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(*Z*)-6-{[1,3-Dihydroxy-2-(hydroxymethyl)propan-2-ylamino]methylene}-2-methoxy-4-[(*E*)-*o*-tolyldiazenyl]cyclohexa-2,4-dienone

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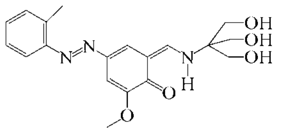
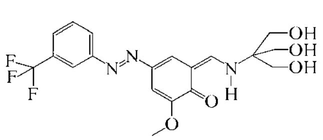
The title compound, $C_{19}H_{23}N_3O_5$, adopts the keto–amine tautomeric form with the hydroxy H atom located on the N atom, where it is involved in a strong intramolecular N—H···O hydrogen bond. The compound exhibits *trans* geometry with respect to the azo N═N double bond, with a dihedral angle between the two benzene rings of 38.03 (6)°. The packing of the molecules in the crystal structure is determined by O—H···O and C—H···O hydrogen bonds. A comparison with closely related compounds is given.

Comment

Schiff base compounds can be classified by their photochromic and thermochromic characteristics (Cohen *et al.*, 1964). Optically active azobenzene polymers are very important because of their photoresponsive properties. Such photochromic compounds have been increasing in number ever since their potential applications were realised in areas such as the control and measurement of radiation intensity, optical computers and display systems (Dürr, 1989; Dürr & Bouas-Laurent, 1990).

In this paper, we report the synthesis and crystal structure of the title compound, (I), and compare it with those of other diazenes (see scheme), namely (*Z*)-6-{[1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylamino]methylene}-2-methoxy-4-{(*E*)-[3-(trifluoromethyl)phenyl]diazenyl}cyclohexa-2,4-dienone, (II) (Ersanlı, Albayrak, Odabaşoğlu & Kazak, 2005), (*Z*)-4-[(*E*)-(4-butylphenyl)diazenyl]-6-{[1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylamino]methylene}-2-methoxycyclohexa-2,4-dienone, (III) (Ersanlı, Albayrak, Odabaşoğlu & Büyükgüngör *et al.*, 2005), (*Z*)-4-(2,6-dichlorophenyldiazenyl)-6-{[1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylamino]methylene}-2-methoxycyclohexa-2,4-dienone and the 3-methoxyphenyldiazenyl and 4-methoxyphenyldiazenyl analogues, (IV) (Özek *et al.*, 2006), 4-[(3-chlorophenyl)diazenyl]-6-methoxy-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2*H*)-one, (V) (Koşar *et al.*, 2004*a*), 4-[(4-methylphenyl)diazenyl]-6-methoxy-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2*H*)-one, (VI) (Koşar *et al.*, 2004*b*), and (*Z*)-6-[1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylamino]methylene-4-[(*E*)-(4-ethylphenyl)diazenyl]cyclohexa-2,4-dienone, (VII) (Şahin *et al.*, 2005).


(I)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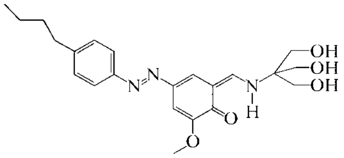
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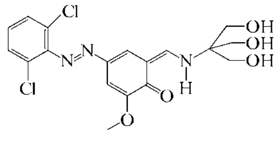
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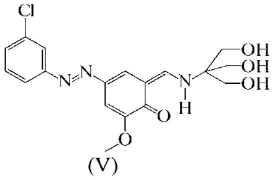
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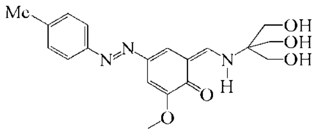
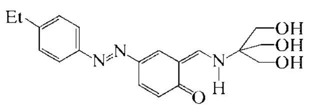

(VI)


(VII)

The structure of (I) (Fig. 1 and Table 1) is very similar to those of diazene (azo) compounds reported previously (Table 3). The molecule consists of two aromatic groups linked through a diazene bridge; we designate the aromatic rings and azo group *A*, *B* and *C*, corresponding to the C1–C6 ring, the C8–C13 ring and the C1—N═N2—C8 group, respectively. The dihedral angles between these groups are *A*/*C* = 27.54 (7)°, *B*/*C* = 10.49 (16)° and *A*/*B* = 38.03 (6)°. Ring *A* is essentially planar, with an r.m.s. deviation of 0.010 (2) Å and a maximum deviation from this plane of 0.016 (2) Å for atom C1. Ring *B* is almost planar [r.m.s. deviaton = 0.016 (1) Å], with a maximum deviation from this plane of 0.025 (1) Å for atom C11. The aromatic rings are in a *trans* configuration with respect to the azo double bond. The N1—C1 and N2—C8 bond lengths indicate single-bond character, and the N═N bond length is indicative of significant double-bond character, as has been observed in other *trans*-azo compounds (Ersanlı, Odabaşoğlu *et al.*, 2004*a*; Ersanlı, Albayrak, Odabaşoğlu, Kazak & Erdönmez, 2004).

