

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

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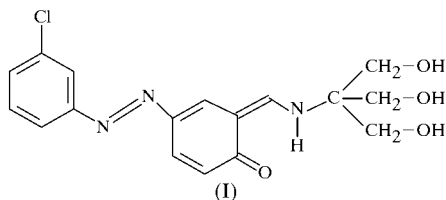
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The title compound, C₁₇H₁₈ClN₃O₄, adopts the keto–amine tautomeric form and displays an intramolecular N–H···O hydrogen bond [N···O = 2.639 (2) Å]. The configuration around the azo N=N double bond is *trans*, and the dihedral angle between the planes of the two aromatic rings is 20.5 (2)°. The molecules are linked by O–H···O hydrogen bonds to form a three-dimensional network.

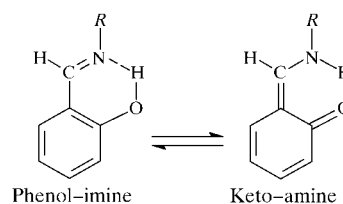
Comment

There is considerable interest in Schiff base ligands and their complexes because of their striking antitumour activities (Zhou *et al.*, 2000). *N*-Substituted *ortho*-hydroxyimines have been reported to display thermochromism and photochromism in the solid state by H-atom transfer from the hydroxyl O atom to the N atom (Hadjoudis *et al.*, 1987; Xu *et al.*, 1994). Azoazomethines have been extensively used as dyestuffs for wool, leather and synthetic fabrics because of their extraordinary colouring properties (Kamel *et al.*, 1971; Gopal & Srinivasan, 1986; Karaer, 1997). As part of our ongoing work on the synthesis and structural characterization of polyhydroxyazoazomethine derivatives, the title compound, (I), was synthesized, and its crystal structure is reported here.



An ORTEP-3 (Farrugia, 1997) view of the molecule of (I) and a packing diagram are shown in Figs. 1 and 2, respectively. The structure of (I) reveals several points of interest. First, the

molecule exists primarily as the keto–amine tautomer, as indicated by the C10–O1, C9–C13, C13–N3 and C9–C10 bond lengths (Table 1). These bonds are 1.356 (3), 1.448 (3), 1.270 (3) and 1.288 (4) Å, respectively, in the phenol–imine tautomer (see *Scheme* below) of 1,8-bis(*N*-2-oxyphenylsaliacylidene)-3,6-dioxaoctane (Yıldız *et al.*, 1998). These data show that there is significant elongation of the C13–N3 bond and contraction of the C10–O1 bond. Secondly, the ‘hydroxyl’ H atom was located on atom N3, thus confirming a preference for the keto–amine tautomer in the solid state. Finally, there is a strong intramolecular N3–H33···O1 hydrogen bond, which is a common feature of *ortho*-hydroxysaliacylidene systems (Filarowski *et al.*, 2003; Nazır *et al.*, 2000; Yıldız *et al.*, 1998).



It has been reported that there may be an orientational disorder in azobenzene, resulting in a shortening of the N=N bond [to 1.189 (6) Å] and an elongation of the N–Ph bonds

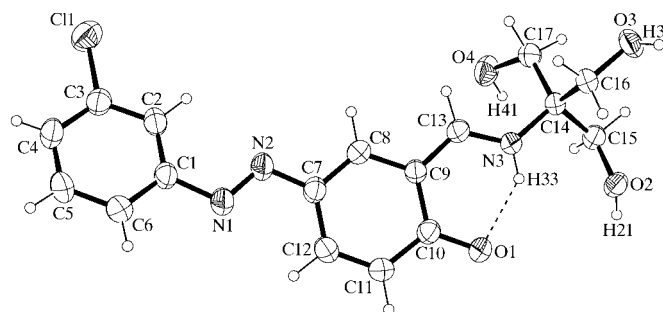


Figure 1
An ORTEP-3 (Farrugia, 1997) view of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

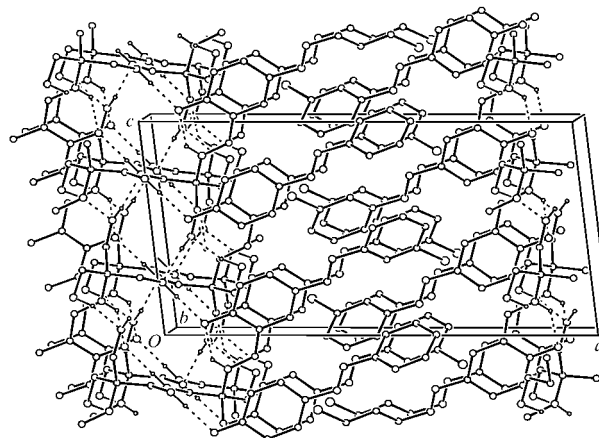


Figure 2
An ORTEP-3 (Farrugia, 1997) packing diagram of (I), viewed along the *b* axis.

