Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

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

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**Key indicators**

Single-crystal X-ray study
$T$ = 291 K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.043
$wR$ factor = 0.116
Data-to-parameter ratio = 11.7

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

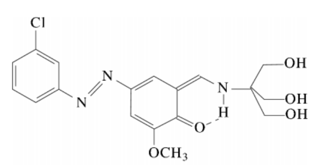


Received 23 December 2003
Accepted 5 January 2004
Online 17 January 2004

The title compound, $C_{18}H_{20}ClN_3O_5$, adopts the keto–amine tautomeric form and displays an intramolecular N—H···O hydrogen bond. The configuration around the azo N=N double bond is *trans* and the dihedral angle between the two aromatic rings is 10.0 (1)°. Intermolecular O—H···O hydrogen bonds form a three-dimensional network.

## Comment

Azo dyes are widely used in the textile, printing, paper manufacturing, pharmaceutial and food industries. The great majority of them are monoazo compounds, which have the common structural unit of the azo chromophore, –N=N–, linking two aromatic systems. There is considerable interest in Schiff base ligands and their complexes due to their striking antitumour activities (Zhou *et al.*, 2000). *N*-substituted *o*-hydroxyimines have been reported to display thermochromism and photochromism in the solid state *via* H-atom transfer from the hydroxy O atom to the N atom (Hadjoudis *et al.*, 1987; Xu *et al.*, 1994). Against this background, we present here the structure of the title compound, (I).



(I)

A displacement ellipsoid plot of (I) and a packing diagram are shown in Figs. 1 and 2, respectively. In this molecule, the bond lengths and angles (Table 1) are very similar to those in the azo compound studied previously (Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann, 2003). The chloro, imino, hydroxy and methoxy group linkages distort the C⋯C bond lengths of the benzene rings [1.353 (3)–1.447 (3) Å] compared with their value in benzene. The N=N bond of 1.260 (2) Å agrees with that in the related compound [1.256 (2) Å; Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann, 2003] and is longer than the calculated value of 1.250 Å in $CH_3$–N=N–$CH_3$ (Baht *et al.*, 2000), suggesting electron delocalization. The dihedral angle between the chlorophenyl and salicylidene rings is 10.0 (1)°. This value agrees with the values of 5–15° observed for *E*-azobenzenes (Brown, 1966).

The molecular structure of (I) is the keto–amine tautomer, as indicated by the following bond lengths: C10—O1 1.272 (2), C7—C8 1.366 (3) and C11—C12 1.353 (3) Å. In our previous work, these bond lengths are 1.2892 (18), 1.360 (3) and 1.364 (2) Å, respectively (Odabaşoğlu, Albayrak, Büyük-

