

3-Methoxy-5-(4-methylphenyl-diazenyl)salicylaldehyde and 3-methoxy-5-(2-methylphenyl-diazenyl)salicylaldehyde

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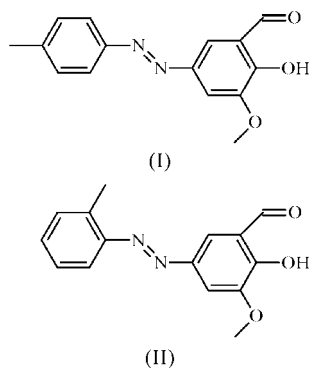
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The two title molecules, both $C_{15}H_{14}N_2O_3$, are roughly planar and display a *trans* conformation with respect to the $-N=N-$ double bond, as found for other diazene derivatives. In both compounds, there are intramolecular $O-H\cdots O$ hydrogen bonds and the crystal packing is governed by weak intermolecular $C-H\cdots O$ hydrogen bonds and $\pi-\pi$ stacking.

Comment

Diazenes have been the most widely used class of dyes owing to their versatile applications in various fields, such as dyeing textile fibres, colouring different materials, plastics, biological-medical studies, lasers, liquid crystalline displays, electro-optical devices and ink-jet printers in high-technology areas (Catino & Farris, 1985; Gregory, 1991). As part of a general study of the crystal chemistry of dyes and to provide templates for molecular modelling studies, the crystal structures of the yellow dye (I) and the light-brown dye (II) have been determined.



In the azo groups, the $N1-C1$ and $N2-C7$ bond lengths [1.426 (2) and 1.426 (2) Å in (I), and 1.427 (3) and 1.418 (3) Å in (II), respectively; Tables 1 and 3] indicate significant single-

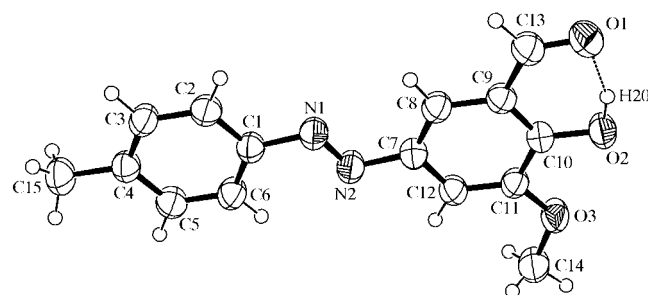


Figure 1
ORTEP-3 (Farrugia, 1997) view of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The dashed line indicates an intramolecular hydrogen bond.

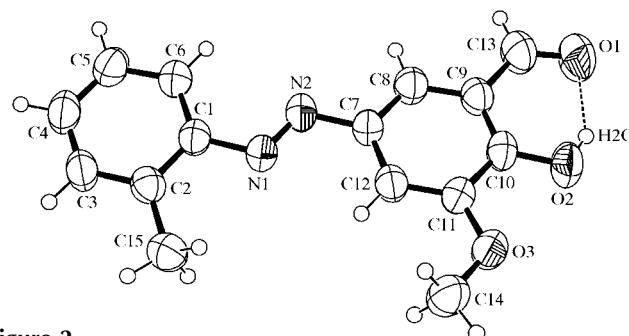
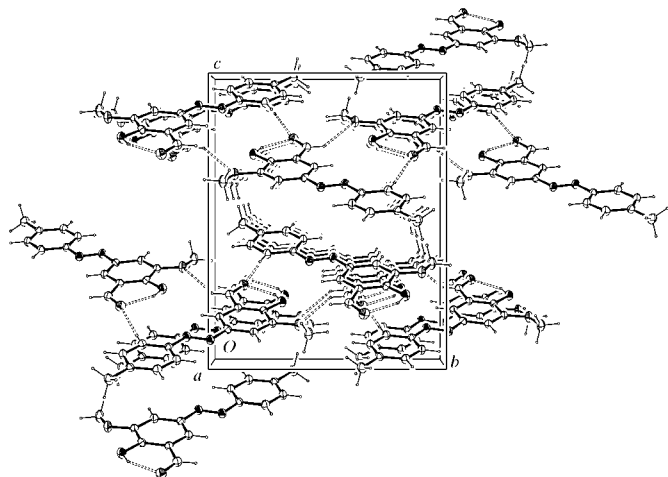


Figure 2
A view of (II), with the atom-numbering scheme and 50% probability displacement ellipsoids. The dashed line indicates an intramolecular hydrogen bond.

