve the intramolecular interactions.