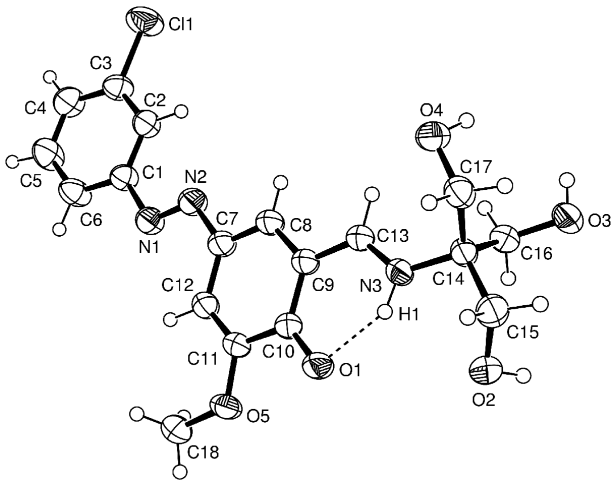



**Figure 1**
A view of the molecule of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

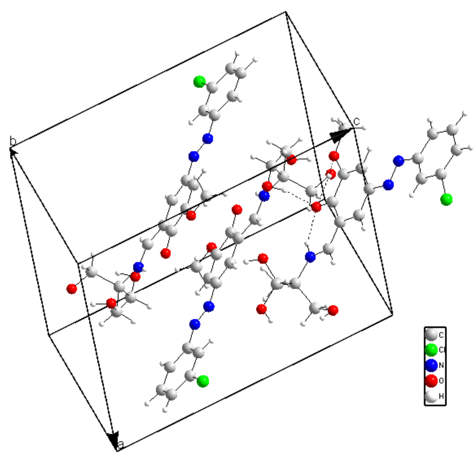


**Figure 2**
A packing diagram for (I). Broken lines indicate hydrogen bonds.

güngör & Lönnecke, 2003). These elongations and contractions are due to the 3-chlorophenyldiazenyl linkage on the salicylidene ring. In addition, the C10—O1 and C11—C12 bond lengths in *N*-(2-fluoro-3-methoxy)-salicylaldimine, which is in the phenol–imine tautomeric form, are 1.347 (3) and 1.374 (3) Å, respectively (Ünver *et al.*, 2002). The hydroxyl H atom was located on N3, thus confirming a preference for the keto–amine tautomer of (I) in the solid state.

There is a strong intramolecular N3—H1···O1 hydrogen bond in (I) (Table 2), which is a common feature of *o*-hydroxysalicylidene systems (Odabaşoğlu, Albayrak, Büyükgüngör & Lönnecke, 2003; Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann, 2003; Filarowski *et al.*, 2003; Nazır *et al.*, 2000; Yıldız *et al.*, 1998). The dihedral angle between the N—H···O hydrogen-bonded ring and the salicylidene ring is 2.1 (1)°.

## Experimental

The title compound, (I), was prepared as described by Odabaşoğlu, Albayrak, Büyükgüngör & Goesmann (2003), using *o*-vanillin, 3-chloroaniline and tris(hydroxymethyl)aminomethane as starting materials. The product was recrystallized from ethanol and well shaped crystals of (I) were obtained by slow evaporation of an acetonitrile solution (yield 85%; m.p. 496–498 K).

*Crystal data*

| | |
|---|---|
| $C_{18}H_{20}ClN_3O_5$ | $D_x$ = 1.363 Mg m$^{-3}$ |
| $M_r$ = 393.82 | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 12 137 reflections |
| $a$ = 10.6950 (8) Å | $\theta$ = 1.9–28.3° |
| $b$ = 12.3204 (10) Å | $\mu$ = 0.23 mm$^{-1}$ |
| $c$ = 14.8486 (12) Å | $T$ = 291 K |
| $\beta$ = 101.144 (6)° | Plate, orange |
| $V$ = 1919.7 (3) Å$^3$ | 0.50 × 0.50 × 0.16 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Stoe IPDS 2 diffractometer | 2571 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int}$ = 0.075 |
| Absorption correction: by integration (*X-RED*; Stoe & Cie, 2002) | $\theta_{max}$ = 26.0° |
| $T_{min}$ = 0.850, $T_{max}$ = 0.963 | $h = -13 \rightarrow 13$ |
| 13 394 measured reflections | $k = -15 \rightarrow 15$ |
| 3776 independent reflections | $l = -18 \rightarrow 18$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | All H-atom parameters refined |
| $R[F^2 > 2\sigma(F^2)]$ = 0.043 | $w = 1/[\sigma^2(F_o^2) + (0.0703P)^2]$ |
| $wR(F^2)$ = 0.116 | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 0.94 | $(\Delta/\sigma)_{max}$ = 0.001 |
| 3776 reflections | $\Delta\rho_{max}$ = 0.64 e Å$^{-3}$ |
| 324 parameters | $\Delta\rho_{min}$ = −0.49 e Å$^{-3}$ |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| C1—N1 | 1.430 (2) | C9—C10 | 1.430 (3) |
| C3—Cl1 | 1.738 (2) | C10—O1 | 1.272 (2) |
| C7—C8 | 1.366 (3) | C11—C12 | 1.353 (3) |
| C7—N2 | 1.402 (2) | C13—N3 | 1.296 (2) |
| C7—C12 | 1.424 (3) | C14—N3 | 1.470 (2) |
| C8—C9 | 1.412 (3) | N1—N2 | 1.260 (2) |
| C9—C13 | 1.410 (3) | | |
| C6—C1—C2 | 119.77 (19) | O1—C10—C9 | 122.98 (17) |
| C6—C1—N1 | 116.47 (18) | C12—C11—O5 | 125.83 (18) |
| C2—C1—N1 | 123.76 (17) | N3—C13—C9 | 123.63 (18) |
| C8—C7—N2 | 115.56 (17) | N3—C14—C17 | 111.37 (15) |
| C8—C7—C12 | 120.08 (18) | C13—N3—C14 | 127.05 (16) |
| N2—C7—C12 | 124.36 (18) | | |
| C10—C9—C13—N3 | −0.4 (3) | C1—N1—N2—C7 | 179.53 (16) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H1···O1 | 0.88 (3) | 1.88 (3) | 2.643 (2) | 145 (3) |
| O2—H22···O3$^{i}$ | 0.88 (3) | 1.88 (3) | 2.759 (2) | 173 (3) |
| O3—H33···O1$^{ii}$ | 0.80 (3) | 2.33 (3) | 3.014 (2) | 144 (3) |
| O3—H33···O5$^{ii}$ | 0.80 (3) | 2.14 (3) | 2.829 (2) | 144 (3) |
| O4—H44···O1$^{ii}$ | 0.91 (3) | 1.85 (3) | 2.747 (2) | 165 (3) |

