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4-(4-Methoxyphenyldiazenyl)-2,6-dimethylphenol

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.131
Data-to-parameter ratio = 12.9

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

The title compound, $C_{15}H_{16}N_2O$, has a *trans* configuration with respect to the diazene double bond, and is approximately planar in the solid state. The dihedral angle between the planes of the two aromatic rings is 8.33 (16)°. In the crystal structure, the molecules are linked to one another, head-to-head, by the hydroxyl groups, forming intermolecular O—H···O hydrogen bonds.

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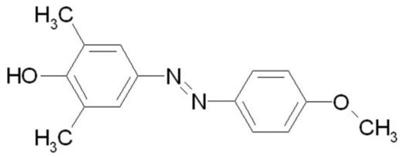
Comment

Diazenes are 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). Hence, because of this wide interest, many experimental studies on diazene compounds have been performed (Huang *et al.*, 2002; Zhang *et al.*, 1998). We have previously reported the structural characterization of compounds with no substituent group [2,6-dimethyl-4-(phenyldiazenyl)phenol, (II); Soylu *et al.*, 2004] and containing a 4-chloro group [2,6-dimethyl-4-(4-chlorophenyldiazenyl)phenol, (III); Kocaokutgen *et al.*, 2003; 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 structure of the title compound, (I), a yellow dye containing a 4-methoxy group, has been determined.



(I)

The molecular structure of the title compound (I) is shown in Fig. 1. It is seen to be very similar to that found in the diazene compounds mentioned above, and consists of two aromatic groups linked through a diazene bridge. In the azo groups, the N1—C1 and N2—C7 bond lengths [1.423 (2) and 1.431 (2) Å, respectively] indicate significant single-bond character, whereas the N═N bond length [1.253 (2) Å] is indicative of significant double-bond character. Similar values have been observed in other *trans*-azo compounds (Huang *et al.*, 2002; Zhang *et al.*, 1998; Maginn, 1993; Jiménez-Cruz *et al.*, 2000). The aromatic rings are in a *trans* configuration with respect to the azo double bond. The dihedral angle, θ_1 between the mean planes of the 4-methoxyphenyl ring and the C1—N1═N2—C7 diazene bridge is 8.24 (26)°, and the angle

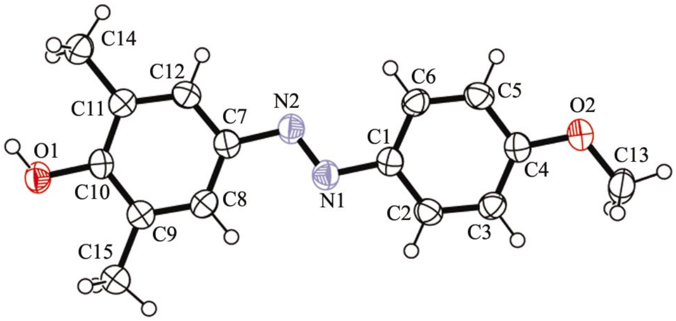


Figure 1

An *ORTEP*-3 (Farrugia, 1997) view of the title compound (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

θ_2 between the C1—N1═N2—C7 diazene group and the 3,5-dimethyl-4-hydroxyphenyl ring is 4.28 (25)°. The angle θ_3 between the planes of the 4-methoxyphenyl and 3,5-dimethyl-4-hydroxyphenyl rings is 8.33 (16)°. As a result, the two substituted phenyl rings, which adopt a *trans* configuration with respect to the diazene double bond, are approximately coplanar.

Table 2 shows a comparison of bond lengths and angles for the diazenes (I), (II) and (III). Comparing the bond lengths of compounds (I)–(III), we find that the N2═N1 bond lengths are very similar, while distance N1—C1 in compounds (I) and (III) is considerably shorter than in compound (II), as a result of the presence of the methoxy and chloro groups in the *para* positions with respect to the diazene linkage. This result can be attributed to the electron-withdrawing groups attached to the benzene ring. When comparing the dihedral angles between the benzene rings, it can be seen that compounds (II) and (III) are more nearly planar than (I). The values of the C1—N1═N2—C2 dihedral angles are consistent with this observation.

Analysis of the crystal packing of (I) shows the presence of intermolecular O—H···O hydrogen bonds (Fig. 2). The H atom of the hydroxyl group forms an O1—H1···O1$^{\rm iii}$ interaction with the same group of the neighbouring molecule (details are given in Table 1). This hydrogen bond connects adjacent molecules head-to-head, running along the *b* axis, and is highly effective in forming polymeric chains which stabilize the crystal structure (Fig. 2).

The results obtained in this study indicate that there are significant differences between the molecular structures of compounds (I), (II) and (III). In (I), the hydroxyl groups are linked to each other by intermolecular hydrogen bonds, forming a one-dimensional network, as shown in Fig. 2. While this bonding arrangement is very similar to that observed in compound (III), which contains a 4-chloro group, it is different from that observed in compound (II), the unsubstituted compound, where a seven-membered chelate ring with O—H···N and C—H···O hydrogen bonds is formed. All of these interactions are highly effective in forming polymeric chains in one dimension in all three compounds. Dipole–dipole and van der Waals interactions are also effective in the molecular packing in the crystal structures.