bond character, whereas the $-N=N-$ bond lengths [1.248 (2) Å in (I) and 1.251 (2) Å in (II)] are indicative of significant double-bond character. Similar values have been observed in other *trans*-azo compounds (Alder *et al.*, 1999, 2001; Dimmock *et al.*, 1997; Odabaşoğlu *et al.*, 2003; Ersanlı, Albayrak *et al.*, 2004; Ersanlı, Odabaşoğlu *et al.*, 2004; Koşar *et al.*, 2004). The aromatic rings are in a *trans* conformation with respect to the azo double bond. The $C14-O3$ bond length [1.413 (2) Å in (I) and 1.429 (4) Å in (II)] is approximately equal to that usually associated with a methyl $C-O$ bond in a methoxy group attached to an aromatic ring (1.424 Å; Allen *et al.*, 1987).

The structures of both (I) and (II) (Figs. 1 and 2) contain two essentially planar fragments, *viz.* one monosubstituted ($C1-C6$) and one trisubstituted phenyl ring ($C7-C12$). The largest deviations from the mean planes of these rings are 0.007 (1) and 0.002 (3) Å for (I), and 0.002 (1) and 0.006 (2) Å for (II), respectively. In (I), the dihedral angle, θ_1 , between the mean planes of the $C1-C6$ phenyl ring and the $C1-N1=N2-C7$ azo bridge is 1.24 (7)°, and the angle, θ_2 , between the planes of the $C1-N1=N2-C7$ azo group and the substituted $C7-C12$ phenyl ring is 1.06 (6)°. The angle, θ_3 , between the planes of the two rings is 0.53 (4)°, *i.e.* the phenyl rings are nearly coplanar. Compound (I) has strong intramolecular $O-H\cdots O$ [$O\cdots O = 2.611$ (2) Å] and weak intermolecular $C-H\cdots O$ [$C\cdots O = 3.205$ (2) Å and $C\cdots O = 3.567$ (2) Å] hydrogen bonds (see Table 2 for details). There is a weak $\pi-\pi$ stacking interaction involving the *p*-tolyl ring. The weak intermolecular hydrogen bonds result in the formation of


Figure 3

A view of the packing structure of (I), illustrating the C–H···O interactions. Dashed lines indicate intramolecular hydrogen bonds.

layers parallel to the (010) plane (Fig. 3), and π – π stacking interactions between these layers form a three-dimensional network. The ring in the molecule at (x, y, z) stacks above the ring at $(1 - x, -y, -z)$, with a distance of 3.812 (3) Å between the ring centroids and a perpendicular distance between the rings of 3.479 (1) Å. In (II), the dihedral angle, θ_1 , between the mean planes of the C1–C6 phenyl ring and the C1–N1=N2–C7 azo bridge is 7.05 (2)°, and the angle, θ_2 , between the planes of the C1–N1=N2–C7 azo group and the substituted C7–C12 phenyl ring is 1.70 (1)°. The dihedral angle, θ_3 , between the planes of the two rings, 8.23 (7)°, is larger than that in (I), and the two phenyl rings are slightly twisted with respect to one another. Like (I), compound (II) has a strong intramolecular O–H···O [O···O = 2.640 (3) Å] hydrogen bond (see Table 4 for details) and there is a weak π – π stacking interaction involving the *o*-tolyl ring. The ring in the molecule at (x, y, z) stacks above the ring at $(x, y, 1 + z)$, with a distance of 3.917 (3) Å between the ring centroids and a perpendicular distance between the rings of 3.410 (1) Å.

Experimental

Compounds (I) and (II) were prepared as described by Odabaşoğlu *et al.* (2003) using *o*-vanillin and 4-methylaniline for (I), and *o*-vanillin and 2-methylaniline for (II), as starting materials. Well shaped crystals of (I) and (II) were obtained by slow evaporation from acetic acid [for (I): m.p. 407–409 K, yield 83%; for (II): m.p. 381–383 K, yield 82%].

Compound (I)

Crystal data

C₁₅H₁₄N₂O₃
M_r = 270.28
 Monoclinic, *P*2₁/*c*
a = 6.746 (5) Å
b = 12.529 (5) Å
c = 15.556 (5) Å
 β = 91.842 (5)°
V = 1314.1 (12) Å³
Z = 4

D_x = 1.366 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 5746 reflections
 θ = 1.6–28.7°
 μ = 0.10 mm^{−1}
T = 293 (2) K
 Prism, yellow
 0.50 × 0.35 × 0.25 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 10 018 measured reflections
 3361 independent reflections
 1784 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.119
 θ_{\max} = 28.7°
h = −9 → 7
k = −16 → 16
l = −20 → 20

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.045
wR(*F*²) = 0.098
S = 0.84
 3361 reflections
 216 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F*_o²) + (0.0583*P*)²]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.32 e Å^{−3}
 Δρ_{min} = −0.20 e Å^{−3}
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.013 (3)

Table 1

Selected geometric parameters (Å, °) for (I).

