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4-[(2-Chlorophenyl)diazenyl]-6-methoxy-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2*H*)-one

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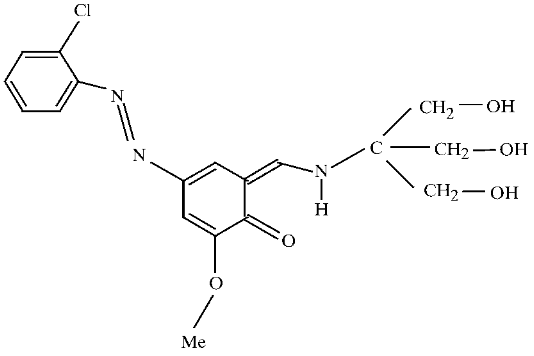
The structure of the title compound, $C_{18}H_{20}ClN_3O_5$, displays the characteristic features of azobenzene derivatives. Intramolecular N—H⋯O, weak intramolecular C—H⋯O, and intermolecular O—H⋯O and C—H⋯O interactions influence the conformation of the molecules and the crystal packing. Intermolecular hydrogen bonds link the molecules into infinite chains, and the title compound adopts the keto–amine tautomeric form. The azobenzene moiety of the molecule has a *trans* configuration. The molecule is not planar, and the dihedral angle between the two phenyl rings is 35.6 (2)°.

Comment

Schiff bases have been used extensively as ligands in the field of coordination chemistry (Calligaris *et al.*, 1972; Garnovski *et al.*, 1993), and Schiff base compounds can be classified by their photochromic and thermochromic characteristics (Cohen *et al.*, 1964; Moustakali *et al.*, 1978; Hadjoudis *et al.*, 1987). Azo compounds are the most widely used class of dyes because of their versatile applications in various fields, such as the dyeing of textiles and fibres, the colouring of different materials, and high-technology areas, such as electro-optical devices and ink-jet printers. The crystal and molecular structures of the title compound, (I), have been investigated in order to determine the conformation and crystal packing, and also to confirm the stereochemistry. Intramolecular hydrogen bonds between O and N atoms in these systems play a vital role in the formation of Schiff base compounds in the solid state by H-atom transfer from the hydroxy O atom to the imine N atom (Hadjoudis *et al.*, 1987; Elerman *et al.*, 1997). X-Ray structure determination reveals that the keto tautomer is favoured over the enol tautomer. X-Ray structure analyses revealed the existance of the NH forms of *N*-(3-hydroxysalicylidene)isopropylamine (Pizzala *et al.*, 2000), 4-[(3-chlorophenyl)diazenyl]-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2*H*)-one (Odabaşoğlu *et al.*, 2003), 2-[(2-hydroxy-4-nitrophenyl)aminomethylene]cyclohexa-3,5-dien-1(2*H*)-one (Ersanlı *et al.*, 2003) and 5-nitro-*N*-salicylideneethylamine (Krygowski *et al.*, 1997), while the OH tautomers have been observed in crystals of 5-chloro-2-[(2-hydroxybenzylidene)aminomethyl]phenol (Kevran *et al.*, 1996), 3-*tert*-butyl-2′-chloro-2-hydroxy-5-methylazobenzene (Işık *et al.*, 1998) and 2-hydroxy-5-*tert*-butylazobenzene (Candan *et al.*, 1999). Transfer of the H atoms in Schiff bases from the O to the N atom is associated with the shortening of the C_{ar}—O bond, which acquires a partial double-bond character as a result of a decrease in the electronegativity of the O atom. In the title compound, (I), the most sensitive bond distance for deciding the tautomer type is the Csp^2—O bond distance. The O2—C10 bond length is consistent with an O═C double bond and is significantly shorter than those of phenols (1.362 Å), indicating significant π character (Allen *et al.*, 1987).



