

## 2,6-Dimethyl-4-(4-chlorophenyldiazenyl)-phenol

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## Key indicators

Single-crystal X-ray study

$T = 213\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

$R$  factor = 0.039

$wR$  factor = 0.109

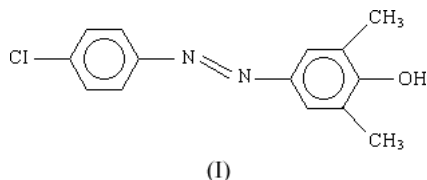
Data-to-parameter ratio = 10.3

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

The crystal structure of the title compound,  $\text{C}_{14}\text{H}_{13}\text{ClN}_2\text{O}$ , determined at 213 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 (azobenzene) derivatives. The dihedral angle between the planes of the two aromatic rings is  $5.48(10)^\circ$ . Hydroxyl groups are linked to each other by intermolecular hydrogen bonds along the *b* axis.

## Comment

Diazene has been the most widely used class of dyes owing to its 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 ongoing work on the synthesis and structural characterization of azoester derivatives, the title compound, (I), was synthesized and its crystal structure is reported here.



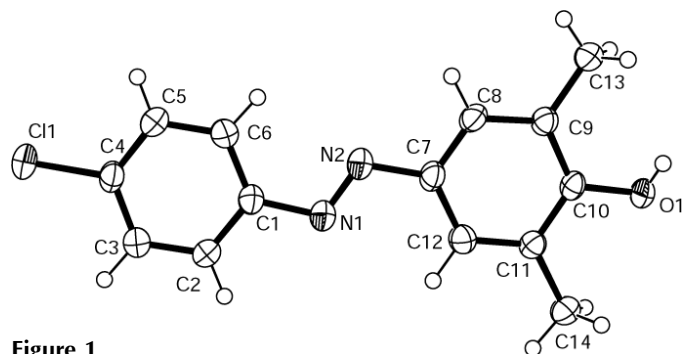
An *ORTEP*-3 (Farrugia, 1997) view of the molecule of the title compound and the molecular packing are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are given in Table 1. The structure of the title compound is very similar to those of azo compounds studied previously (Huang *et al.*, 2002; Zhang *et al.*, 1998; Maginn, 1993; Işık *et al.*, 1998). The two rings are in a *trans* configuration with respect to the azo double bond.

The dihedral angle  $\Theta_1$  between the mean planes of the 4-chlorophenyl ring and the  $\text{C1}-\text{N1}=\text{N2}-\text{C7}$  azo bridge is  $2.65(15)^\circ$  and the angle  $\Theta_2$  between the  $\text{C1}-\text{N1}=\text{N2}-\text{C7}$  azo group and the 3,5-dimethyl-4-hydroxyphenyl ring is  $2.84(15)^\circ$ . The angle  $\Theta_3$  between the planes of the rings is  $5.48(10)^\circ$ , *i.e.* the two substituted phenyl rings are approximately coplanar. The  $\text{N1}-\text{C1}$  and  $\text{N2}-\text{C7}$  bond lengths of  $1.431(2)$  and  $1.424(2)$  Å, respectively, indicate single-bond character, the  $-\text{N}=\text{N}-$  bond length of  $1.254(2)$  Å is indicative of significant double-bond character. The  $\text{C}-\text{Cl}$  bond distance is  $1.744(2)$  Å. These values are consistent with those for similar compounds (Huang *et al.*, 2002; Zhang *et al.*, 1998; Maginn, 1993; Işık *et al.*, 1998). The hydroxyl groups are linked

