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# 5-[(4-Methylphenyl)diazenyl]salicylaldehyde

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ factor = 0.046
$wR$ factor = 0.102
Data-to-parameter ratio = 11.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.



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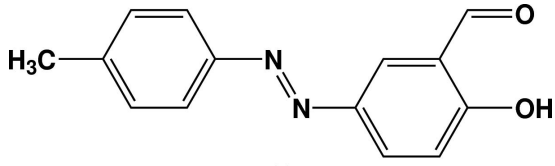
The title compound, $C_{14}H_{12}N_2O_2$, was isolated from the reaction between 4-methylphenyldiazonium nitrite and salicylaldehyde in sodium hydroxide. Structural analysis revealed a nearly planar molecule with the aromatic rings in *trans* positions about the azo group. The molecular packing shows interdigitated stacks of 12-membered hydrogen-bonded dimers.

## Comment

Azo compounds and their metal complexes have attracted much attention, in part because of their physicochemical properties, reactivity patterns and applications in many important areas that include molecular devices, chemical analysis, dyes, pharmaceuticals, *etc*. (Fryszkowska *et al.*, 2005; Ikeya & Okada, 2003; Ichimura, 2000). The reversible interconversion between the *cis* and *trans* isomers of azo compounds facilitates the use of these compounds in optical data storage, switching devices (Ichimura, 2000), non-linear optics (Jeon *et al.*, 2002; Qiu *et al.*, 2004) and photochromic materials (Atassi *et al.*, 1998), among others. The convenient synthesis of azo compounds from the coupling of aryl-substituted diazonium salts with electron-rich aromatic compounds led to the isolation of a large number of arylazo compounds of the donor–acceptor type. Although a series of Schiff base ligands derived from arylazosalicylaldehyde compounds have been reported (Khandar & Nejati, 2000; Khandar & Rezvani, 1998) and the structure of 2-chlorophenylazosalicylaldehyde (Albayrak *et al.*, 2004) has been described, to our knowledge the synthesis, characterization and structure of the title compound, (I), have not been previously reported.




(I)

When 4-methylphenyldiazonium nitrite was allowed to react with salicylaldehyde in sodium hydroxide, 5-[(4-methylphenyl)diazenyl]salicylaldehyde, (I), was obtained as a mustard-brown solid. This procedure is similar to that reported for the synthesis of a variety of arylazosalicylaldehydes (Khandar & Rezvani, 1998).

The $^1$H NMR spectrum of (I) measured in $d_6$-DMSO [$d_6$-DMSO is $d_6$-dimethyl sulfoxide] shows the aldehyde H atom at 10.35 p.p.m., the methyl H atoms at 2.39 p.p.m. and a series