There is a strong intramolecular N3—H3N···O2 hydrogen bond, with the N3···O2 distance shorter than the sum of the van der Waals radii of O and N (3.07 Å; Bondi, 1964) and comparable with the distances observed in (II) [2.585 (2) Å] and (IV) [2.587 (2) Å].

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A comparison of bond lengths and angles associated with the azo group is given in Table 3 for structures (I)–(VII). The steric effect of the *ortho*-methyl group has caused an enlargement in (I) of the dihedral angle between the ring planes [38.03 (6)°] similar to that found in the *o*-chloro derivative, (IV), but it has no significant affect on the C1—N1, N2—C8 and N1—N2 bonds. However, the *A*/*B* dihedral angles of most of the compounds which do not have *ortho* substituents on ring *A* [*viz.* (II), (III), (V) and (VII)] range from 7.81 (4) to 13.99 (18)°, in contrast with the value of 34.88 (21)° for compound (VI). Accordingly, it can be said that the dihedral angles *A*/*B* may be affected by both the positions of the substituents and by the crystal packing.

The structural data clearly show that (I) adopts the keto–amine form, as indicated by the C11—O2, N3—C15, C12—C15 and C11—C12 bond lengths (Fig. 1 and Table 1). There are significant elongations of the N3—C15 bonds and contractions of the C11—O2 bonds. Similar *o*-hydroxy Schiff bases have been found to adopt the keto (Ersanlı *et al.*, 2003; Ersanlı, Albayrak, Odabaşoğlu, Thöne & Erdönmez, 2004), enol (Ersanlı, Albayrak, Odabaşoğlu & Erdönmez, 2004; Ersanlı, Odabaşoğlu *et al.*, 2004*b*) or enol/keto mixture form (Nazır *et al.*, 2000). The N3—C15 and O2—C11 bond distances (Table 1) are reasonably similar, a characteristic of systems in the keto–amine form, comparable with those found in (II) [1.291 (2) and 1.281 (2) Å] and (III) [1.289 (5) and 1.276 (5) Å]. In contrast, the same bonds can be compared with the corresponding distances in 2-[2-(hydroxymethyl)-phenyliminomethyl]phenol [1.275 (2) and 1.354 (2) Å; Ersanlı, Odabaşoğlu *et al.*, 2004*b*] and 4-(2-hydroxyphenylimino-methylene)phenol [1.278 (2) and 1.355 (2) Å; Ersanlı, Albayrak, Odabaşoğlu & Erdönmez, 2004], which exist in the enol–imine tautomeric form.

In the crystal structure of (I), O—H···O and C—H···O hydrogen bonds (Fig. 2 and Table 2) generate edge-fused $R_2^2(8)$ and $R_2^2(9)$ rings (Etter, 1990), forming a three-dimensional network.

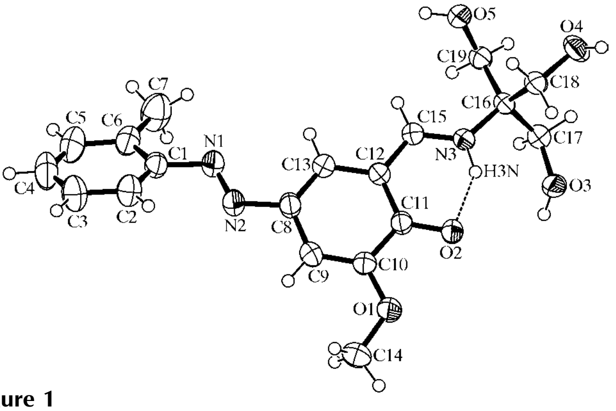

Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the intramolecular hydrogen bond.