[to 1.473 (4) Å]; these bond lengths are 1.249 (4) and 1.431 (4) Å, respectively, in azobenzene with no disorder (Harada *et al.*, 1997). The N1=N2, N1—C1 and N2—C7 bonds in (I) are 1.256 (2), 1.429 (3) and 1.414 (2) Å, respectively, indicating that there is no orientational disorder. The two phenyl rings are planar but not coplanar with one another. The dihedral angle, θ_1 , between the mean planes of the chlorophenyl ring and the C—N—N—C bridge is 11.6 (3)°, and the angle, θ_2 , between the planes of the C—N—N—C link and the salicylidene ring is 8.9 (3)°. The angle, θ_3 , between the planes of the chlorophenyl and salicylidene rings is 20.47 (10)°, which is equal to the sum of θ_1 and θ_2 [20.5 (3)°]. This value of θ_3 is a little larger than those in (*E*)-azobenzenes (5–15°; Brown, 1966). Atoms C1 and C7 are angularly asymmetric (Table 1). This asymmetry seems to be caused by the tendency of the azo system to be partially coplanar with the aromatic rings because of the π -conjugation and steric hindrance involving both the C2—H2 group with N2 and the C12—H12 group with N1. The same angular asymmetry occurs for atoms C13, N3 and C14 because of their asymmetric coordination, and so the N3—C13—C9, C13—N3—C14 and N3—C14—C17 angles are larger according to their optimal hybridization degree.

In addition to the intramolecular hydrogen bond, molecules of (I) are linked by intermolecular O—H...O hydrogen bonds into a three-dimensional network (Fig. 2 and Table 2). There is also a π -ring interaction [3.318 (19) Å] between C12—H12 and the salicylidene ring at $(x, -y + \frac{3}{2}, z + \frac{1}{2})$.

Experimental

A mixture of 3-chloroaniline (1.275 g, 10 mmol), water (50 ml) and concentrated hydrochloric acid (2.5 ml, 30 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 (0.96 g, 14 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. Salicylaldehyde (1.22 g, 10 mmol) solution (pH 9) was gradually added to a cooled solution of 3-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 ethyl alcohol to obtain solid 5-(3-chlorophenylazo)salicylaldehyde (m.p. 400–402 K). To a solution of this solid (1.302 g, 5 mmol) in butan-1-ol (75 ml) was added a solution of tris(hydroxymethyl)aminomethane (0.605 g, 5 mmol) in butan-1-ol (25 ml). The mixture was stirred under reflux and the water produced in the reaction was distilled out. The resulting orange precipitate was filtered off and recrystallized from ethyl alcohol. Crystals of (I) were obtained after 2 d by slow evaporation from acetonitrile (yield 90%; m.p. 455–457 K).

Crystal data

C₁₇H₁₈ClN₃O₄
M_r = 363.79
 Monoclinic, *P*₂₁/*c*
a = 18.418 (4) Å
b = 9.821 (2) Å
c = 9.5020 (19) Å
 β = 96.64 (3)°
V = 1707.2 (6) Å³
Z = 4

D_x = 1.415 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 100 reflections
 θ = 3.0–25.0°
 μ = 0.25 mm⁻¹
T = 295 K
 Prism, orange
 0.40 × 0.30 × 0.10 mm

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.429 (3)	C9—C10	1.436 (3)
C3—C11	1.743 (2)	C10—O1	1.286 (2)
C7—C8	1.367 (3)	C10—C11	1.426 (3)
C7—C12	1.413 (3)	C11—C12	1.360 (3)
C7—N2	1.414 (2)	C13—N3	1.298 (3)
C8—C9	1.408 (3)	C14—N3	1.470 (2)
C9—C13	1.411 (3)	N1—N2	1.256 (2)
C6—C1—C2	120.2 (2)	C12—C7—N2	124.94 (18)
C6—C1—N1	116.2 (2)	O1—C10—C9	121.02 (18)
C2—C1—N1	123.59 (19)	N3—C13—C9	124.52 (19)
C8—C7—C12	119.23 (18)	N3—C14—C17	111.44 (15)
C8—C7—N2	115.82 (18)	C13—N3—C14	126.55 (18)
C10—C9—C13—N3	−0.6 (3)	C1—N1—N2—C7	−177.64 (17)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H33...O1	0.86 (3)	1.93 (2)	2.639 (2)	139 (2)
O2—H21...O1 ⁱ	0.83 (2)	1.78 (2)	2.610 (2)	172.2 (8)
O3—H31...O2 ⁱⁱ	0.78 (2)	1.89 (2)	2.655 (2)	166.1 (17)
O4—H41...O3 ⁱⁱⁱ	0.98 (2)	1.81 (2)	2.780 (2)	167.1 (11)

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

Data collection

Stoe Stadi-4 diffractometer
 ω scans
 6136 measured reflections
 3005 independent reflections
 2314 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.020
 θ _{max} = 25.0°

h = −21 → 21
k = −11 → 0
l = −11 → 11
 2 standard reflections
 frequency: 120 min
 intensity decay: 2%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.037
wR(*F*²) = 0.104
S = 1.06
 3005 reflections
 265 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.5398P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.50 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$

The H atoms attached to atoms O2, O3 and O4 were refined using a riding model, with O—H distances free to refine and *U*_{iso} values equal to 1.2*U*_{eq} of the parent atom. The H atoms attached to atoms C15, C16 and C17 were refined using a riding model, with C—H distances of 0.96 Å. H atoms bonded to the other C atoms and to N3 were refined isotropically. The calculated C—H bond lengths were in the range 0.89 (3)–0.98 (2) Å.

Data collection: *STADIA* (Stoe & Cie, 1996); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1106). Services for accessing these data are described at the back of the journal.

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