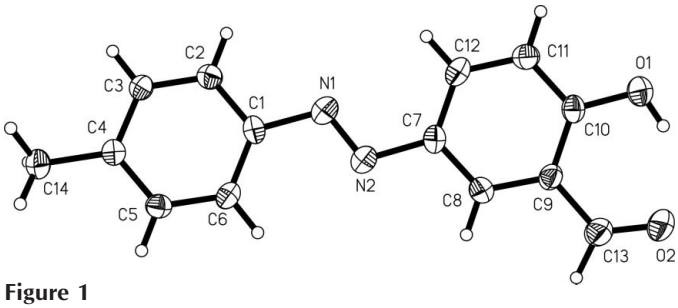



**Figure 1**
The molecular structure of (I), with ellipsoids drawn at the 30% probability level.

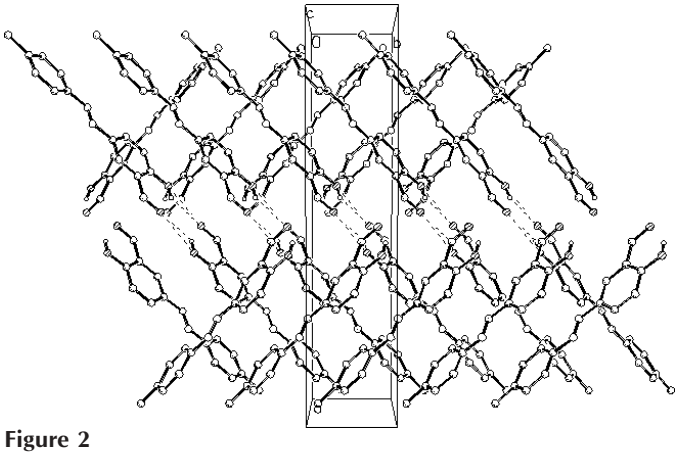


**Figure 2**
The molecular packing of (I), viewed along the *c* axis. Dashed lines indicate hydrogen bonds.

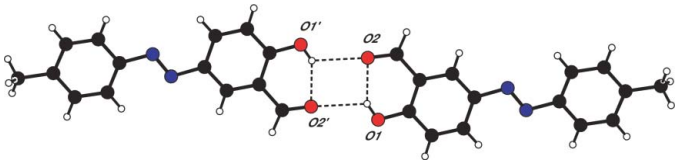



**Figure 3**
A perspective view of the centrosymmetric dimer formed by O—H···O hydrogen bonds, shown as dashed lines [symmetry code: (i) $1-x, 1-y, 1-z$].

of resonances in the range 8.20–7.00 p.p.m. due to the aromatic H atoms. The $^{13}$C NMR spectrum of (I) measured in $d_6$-DMSO shows signals at 191.00 and 163.64 p.p.m. due to the C atoms bearing the carbonyl and hydroxy group, respectively, and a series of resonances at 132.00–117.85 p.p.m. due to the C atoms of the aromatic rings; the methyl C atom appeared at 21.34 p.p.m. The DEPT-135 $^{13}$C NMR spectrum confirmed the assignment of H and C atoms. The electronic absorption spectrum of (I) measured in dimethylformamide (DMF) shows highly intense absorption bands at 270 nm ($\pi$–$\pi^*$ of C═C), 376 nm ($n$–$\pi^*$ of N═N) and 422 nm ($\pi$–$\pi^*$ of N═N), with extinction coefficients of $1.40 \times 10^4$, $2.20 \times 10^4$ and $1.40 \times 10^4$ $M^{-1}$cm$^{-1}$, respectively. The IR spectrum of (I) measured in KBr shows the $\nu$(C═O) at 1655 cm$^{-1}$ and $\nu$(C═C) at 1619 cm$^{-1}$, and $\nu$(O—H) as a broad band at 3448 cm$^{-1}$. The broad character of the hydroxy stretching frequency suggests the participation of the hydroxy group in hydrogen bonding.

The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The molecule adopts the *trans* C—N═N—C configuration with a nearly planar geometry and with torsion angles N2—N1—C1—C2 and N1—N2—C7—C8 of 177.2 (2) and 4.4 (3)°, respectively. This suggests delocalization of electron density between the aromatic rings and the azo group. The bond distances and angles are normal and similar to those reported for 2-chlorophenylazosalicylaldehyde (Albayrak *et al.*, 2004).

In the crystal structure, the packing of the molecules, as seen in Fig. 2, shows interdigitated stacks of 12-membered hydrogen-bonded dimeric units. These are illustrated in Fig. 3. With the exception of the hydrogen bonds between the hydroxy and keto groups (see Table 2), there are no additional hydrogen bonds in the crystal structure. The bond distances and angles of the hydrogen bonds are of the classic O—H···O type and are similar to those in 2-chlorophenylazosalicylaldehyde (Albayrak *et al.*, 2004). The face-to-face interplanar distance between the C atoms of adjacent stacks is *ca* 3.57 Å and the side-to-side distance between H atoms of intercalated stacks is *ca* 6.91 Å.

In conclusion, the X-ray structural analysis of (I) is consistent with spectroscopic data and confirms the presence of hydrogen bonds inferred from IR analysis. In view of their facile synthesis and interesting physicochemical properties, together with our continued interest in the coordination chemistry of azo compounds, further studies are in progress in our laboratories to explore the synthesis and coordination chemistry of a variety of azosalicyaldehyde compounds.

