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5-(2-Chlorophenyldiazenyl)salicylaldehyde and 4-(2-chlorophenyldiazenyl)-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2*H*)-one

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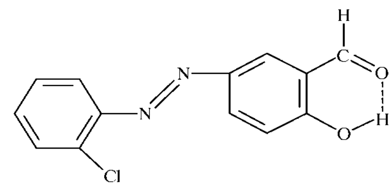
The molecule of the former title compound, $C_{13}H_9ClN_2O_2$, (I), is nearly planar, with an intramolecular O···O hydrogen bond of 2.692 (2) Å. The latter title compound, $C_{17}H_{18}ClN_3O_4$, (II), exists in the keto–amine tautomeric form, with a strong intramolecular hydrogen bond of 2.640 (2) Å between the O and N atoms, the H atom being bonded to the N atom. The azobenzene moieties of both molecules have *trans* configurations, and the dihedral angle between the planes of the two aromatic rings is 4.1 (1)° in (I) and 9.9 (1)° in (II). The N—H···O hydrogen-bonded rings are almost planar and coupled with the cyclohexadiene rings in (II).

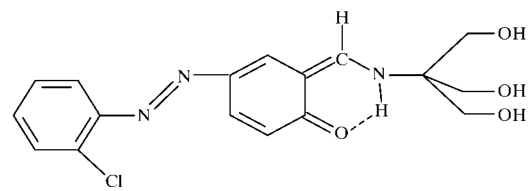
Comment

Azo compounds are the most widely used class of dyes, due to their versatile application 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 (Peters & Freeman, 1991). Schiff bases have been used extensively as ligands in the field of coordination chemistry (Garnovskii *et al.*, 1993). There is considerable interest in Schiff base complexes due to their striking anti-tumour activities (Zhou *et al.*, 2000). Schiff base compounds show photochromism and thermochromism in the solid state by proton transfer from the hydroxyl O atom to the imine N atom (Hadjoudis *et al.*, 1987). Photochromic compounds are of great interest for the control and measurement of radiation intensity, optical computers and display systems (Dürr & Bouas-Laurent, 1990). Azo-azomethine compounds are also widely used in the textile industry as synthetic colouring materials (Kamel *et al.*, 1971).

2-Hydroxy Schiff base ligands are of interest mainly due to the existence of O—H···N and N—H···O hydrogen bonds and tautomerism between enol and keto forms. In the aldimine compounds made from 2-hydroxy-1-naphthaldehyde, both types of hydrogen bonds were found (Fernández *et al.*, 2001). The structures of Schiff bases derived from salicylaldehyde generally exist in the phenol–imine form (Elmalı *et al.*, 1999; Filarowski *et al.*, 1999). In contrast, the structures of Schiff bases derived from the condensation of salicylaldehyde and substituted salicylaldehyde with tris(hydroxymethyl)aminomethane only exist in the keto–amine form (Odabaşoğlu, Albayrak, Büyükgüngör & Lönnecke, 2003).



(I)



(II)

As part of a general study of the crystal chemistry of dyes, and to provide templates for molecular-modelling studies, the crystal structures of the title compounds, (I) and (II), have been determined. The molecular structures of (I) and (II), with the atom-labelling schemes, are shown in Figs. 1 and 2, respectively, and selected bond lengths and angles are given in Tables 1 and 3, respectively.

In (I), the aromatic rings, which adopt a *trans* configuration about the N=N double bond, are nearly coplanar, with a dihedral angle of 4.1 (1)° between them. A significant intramolecular interaction is noted, involving phenol atom H1 and carbonyl atom O2, such that a six-membered ring is formed (Table 2). The C—Cl bond distance in (I) is consistent with that in 4-[(3-chlorophenyl)diazenyl]-2-{[tris(hydroxymethyl)methyl]aminomethylene}cyclohexa-3,5-dien-1(2*H*)-one, (III) (Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann, 2003). The C13—O2 bond distance in (I) is also consistent with the value of the C=O double bond in carbonyl compounds (Loudon, 2002).