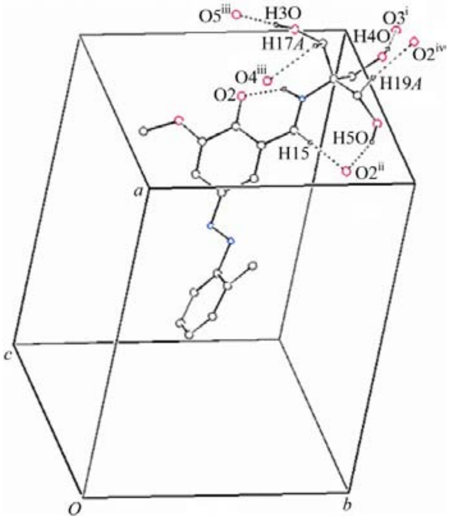

Figure 2
A packing diagram for (I), with hydrogen bonds drawn as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity. The symmetry codes are as given in Table 2.

Experimental

The title compound, (I), was prepared as previously described by Ersanlı, Albayrak, Odabaşoğlu, Thöne & Erdönmez (2004). The product was recrystallized from ethanol and well shaped crystals were obtained by slow evaporation of a methanol solution (yield 88%; m.p. 490–492 K).

Crystal data

$C_{19}H_{23}N_3O_5$
$M_r = 373.40$
Monoclinic, $P2_1/c$
$a = 15.6582$ (7) Å
$b = 10.6380$ (6) Å
$c = 11.1041$ (5) Å
$\beta = 98.238$ (4)°
$V = 1830.55$ (16) Å^3
$Z = 4$
$D_x = 1.355$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 296$ (2) K
Plate, orange
0.50 × 0.28 × 0.06 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.964$, $T_{\max} = 0.994$
30866 measured reflections
4371 independent reflections
2882 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.074$
$\theta_{\max} = 28.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.089$
$S = 0.87$
4371 reflections
262 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.428 (2)	C12—C15	1.418 (2)
C8—N2	1.416 (2)	C15—N3	1.291 (1)
C10—O1	1.361 (1)	C16—N3	1.468 (1)
C11—O2	1.286 (1)	N1—N2	1.250 (2)
C11—C12	1.428 (2)		
C9—C10—O1	126.1 (1)	N2—N1—C1	112.28 (11)
O2—C11—C12	123.28 (10)	N1—N2—C8	116.17 (11)
C11—C12—C15—N3	−0.75 (18)	C1—N1—N2—C8	178.87 (10)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4O···O3^{i}	0.92 (2)	1.81 (2)	2.7282 (13)	174.8 (16)
O5—H5O···O2^{ii}	0.88 (2)	2.00 (2)	2.8430 (12)	159.3 (17)
O3—H3O···O5^{iii}	0.89 (2)	1.872 (18)	2.7576 (13)	179.7 (18)
C15—H15···O2^{ii}	0.93	2.48	3.3951 (14)	167
C17—H17*A*···O4^{iii}	0.97	2.57	3.3157 (15)	134
C19—H19*A*···O2^{iv}	0.97	2.47	3.4223 (15)	167
N3—H3N···O2	0.94 (2)	1.772 (17)	2.5873 (13)	143.4 (15)

Symmetry codes: (i) $-x+2, -y+2, -z+2$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$.

Table 3
Comparison of geometric parameters (Å, °) for (I) with those in the related compounds (II), (III), (IV), (V), (VI) and (VII).

A is the ring C1–C6, *B* is ring C8–C13 and *C* is the azo group C1—N═N2—C8.

Bond	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
N1—N2	1.250 (2)	1.264 (2)	1.238 (5)	1.243 (3)	1.260 (2)	1.247 (5)	1.253 (7)
N1—C1	1.428 (2)	1.426 (2)	1.427 (7)	1.443 (3)	1.430 (2)	1.429 (6)	1.428 (9)
N2—C8	1.416 (2)	1.411 (2)	1.406 (6)	1.417 (3)	1.402 (2)	1.417 (5)	1.428 (8)
C1—N1—N2—C8	178.87 (10)	−178.75 (10)	−175.6 (5)	179.2 (2)	179.53 (16)	172.2 (4)	−175.9 (5)
A/*B*	38.03 (6)	7.81 (4)	13.99 (18)	58.94 (1)	10.05 (5)	34.88 (21)	8.94 (2)
A/*C*	27.54 (7)	8.36 (7)	7.26 (25)	61.51 (1)	8.10 (10)	29.73 (34)	12.14 (3)
B/*C*	10.49 (16)	8.20 (5)	7.34 (18)	2.91 (1)	2.13 (7)	7.29 (22)	8.55 (2)

H atoms attached to N and O atoms were refined with isotropic displacement parameters. All H atoms bound to C atoms were refined using a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms, C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene H atoms, and C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

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, 1997); 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3007). Services for accessing these data are described at the back of the journal.

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