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2,6-Dimethyl-4-(phenyldiazenyl)-phenol

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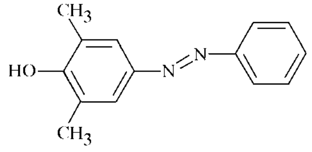
The crystal structure of the title compound, $C_{14}H_{14}N_2O$, determined at 293 K, shows that the molecule is approximately planar in the solid state and that the aromatic rings have a *trans* configuration with respect to the azo double bond, as found for other diazene derivatives. The packing can be described as a polymeric arrangement of molecules linked through O—H···N and C—H···O hydrogen bonds and close contacts. These intermolecular interactions result in the formation of infinite chains parallel to the *b* axis.

Comment

Diazenes have been widely used as dyes, owing to their versatility in various fields and in advanced technologies, including textiles, plastics, biological staining, lasers, liquid crystalline displays, electro-optical devices and ink-jet printers (Catino & Ferris, 1985; Gregory, 1991). Because of their wide spread use, diazenes have been the subject of many experimental studies (Huang *et al.*, 2002; Zhang *et al.*, 1998; Kocaokutgen, Gür *et al.*, 2003; Kocaokutgen, Soylu *et al.*, 2003). In this paper, we report the synthesis and crystal structure of the title compound, (I), recrystallized from ethanol. We also include here a comparison of the present structure with those of other diazenes, namely 2,6-dimethyl-4-(4-chlorophenyldiazenyl)phenol, (II) (Kocaokutgen, Gür *et al.*, 2003), and 2-*tert*-butyl-4-methyl-6-(phenyldiazenyl)phenol, (III) (Kocaokutgen, Soylu *et al.*, 2003).



(I)

The structure of (I) (Fig. 1) is very similar to those of diazene (azo) compounds reported previously. The molecule consists of two aromatic groups linked through a diazene bridge. The dihedral angles between the azo bridge *A* (C1—N1═N2—C7) and the coplanar substituted and unsubstituted benzene rings *B* (C1–C6) and *C* (C7–C12) are *A*/*B* 13.48 (22), *A*/*C* 10.90 (21) and *B*/*C* 6.57 (15)°, *i.e.* the two substituted benzene rings are approximately coplanar. Some related torsion angles are reported in Table 1. The aromatic rings are in a *trans* configuration with respect to the azo double bond. The N1—C1 and N2—C7 bond lengths of 1.451 (3) and 1.428 (3) Å, respectively, indicate single-bond character, and the N═N bond length of 1.252 (3) Å is indicative of significant double-bond character.

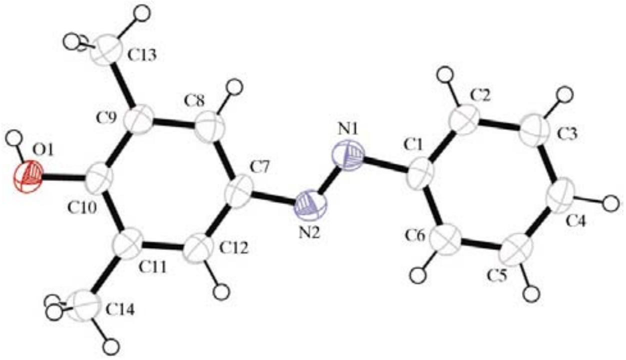


Figure 1
A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

In the structure of (I), the hydroxyl group forms two close intermolecular contacts with a symmetry-related molecule

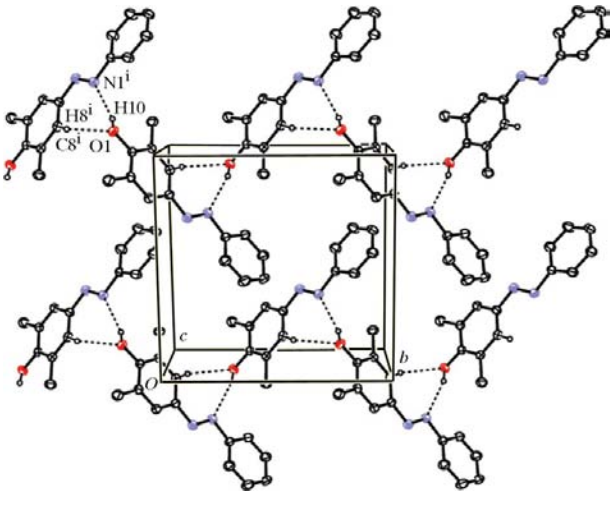


Figure 2
Diagram of the hydrogen-bonding interactions in (I) (dashed lines). Displacement ellipsoids are drawn at the 30% probability level and H atoms not involved in hydrogen-bond interactions have been omitted for clarity. [Symmetry code: (i) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$.]

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(Table 2). In the first interaction, the hydroxyl group (atom O1) serves as a hydrogen-bond donor to one of the azo N atoms in a neighbouring molecule and in the second it is in close contact with the H atom bonded to atom C8 of the benzene ring of the same molecule. These intermolecular interactions link neighbouring molecules in one dimension and are highly effective in forming polymeric chains which stabilize the crystal structure (Fig. 2). As shown in Fig. 2, the chains extend parallel to the *b* axis.