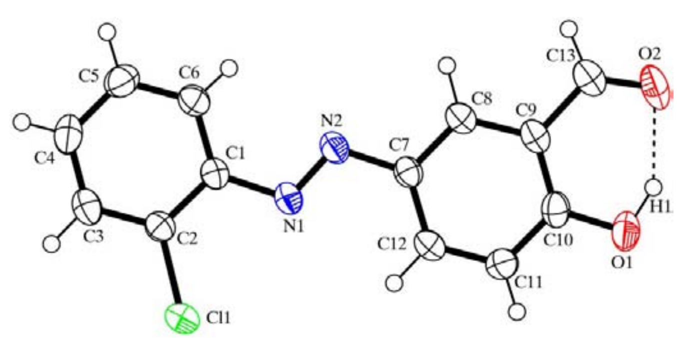


Figure 1
A view of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

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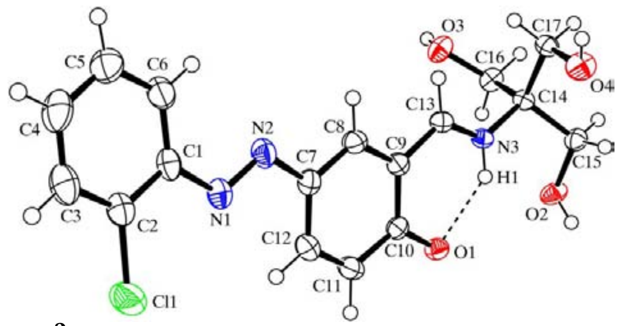

Figure 2
A view of (II), with the atom-numbering scheme and 50% probability displacement ellipsoids.

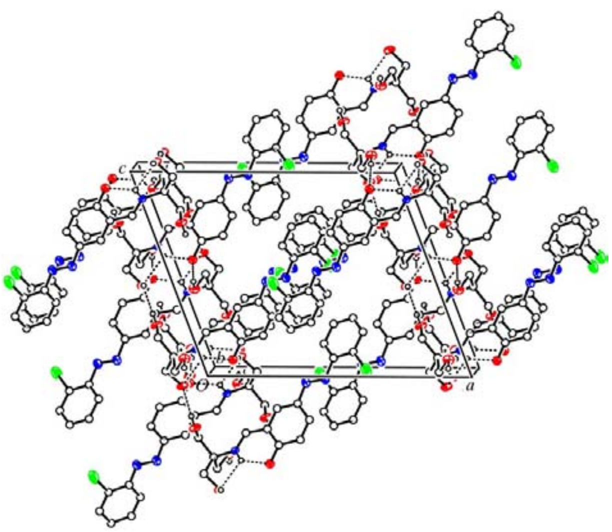

Figure 3
A packing diagram for (II), viewed along the *b* axis.

In compound (II), the azobenzene moieties of the molecule have a *trans* configuration, and the dihedral angle between the planes of the two aromatic rings is 9.9 (1)°. In our previous work, the same dihedral angle was 20.47 (10)° in (III) (Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann, 2003). The present X-ray structure determination reveals that, in the solid state, the keto–amine tautomer exists in the molecule of (II). This is evident from the observed contraction of the C10—O1, C9—C13, C7—C8 and C11—C12 distances and the elongation of the C8—C9, C9—C10 and C10—C11 distances, relative to the starting material, (I) (Tables 1 and 3). Furthermore, the C13—N3 bond in (II) is elongated relative to the C═N bond in 2-[2-(hydroxymethyl)phenyliminomethyl]-phenol, which exists in the phenol–imine form [1.275 (2) Å; Ersanlı *et al.*, 2004]. The N1═N2, N1—C1 and N2—C7 bond lengths are approximately the same in both (I) and (II). That is to say, transformation to the keto–amine form of the salicylidene ring does not affect bond distances but slightly changes the torsion angle (C1—N1—N2—C7) in the azo moiety.

The intra- and intermolecular hydrogen bonding in (II) is shown in Fig. 3 and the geometric values are given in Table 4. Atom H33 bonded to N3 forms a strong intramolecular hydrogen bond with atom O1 [2.640 (2) Å], as in our previous work (Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann, 2003; Odabaşoğlu, Albayrak, Büyükgüngör & Lönnecke, 2003).

Experimental

The title compounds were obtained as described in our previous work (Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann, 2003), using 2-chloroaniline, salicylaldehyde and tris(hydroxymethyl)aminomethane as starting materials. Suitable single crystals of (I) were obtained by slow evaporation from ethanol (yield 85%; m.p. 424–426 K) and crystals of (II) were obtained from acetonitrile (yield 72%; m.p. 479–481 K).