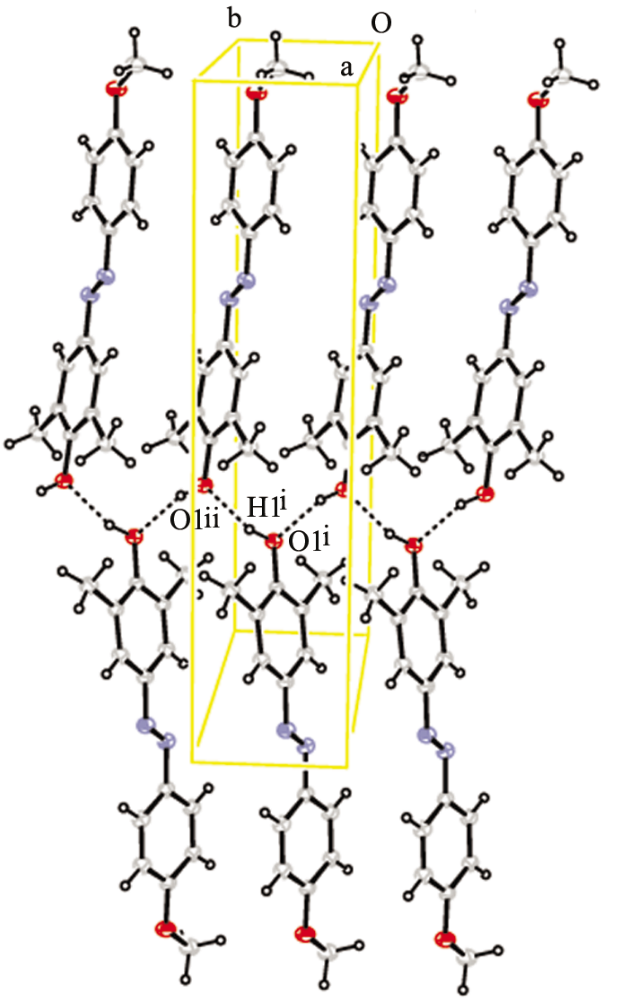


Figure 2

Crystal packing of the title compound (I), showing the hydrogen-bonding interactions (dashed lines). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $x, y, z-1$; (ii) $\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$.]

Experimental

2,6-Dimethyl-4-(4-methoxyphenyldiazenyl)phenol was synthesized by the method of Kocaokutgen *et al.* (2003). The product obtained was crystallized from ethyl alcohol, giving crystals of (I) (m.p. 397–399 K) of suitable quality for X-ray diffraction analysis.

Crystal data

$C_{15}H_{16}N_2O_2$
$M_r = 256.30$
Monoclinic, $P2_1/n$
$a = 17.049$ (4) Å
$b = 4.154$ (9) Å
$c = 19.130$ (4) Å
$\beta = 102.695$ (4)°
$V = 1322$ (3) Å^3
$Z = 4$

$D_x = 1.288$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7798 reflections
$\theta = 2.5$–29.2°
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Prism, orange
0.50 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\rm min} = 0.958$, $T_{\rm max} = 0.991$
6146 measured reflections

2303 independent reflections
1747 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\rm max} = 25.0°$
$h = -20 \rightarrow 20$
$k = -4 \rightarrow 4$
$l = -22 \rightarrow 22$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.131$
$S = 1.11$
2303 reflections
178 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.2962P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O1$^{\rm iii}$	0.91 (3)	1.89 (3)	2.730 (4)	152 (2)

Symmetry code: (iii) $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

Table 2
A comparison of geometrical parameters (Å, °) for compound (I) and related compounds (II) and (III).

	(I)	(II)	(III)
C7—N2	1.431 (2)	1.428 (3)	1.424 (2)
N2—N1	1.253 (2)	1.252 (3)	1.256 (2)
N1—C1	1.423 (2)	1.451 (3)	1.430 (2)
C1—N1—N2—C7	−177.53 (16)	−178.00 (17)	−177.66 (16)
(C1–C6)/(C7,N2,N1,C2)	8.24 (26)	13.48 (22)	2.65 (15)
(C7–C12)/(C7,N2,N1,C2)	4.29 (25)	10.90 (21)	2.84 (15)
(C1–C6)/(C7–C12)	8.33 (16)	6.57 (15)	5.48 (10)

The hydroxyl H atom was located in a Fourier difference map and refined isotropically. The remainder of the H atoms were included in calculated positions and treated as riding atoms; C—H = 0.96 Å for CH_3 and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(parent C atom), and C—H = 0.93 Å for $CH_{\rm ar}$ and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent C atom).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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