C1–N1	1.426 (2)	C13–O1	1.224 (2)
C7–N2	1.426 (2)	C14–O3	1.413 (2)
C10–O2	1.350 (2)	N1–N2	1.248 (2)
C11–O3	1.362 (2)		
C2–C1–N1	116.1 (1)	O3–C11–C12	125.7 (2)
C6–C1–N1	124.6 (1)	O3–C11–C10	114.9 (2)
C8–C7–N2	125.2 (1)	O1–C13–C9	124.1 (1)
C12–C7–N2	115.1 (1)	N2–N1–C1	114.2 (2)
O2–C10–C11	118.6 (2)	N1–N2–C7	114.1 (2)
O2–C10–C9	121.7 (2)	C11–O3–C14	117.9 (2)
C11–C10–C9	119.7 (1)		

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C13–H13···O3 ⁱ	1.01 (2)	2.39 (1)	3.205 (2)	137.3 (10)
C2–H2···O1 ⁱ	0.97 (2)	2.60 (2)	3.567 (2)	172.7 (11)
O2–H2O···O1	0.97 (2)	1.68 (2)	2.611 (2)	159.1 (16)

Symmetry code: (i) 2 − *x*, *y* − ½, ½ − *z*.

Compound (II)

Crystal data

C₁₅H₁₄N₂O₃
M_r = 270.28
 Monoclinic, *Cc*
a = 10.734 (5) Å
b = 14.786 (5) Å
c = 8.533 (5) Å
 β = 97.053 (5)°
V = 1344.0 (11) Å³
Z = 4
D_x = 1.336 Mg m^{−3}

Mo *K*α radiation
 Cell parameters from 8228 reflections
 θ = 2.4–25.9°
 μ = 0.10 mm^{−1}
T = 293 K
 Prism, light brown
 0.60 × 0.33 × 0.13 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 9238 measured reflections
 1307 independent reflections
 1052 reflections with $I > 2\sigma(I)$
*R*_{int} = 0.077

θ_{\max} = 25.9°
h = −13 → 13
k = −18 → 18
l = −9 → 10

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 0.93$	$\Delta\rho_{\max} = 0.12 \text{ e } \text{\AA}^{-3}$
1307 reflections	$\Delta\rho_{\min} = -0.11 \text{ e } \text{\AA}^{-3}$
185 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.016 (3)

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

C1—N1	1.427 (3)	C13—O1	1.234 (4)
C7—N2	1.418 (3)	C14—O3	1.429 (4)
C10—O2	1.344 (4)	N1—N2	1.251 (3)
C11—O3	1.364 (3)		
C6—C1—N1	123.7 (2)	O3—C11—C12	126.1 (2)
C2—C1—N1	116.0 (2)	O3—C11—C10	113.8 (2)
C8—C7—N2	116.1 (2)	O1—C13—C9	124.5 (3)
C12—C7—N2	124.2 (2)	N2—N1—C1	114.4 (2)
O2—C10—C9	122.3 (2)	N1—N2—C7	114.6 (2)
O2—C10—C11	118.1 (3)	C11—O3—C14	116.6 (2)
C9—C10—C11	119.6 (2)		

Table 4

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2O \cdots O1	0.82	1.92	2.640 (3)	146

For (I), C—H distances are in the range 0.94 (1)–1.01 (1) \AA and $U_{\text{iso}}(\text{H})$ values are in the range 0.049 (4)–0.072 (5) \AA^2 . For the hydroxy H atom, the O—H distance is 0.97 (2) \AA . The remaining H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96 \AA for atoms C14 and C15. The $U_{\text{iso}}(\text{H})$ values were constrained as $1.5U_{\text{eq}}(\text{methyl C})$. For (II), all H atoms were positioned geometrically and refined as riding, with C—H distances of 0.93–0.96 \AA and an O—H distance of 0.82 \AA . The $U_{\text{iso}}(\text{H})$ values were constrained as $1.2U_{\text{eq}}(\text{C})$ [$1.5U_{\text{eq}}(\text{methyl C})$]. Owing to the absence of atoms heavier than Si and to the use of Mo

$K\alpha$ radiation, the absolute structure could not be determined reliably and Friedel pairs were merged, resulting in a low data/parameter ratio.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1045). Services for accessing these data are described at the back of the journal.

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