A comparison of bond lengths and angles associated with the azo group is given in Table 3 for structures (I), (II) and (III). A general conclusion is that the molecular geometry of the diazene moiety of (III) is significantly different from that of (I) and (II). The C—N bond lengths of (I) and (II) are longer than the corresponding values reported for (III), while their N═N bond lengths are shorter. In the chemical structure of (III), there is a hydroxyl group *ortho* to the azo group which forms an intramolecular hydrogen bond to the distal N atom. We believe that the presence of this intramolecular hydrogen bond is related to the relative expansion of the diazene N═N double bond observed for (III).

The results obtained in this study indicate that there are also significant differences when comparing the molecular structures of (I) and (II). In the previously reported structure of (II), the crystal packing is mainly stabilized by intermolecular O—H···O hydrogen bonds, which form a dimeric arrangement. From the results presented in this paper, it can be said that the crystal structure is stabilized by a seven-membered chelate ring *via* O—H···N hydrogen bonds and close C—H···O interactions, which are highly effective in forming polymeric chains in one dimension (Fig. 2). Dipole–dipole and van der Waals interactions are also effective in the molecular packing in the crystal structure.

Experimental

A mixture of aniline (0.02 mol), water (40 ml) and concentrated hydrochloric acid (0.06 mol) was stirred. This solution was cooled to 273–278 K and a solution of sodium nitrite (0.02 mol) in water (10 ml) was added dropwise, while maintaining the temperature below 278 K. The resulting mixture was stirred for an additional 30 min in an ice bath and then buffered with solid sodium acetate. 2,6-Dimethylphenol (0.02 mol), dissolved with sodium hydroxide (0.02 mol) in water (10 ml), was cooled to 273–278 K in an ice bath and then gradually added to the above solution of benzenediazonium chloride. The resulting mixture was stirred for 60 min. The crude precipitate was filtered off, washed several times with water and recrystallized from ethanol (m.p. 364–365 K; yield 86%). Purity was monitored by thin-layer chromatography. The compound was recrystallized from ethanol to produce crystals of (I) of suitable quality for X-ray diffraction analysis. The IR spectrum of (I) was recorded using an IASCO FT–IR-430 spectrophotometer. IR spectroscopic data (ν, cm^{-1}): 3350 (O—H), 2953–2920 (CH_3). Elemental analysis calculated: C 74.34, H 6.19, N 12.39%; found: C 74.28, H 6.35, N 12.03%. UV–Vis measurements [λ (nm), log ε (l/mol cm), CH_3CH_2OH]: 353 (4.713), 444 (3.454). ^{1}H NMR (200 MHz, DMSO-d_6, δ): 8.98 (*s*, H, OH), 740–7.85 (*m*, 7H, Ar), 2.29 (*s*, 3H, CH_3).

Crystal data

$C_{14}H_{14}N_2O$
$M_r = 226.27$
Monoclinic, $P2_1/c$
$a = 11.1447\ (16)$ Å
$b = 10.7602\ (14)$ Å
$c = 10.5103\ (15)$ Å
$\beta = 106.775\ (2)^\circ$
$V = 1206.8\ (3)$ Å^3
$Z = 4$
$D_x = 1.245$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 915 reflections
$\theta = 2.7$–28.3°
$\mu = 0.08$ mm^{-1}
$T = 210\ (2)$ K
Prism, orange
$0.30 \times 0.30 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.976$, $T_{max} = 0.992$
4421 measured reflections
2896 independent reflections
2063 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 28.3^\circ$
$h = -8 \rightarrow 14$
$k = -8 \rightarrow 14$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.170$
$S = 1.09$
2896 reflections
210 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.6654P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C10	1.360 (3)	C11—C14	1.498 (3)
C9—C13	1.509 (3)		
N2—N1—C1	112.58 (17)	C6—C1—N1	124.8 (2)
N1—N2—C7	115.25 (18)	C12—C7—N2	114.72 (19)
C2—C1—N1	115.28 (18)	C8—C7—N2	125.8 (2)
C1—N1—N2—C7	177.99 (18)	C13—C9—C10—O1	−1.5 (3)
C8—C9—C10—O1	178.5 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···N1^i	0.81 (3)	2.21 (3)	2.963 (2)	155 (3)
C8—H8···O1^{ii}	0.93 (2)	2.51 (3)	3.328 (3)	147.4 (19)

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

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

	(I)	(II)	(III)
C7—N2	1.428 (3)	1.424 (2)	1.411 (3)
N2—N1	1.252 (3)	1.256 (2)	1.268 (2)
N1—C1	1.451 (3)	1.430 (2)	1.429 (3)
C7—N2—N1—C1	−178.00 (17)	−177.66 (16)	−179.46 (19)

H-atom parameters were refined freely; C—H distances are in the range 0.91 (3)–1.03 (3) Å.

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).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1136). Services for accessing these data are described at the back of the journal.

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