(I)

A view of a molecule of (I), with the atom-labelling scheme, is shown in Fig. 1 and the crystal packing is shown in Fig. 2. The N2—N1 and N2—C7 bond lengths (Table 1) indicate

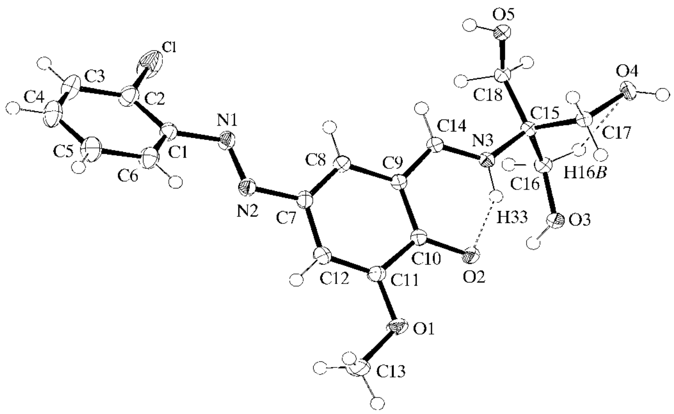


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title compound, with atomic labelling. Displacement ellipsoids are drawn at the 50% probability level.

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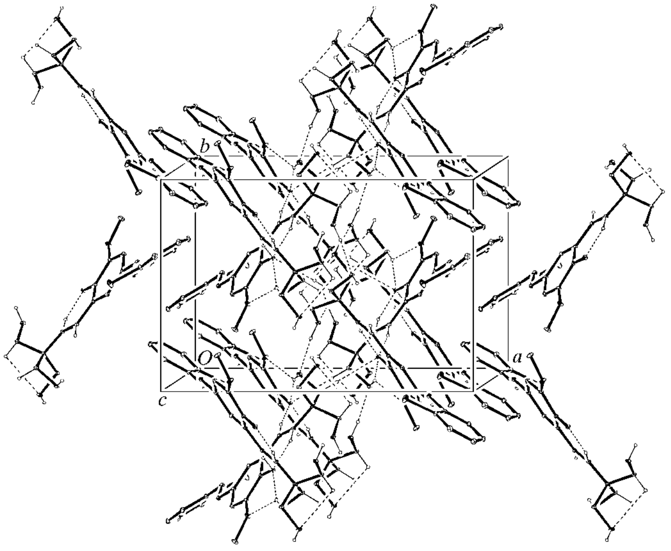

Figure 2
An *ORTEP*-3 (Farrugia, 1997) packing diagram of (I). H atoms have been omitted for clarity.

single-bond character, a result consistent with those found for other azobenzene derivatives studied recently (Işık, 1997, 1998; Odabaşoğlu *et al.*, 2003). Similar values have been observed in other *trans*-azo compounds (Özbey *et al.*, 1993, 1994, 1995). The N=N bond length is indicative of significant double-bond character.

The dihedral angle between the planes of the C1—N1=N2—C7 azo moiety and the chloro-substituted ring is 27.0 (2)°, that between the planes of the azo group and the other aromatic ring is 8.7 (2)°, and that between the planes of the two rings is 35.6 (2)°.

In (I), a moderate intramolecular hydrogen bond occurs between atoms N3 and O2 [2.584 (2) Å; Table 2] (Jeffrey, 1997), the H atom being essentially bonded to the N atom. The sum of the van der Waals radii of O and N atoms (3.07 Å) is significantly longer than the intramolecular N···O hydrogen-bond length (Bondi, 1964).