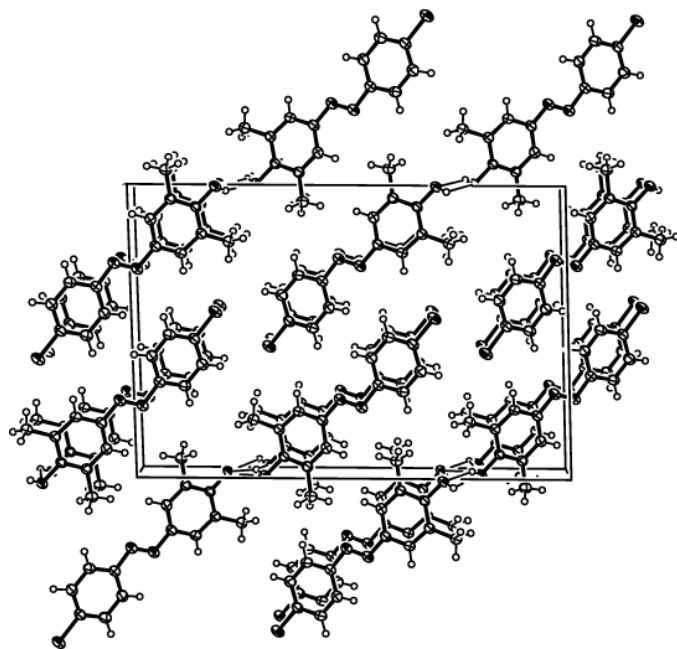
Received 16 September 2003

Accepted 24 September 2003

Online 7 October 2003



**Figure 1**  
An ORTEP-3 (Farrugia, 1997) view of the title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids.



**Figure 2**  
An ORTEP-3 (Farrugia, 1997) display of the molecular packing, viewed along the *b* axis

to each other by intermolecular hydrogen bonds, forming a three dimensional network, as shown in Fig. 2 and Table 2.

## Experimental

A mixture of *p*-chloroaniline (0.02 mol), 40 ml water 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 10 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. 2,6-dimethylphenol (0.02 mol), dissolved with sodium hydroxide (0.02 mol) in 10 ml water, was cooled to 273–278 K in an ice bath, and then gradually added to the solution of *p*-chlorobenzendiazonium chloride. The resulting mixture was stirred for 60 min. The crude precipitate was filtered, washed several times with water and recrystallized from ethyl alcohol to give a product of m.p. 408–411 K; yield %85. Its purity was monitored by TLC. The compound was recrystallized from ethyl alcohol to produce crystals of suitable quality for X-ray diffraction analysis.

## Crystal data

$C_{14}H_{13}ClN_2O$   
 $M_r = 260.71$   
Monoclinic,  $P2_1/c$   
 $a = 14.618$  (3) Å  
 $b = 3.9575$  (8) Å  
 $c = 21.643$  (4) Å  
 $\beta = 91.887$  (3)°  
 $V = 1251.4$  (4) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.384$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 7535 reflections  
 $\theta = 1.9$ – $29.3$ °  
 $\mu = 0.29$  mm<sup>-1</sup>  
 $T = 213$  (2) K  
Prism, orange  
0.20 × 0.10 × 0.10 mm

## Data collection

Bruker AXS SMART CCD diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Bruker, 1998)  
 $T_{min} = 0.944$ ,  $T_{max} = 0.971$   
5900 measured reflections

2206 independent reflections  
1790 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.036$   
 $\theta_{max} = 25.0$ °  
 $h = -17 \rightarrow 15$   
 $k = -4 \rightarrow 3$   
 $l = -23 \rightarrow 25$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.109$   
 $S = 1.03$   
2206 reflections  
215 parameters  
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 0.2052P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.25$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cl1–C4	1.7437 (19)	N1–C1	1.430 (2)
O1–C10	1.386 (2)	N2–C7	1.424 (2)
N1–N2	1.256 (2)	C11–C14	1.507 (3)
N2–N1–C1	112.73 (15)	C12–C7–N2	125.37 (17)
N1–N2–C7	115.56 (15)	C8–C9–C13	120.95 (17)
C2–C1–N1	116.74 (16)	C10–C9–C13	121.74 (16)
C6–C1–N1	124.14 (17)	O1–C10–C9	121.00 (16)
C5–C4–Cl1	119.25 (15)	O1–C10–C11	116.17 (15)
C3–C4–Cl1	119.30 (16)	C12–C11–C14	121.65 (18)
C8–C7–N2	114.75 (16)	C10–C11–C14	120.28 (16)
C1–N1–N2–C7	–177.66 (16)	N1–N2–C7–C8	179.53 (17)
N2–N1–C1–C2	–179.88 (18)	N1–N2–C7–C12	1.6 (3)
N2–N1–C1–C6	1.0 (3)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1O <sup>1</sup> ···O1 <sup>1</sup>	0.77 (2)	2.06 (2)	2.7762 (19)	154 (2)

Symmetry code: (i)  $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$ .

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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