organic papers

2-*tert*-Butyl-4-methyl-6-(phenyldiazenyl)phenol

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The crystal structure of the title compound, $C_{17}H_{20}N_2O$, determined at 208 K, shows that the molecule is approximately planar in the solid state, having a *trans* configuration with respect to the azo double bond, as found for other diazene derivatives. The dihedral angle between the planes of the two aromatic rings is 5.04 (12)°. The hydroxy group and an N atom of the azo group are linked by an intramolecular O—H···N hydrogen bond.

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 our studies on azo derivatives, the title compound, (I), was synthesized and its crystal structure is reported here.

(I)
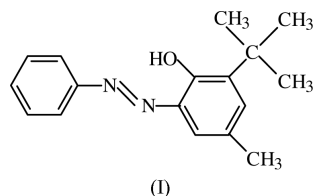
An *ORTEP*-3 (Farrugia, 1997) view of the molecule of (I) and the molecular packing are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are given in Table 1. The structure of (I) is very similar to an azo
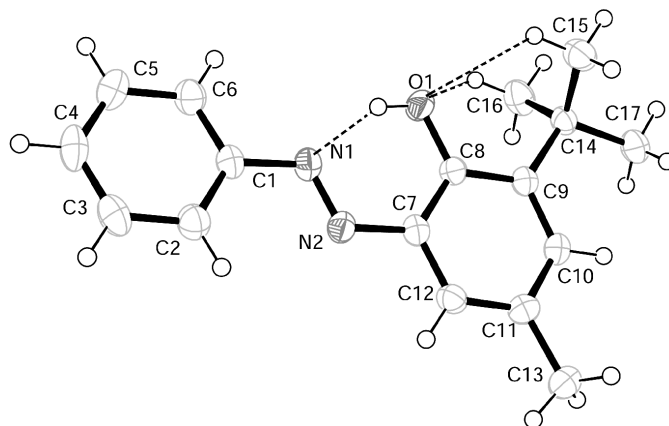

Figure 1

An *ORTEP*-3 (Farrugia, 1997) view of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. Dashed lines indicate intramolecular hydrogen bonds.

compound studied previously (Işik, 1998). 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 phenyl ring (C1–C6) and the C1—N1=N2—C7 azo bridge is 6.8 (2)°, and the angle Θ_2 between the C1—N1=N2—C7 azo group and the substituted phenyl ring (C7–C12) is 1.9 (2)°. The angle Θ_3 between the planes of the rings is 5.11 (14)°, *i.e.* the substituted and unsubstituted phenyl rings are approximately coplanar. The N1—C1 and N2—C7 bond lengths of 1.429 (3) and 1.411 (3) Å, respectively, indicate single-bond character and the N=N bond length of 1.268 (2) Å is indicative of significant double-bond character. These values are comparable with those found for similar compounds (Huang *et al.*, 2002; Zhang *et al.*, 1998; Maginn, 1993; Jimenez-Cruz *et al.*, 2000; Kocaokutgen *et al.*, 2003).

The near coplanarity of the aromatic rings with the azo bridge is facilitated by an O1—H1···N1 intramolecular hydrogen bond. C16—H16B···O1 and C15—H15B···O1 hydrogen bonds are also observed in the molecular structure (see Table 2 for details).

The molecules are stacked along the *a* axis such that the centroid of the unsubstituted ring and that of the substituted ring in the molecule at $(1 + x, y, z)$ are separated by 3.770 (1) Å. The molecular packing is further stabilized by C—H···π interactions (Table 2), involving the unsubstituted ring (centroid $Cg1$).

Experimental

A mixture of aniline (0.91 ml, 0.01 mol), water (12 ml) and concentrated hydrochloric acid (3.47 ml, 0.04 mol) was heated while stirring until a clear solution was obtained. This solution was cooled to 273–278 K and a solution of sodium nitrite (0.76 g, 0.01 mol) in 5 ml water was then added dropwise while maintaining the temperature below 278 K. The resulting mixture was stirred for an additional 30 min in an ice bath. This solution was buffered with solid sodium acetate at pH 4–5. 2-*tert*-Butyl-4-methylphenol (1.47 g, 0.01 mol) dissolved with sodium acetate in 5 ml ethyl alcohol was cooled to 273–278 K in an ice bath and then gradually added to the solution of cooled benzenediazonium chloride, prepared as described above. The resulting mixture was stirred for 60 min in an ice bath. The crude oily product was decanted, washed several times with water and dried under vacuum. The product was crystallized from ethyl alcohol to give the title compound (m.p. 379–380 K; yield 25%). Its purity was monitored by thin-layer chromatography. The compound was recrystallized from ethyl alcohol to produce crystals of suitable quality for X-ray diffraction analysis. Elemental analysis found: C 76.05, H 7.61, N 10.26%; calculated: C 76.12, H 7.46, N 10.45%.

Crystal data

Figure 2
An *ORTEP*-3 (Farrugia, 1997) view of the molecular packing along the *c* axis.

Data collection

Bruker AXS SMART CCD diffractometer	1543 independent reflections
ω scans	1355 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.042$
(*SADABS*; Bruker, 1998)	$\theta_{max} = 25.0°$
$T_{min} = 0.985$, $T_{max} = 0.985$	$h = -7 \rightarrow 7$
8784 measured reflections	$k = -12 \rightarrow 10$
	$l = -23 \rightarrow 27$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 0.273P]$
$wR(F^2) = 0.089$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1543 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
181 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C8	1.350 (3)	N1—C1	1.429 (3)
N1—N2	1.268 (2)	N2—C7	1.411 (3)
N2—N1—C1	115.24 (19)	C10—C9—C14	121.9 (2)
N1—N2—C7	116.48 (19)	C9—C10—C11	124.5 (2)
C6—C1—N1	116.6 (2)	C12—C11—C10	117.1 (2)
C2—C1—N1	123.3 (2)	C12—C11—C13	122.1 (2)
C12—C7—N2	114.7 (2)	C16—C14—C15	110.1 (2)
O1—C8—C9	120.07 (19)	C16—C14—C9	110.58 (18)
O1—C8—C7	120.32 (19)	C17—C14—C9	111.16 (19)
C10—C9—C8	117.0 (2)		
C1—N1—N2—C7	−179.46 (19)	N1—N2—C7—C12	178.03 (19)
N2—N1—C1—C6	−173.4 (2)	N1—N2—C7—C8	−0.7 (3)
N2—N1—C1—C2	6.6 (3)	N2—C7—C8—O1	0.9 (3)

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
O1—H1···N1	0.82	1.83	2.551 (2)	145
C16—H16B···O1	0.96	2.30	2.958 (3)	125
C15—H15C···O1	0.96	2.44	3.063 (3)	123
C4—H4···$Cg1^{\mathrm{i}}$	0.93	2.90	3.625 (3)	136

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -z$. $Cg1$ is the centroid of the unsubstituted phenyl ring C1–C6.

H atoms were placed in calculated positions [O—H = 0.82 Å and C—H = 0.93–0.96 Å], with U_{iso} values constrained to be $1.5U_{\mathrm{eq}}$ of the carrier atom for the methyl H atoms and $1.2U_{\mathrm{eq}}$ for the remaining H atoms. Friedel reflections were merged before the final refinement because of the absence of significant anomalous scattering effects.

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 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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