## Experimental

5-[(4-Methylphenyl)diazenyl]salicylaldehyde, (I), was prepared from the reaction between *p*-tolyldiazonium nitrite and salicyladehyde in sodium hydroxide, following a standard literature procedure as described for the synthesis of arylazo compounds of salicyladehyde (Khandar & Rezvani, 1998). Analysis calculated for $C_{14}H_{12}N_2O_2$: C 70.00, H 5.03, N 11.66%; found: C 70.02, H 4.94, N 11.58%. $^1$H NMR ($d_6$-DMSO): $\delta$ 10.35 (*s*, 1H), 8.17 (*s*, 1H), 8.07 (*d*, 1H), 7.84 (*d*, 2H), 7.55 (*d*, 1H), 7.18 (*d*, 1H) and 2.39 (*s*, 3H). $^{13}$C NMR ($d_6$-DMSO): $\delta$ 190.98 (1C), 163.56 (1C), 150.24 (1C), 145.06 (1C), 141.55 (1C), 130.22 (2C), 129.88 (1C), 123.87 (1C), 122.7 (2C), 118.70 (1C) and 21.34 (1C). DEPT-135 $^{13}$C NMR ($d_6$-DMSO): $\delta$ 191.00 (C═O), 163.64 (C—OH), 150.24, 145.06, 130.22, 129.90, 123.90, 122.70, 118.70 (C-aromatic rings) and 21.34 ($CH_3$). (IR (KBr disk), cm$^{-1}$: $\nu$ (C—O) 1206, $\nu$(OH) def 1378, $\nu$(C═O) 1655, $\nu$(C—H) 3101 and $\nu$(O—H) 3434. Single crystals of (I) were obtained, after several days, by slow evaporation of a DMSO solution.

*Crystal data*

$C_{14}H_{12}N_2O_2$
$M_r$ = 240.26
Monoclinic, $P2_1/c$
$a$ = 21.578 (5) Å
$b$ = 4.674 (5) Å
$c$ = 11.709 (5) Å
$\beta$ = 95.829 (5)°
$V$ = 1174.8 (14) Å$^3$
$Z$ = 4
$D_x$ = 1.358 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 39 reflections
$\theta$ = 3.8–25.0°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 (2) K
Block, brown
0.44 × 0.30 × 0.26 mm

*Data collection*

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2985 measured reflections
2061 independent reflections
1131 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 25.0°$
$h = -25 \rightarrow 25$
$k = -1 \rightarrow 5$
$l = -13 \rightarrow 1$
3 standard reflections
every 97 reflections
intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.103$
$S = 1.29$
2061 reflections
180 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.008P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å$^{-3}$
$\Delta\rho_{min} = -0.17$ e Å$^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0049 (6)

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

| | | | |
|---|---|---|---|
| O1—C10 | 1.344 (3) | C1—C6 | 1.393 (3) |
| O2—C13 | 1.220 (3) | C1—N1 | 1.439 (3) |
| N2—N1 | 1.237 (2) | C4—C14 | 1.496 (3) |
| N2—C7 | 1.446 (3) | C7—C8 | 1.368 (3) |
| C1—C2 | 1.376 (3) | C7—C12 | 1.401 (3) |
| | | | |
| N1—N2—C7 | 112.5 (2) | C8—C7—N2 | 116.5 (2) |
| C2—C1—C6 | 118.8 (2) | C12—C7—N2 | 125.0 (2) |
| C2—C1—N1 | 114.9 (2) | C8—C9—C13 | 120.5 (2) |
| C6—C1—N1 | 126.3 (2) | O1—C10—C11 | 117.7 (2) |
| C3—C2—C1 | 121.1 (2) | O1—C10—C9 | 122.9 (2) |
| C5—C4—C14 | 121.3 (2) | O2—C13—C9 | 124.5 (3) |
| C3—C4—C14 | 121.2 (2) | N2—N1—C1 | 113.4 (2) |
| C8—C7—C12 | 118.5 (2) | | |
| C1—N1—N2—C7 | −179.40 (18) | N2—N1—C1—C6 | 3.2 (3) |
| N1—N2—C7—C12 | 4.4 (3) | N2—N1—C1—C2 | −177.2 (2) |
| N1—N2—C7—C8 | −176.1 (2) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···O2 | 0.82 | 1.96 | 2.672 (3) | 145 |
| O1—H1···O2$^{i}$ | 0.82 | 2.34 | 2.863 (3) | 122 |

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

The methyl H atoms were refined isotropically [C—H = 0.89 (3)–0.94 (3) Å]. The other H atoms were assigned by assuming idealized geometry and were treated as riding atoms: aromatic C—H = 0.93 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C); O—H = 0.82 Å and $U_{iso}$(H) = 1.5$U_{eq}$(O).

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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