Experimental

A mixture of 2-chloroaniline (1 g, 8.8 mmol), water (50 ml) and concentrated hydrochloric acid (2.2 ml, 26.4 mmol) was heated with stirring until a clear solution was obtained. This solution was cooled to 273–278 K, and a solution of sodium nitrite (0.85 g, 12.3 mmol) in water was added dropwise while the temperature was maintained below 278 K. The resulting mixture was stirred for 30 min in an ice bath. *o*-Vanillin (1.19 g, 8.8 mmol) solution (pH 9) was added gradually to the solution of cooled 2-chlorobenzenediazonium chloride, prepared as described above, and the resulting mixture was stirred at 273–278 K for 60 min in an ice bath. The product was recrystallized from glacial acetic acid to obtain solid 3-(2-chlorophenylazo)-5-methoxysalicylaldehyde. To a solution of this solid (0.5 g, 1.7 mmol) in butan-1-ol (25 ml) was added a solution of tris(hydroxymethyl)aminomethane (0.2 g, 1.7 mmol) in butan-1-ol (15 ml). The mixture was stirred under reflux, and the water produced in the reaction was distilled out of the reaction mixture. The resulting orange precipitate was filtered off and recrystallized from ethyl alcohol. Crystals of (I) were obtained by slow evaporation from ethyl alcohol over a period of 2 d (yield 90%).

Crystal data

$C_{18}H_{20}ClN_3O_5$
$M_r = 393.82$
Monoclinic, $P2_1/c$
$a = 15.4723$ (2) Å
$b = 10.5669$ (8) Å
$c = 11.1850$ (8) Å
$\beta = 98.900$ (3)°
$V = 1806.7$ (2) Å^3
$Z = 4$
$D_x = 1.448$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5368 reflections
$\theta = 2.3$–30.5°
$\mu = 0.25$ mm^{-1}
$T = 133$ (2) K
Prism, orange
0.35 × 0.19 × 0.16 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.831$, $T_{\max} = 0.928$
35 639 measured reflections
5276 independent reflections
3951 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 30.0°$
$h = -21 \rightarrow 21$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.105$
$S = 1.04$
5276 reflections
261 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.067P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl—C2	1.734 (2)	C9—C14	1.429 (2)
C1—N1	1.427 (2)	O1—C13	1.425 (2)
N1—N2	1.260 (2)	C14—N3	1.294 (2)
N2—C7	1.413 (2)	N3—C15	1.469 (2)
C11—O1	1.360 (2)	C17—O4	1.416 (2)
C11—C10	1.440 (2)	C18—O5	1.425 (2)
C10—O2	1.287 (2)	C16—O3	1.430 (2)
C10—C9	1.435 (2)		
C2—C1—N1	118.6 (2)	N1—N2—C7	115.7 (2)
C6—C1—N1	122.7 (2)	O2—C10—C9	123.4 (2)
C3—C2—Cl	118.8 (2)	O2—C10—C11	120.2 (2)
C1—C2—Cl	120.3 (2)	N3—C14—C9	121.2 (2)
N2—N1—C1	111.7 (2)	C14—N3—C15	128.9 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H31···O5$^{\rm i}$	0.85 (2)	1.88 (2)	2.723 (1)	173.1 (15)
O4—H41···O3$^{\rm ii}$	0.85 (2)	1.88 (2)	2.719 (1)	170.2 (16)
O5—H51···O1$^{\rm iii}$	0.76 (2)	2.28 (2)	2.785 (1)	125.5 (18)
O5—H51···O2$^{\rm iii}$	0.76 (2)	2.11 (2)	2.835 (1)	161.2 (19)
C14—H14···O2$^{\rm iii}$	0.95	2.44	3.376 (1)	169
C18—H18*A*···O2$^{\rm iv}$	0.99	2.43	3.398 (1)	165
N3—H33···O2	0.93 (2)	1.77 (2)	2.584 (2)	144.4 (14)
C16—H16*B*···O4	0.99	2.57	2.941 (1)	102

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

All H-atom positions (except for those of the hydroxy H atoms and atom H33) were refined using a riding model, with $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$ of the attached atom. The hydroxy H atoms and atom H33 were found as peaks of small positive electron density in difference Fourier maps calculated at the end of the refinement, and the parameters of these atoms were refined.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (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).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1451). Services for accessing these data are described at the back of the journal.

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