Compound (I)

Crystal data

$C_{13}H_9ClN_2O_2$
M_r = 260.67
Monoclinic, $P2_1/n$
a = 6.9938 (11) Å
b = 21.636 (3) Å
c = 8.1078 (13) Å
β = 108.724 (3)°
V = 1161.9 (3) Å^3
Z = 4
D_x = 1.490 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2275 reflections
θ = 1.9–26.0°
μ = 0.32 mm^{-1}
T = 213 (2) K
Prism, dark red
0.40 × 0.40 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
T_{min} = 0.882, T_{max} = 0.909
6246 measured reflections
2275 independent reflections
1783 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 26.0°
$h = -8 \rightarrow 8$
$k = -19 \rightarrow 26$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.108
S = 1.04
2275 reflections
199 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.066P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cl1—C2	1.733 (2)	N2—C7	1.422 (2)
O2—C13	1.213 (2)	C7—C8	1.383 (3)
O1—C10	1.348 (2)	C9—C10	1.395 (3)
N1—N2	1.255 (2)	C9—C13	1.461 (3)
N1—C1	1.427 (2)	C11—C12	1.370 (3)
N2—N1—C1	113.6 (2)	O1—C10—C9	123.0 (2)
N1—N2—C7	113.9 (2)	O2—C13—C9	124.5 (2)
C1—N1—N2—C7	179.8 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.95 (3)	1.83 (3)	2.692 (2)	149 (2)
O1—H1···O2^{i}	0.95 (3)	2.38 (3)	2.952 (2)	118 (2)

Symmetry code: (i) $1 - x, 1 - y, 3 - z$.

Compound (II)

Crystal data

$C_{17}H_{18}ClN_3O_4$	D_x = 1.430 Mg m^{-3}
M_r = 363.79	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3332 reflections
a = 16.122 (3) Å	θ = 1.4–26.0°
b = 8.3847 (12) Å	μ = 0.25 mm^{-1}
c = 13.359 (2) Å	T = 213 (2) K
β = 110.689 (3)°	Prism, orange
V = 1689.4 (5) Å^3	0.35 × 0.25 × 0.10 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	3332 independent reflections
ω scans	2501 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)	R_{int} = 0.026
T_{min} = 0.916, T_{max} = 0.975	θ_{max} = 26.0°
10 407 measured reflections	$h = -19 \rightarrow 15$
	$k = -8 \rightarrow 10$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.0074P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.034	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.109	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
S = 1.09	$\Delta\rho_{min}$ = −0.33 e Å^{-3}
3332 reflections	
298 parameters	
All H-atom parameters refined	

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C10	1.306 (2)	C7—C8	1.371 (2)
N1—N2	1.258 (2)	C9—C13	1.427 (2)
N1—C1	1.422 (2)	C9—C10	1.431 (2)
N2—C7	1.418 (2)	C11—C12	1.365 (2)
N3—C13	1.292 (2)		
N2—N1—C1	114.1 (2)	O1—C10—C9	121.7 (2)
N1—N2—C7	113.6 (1)	N3—C13—C9	123.2 (2)
C8—C7—N2	116.4 (2)		
C1—N1—N2—C7	−178.7 (1)	C10—C9—C13—N3	−2.4 (2)

All H atoms were refined freely. For (I), the refined C—H distances are in the range 0.87 (2)–1.00 (2) Å and U_{iso}(H) values are in the range 0.031 (5)–0.052 (6) Å^2. For (II), the refined C—H distances are in the range 0.92 (2)–1.02 (2) Å and U_{iso}(H) values are in the range 0.024 (4)–0.054 (6) Å^2.

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); 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).

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H22···O1^{i}	0.86 (3)	1.78 (3)	2.635 (2)	177 (2)
O4—H44···O2^{ii}	0.77 (3)	2.03 (3)	2.791 (2)	172 (3)
O3—H33···O1^{iii}	0.86 (2)	1.96 (2)	2.803 (2)	167 (2)
N3—H1···O1	0.87 (2)	1.95 (2)	2.640 (2)	134.6 (19)
N3—H1···O2	0.87 (2)	2.21 (2)	2.665 (2)	112.4 (18)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1474). Services for accessing these data are described at the back of the journal.

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