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

All H-atom parameters were freely refined. The C—H distances are in the range 0.92 (2)–1.04 (3) Å and $U_{iso}$(H) values are in the range 0.44 (5)–0.88 (10) Å$^2$. Although the structure contains solvent accessible voids of 48 Å$^3$, no small molecules can be detected in the structure, as evidenced from the difference Fourier map.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); 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, 1998).

## References


Baht, K. L., Freeman, H. S., Velga, J., Sztandera, L., Tracthman, M. & Bock, C. W. (2000). *Dyes Pigm.* **46**, 109–119.
Brown, C. J. (1966). *Acta Cryst.* **21**, 146–152.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1998). *WinGX*. University of Glasgow, Scotland.
Filarowski, A., Koll, A. & Glowiaka, T. (2003). *J. Mol. Struct.* **644**, 187–195.
Hadjoudis, E., Vitterakis, M. & Maviridis, I. M. (1987). *Tetrahedron*, **43**, 1345–1360.
Nazır, H., Yıldız, M., Yılmaz, H., Tahir, M. N. & Ülkü, D. (2000). *J. Mol. Struct.* **524**, 241–250.
Odabaşoğlu, M., Albayrak, Ç., Büyükgüngör, O. & Goesmann, H. (2003). *Acta Cryst.* C**59**, o234–o236.
Odabaşoğlu, M., Albayrak, Ç., Büyükgüngör, O. & Lönnecke, P. (2003). *Acta Cryst.* C**59**, o616–o619.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Stoe & Cie (2002). *X-AREA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
Ünver, H., Kendi, E., Güven, K. & Durlu, T. (2002) *Z. Naturforsch. Teil B*, **57**, 685–690.
Xu, X., You, X., Sun, Z., Wang, X. & Liu, H. (1994). *Acta Cryst.* C**50**, 1169–1171.
Yıldız, M., Kılıç, Z. & Hökelek, T. (1998). *J. Mol. Struct.* **441**, 1–10.
Zhou, Y.-S., Zhang, L.-J., Zeng, X.-R., Vital, J. J. & You, X.-Z. (2000). *J. Mol. Struct.* **553**, 25–30.