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5-Chloro-2-[(2-hydroxybenzylidene)aminomethyl]phenol

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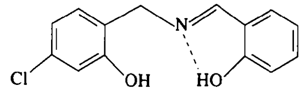
Abstract

The crystal structure of the title compound, $C_{14}H_{12}ClNO_2$, has been determined. The molecule is not planar and contains an intramolecular O—H···N hydrogen bond.

Comment

Although Schiff bases have been widely used as ligands in the formation of transition metal complexes which have been structurally characterized, a relatively small number of free Schiff bases have been similarly characterized (Calligaris & Randaccio, 1987). In the course of a systematic structural investigation of Schiff bases, the structure of the title compound, (I), formed by the reaction of amine with aldehyde compounds, was determined (Elerman, Svoboda & Fuess, 1991; Elerman, Paulus, Svoboda & Fuess, 1992; Elerman, Elmali, Kabak, Aydin & Peder, 1994; Elerman, Elmali & Svoboda, 1995; Elmali, Özbey, Kendi, Kabak & Elerman, 1995). N-Substituted salicylaldimines are of interest because of their thermochromic and photochromic properties in the solid state, which is the result of proton transfer from the hydroxyl O atom to the imine N atom which may be reversible (Hadjoudis, Vittorakis & Mavridis, 1987).



(I)

On the basis of some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromism are planar, while those exhibiting photochromism are non-planar (Mavridis, Hadjoudis & Mavridis, 1978, 1980). The title molecule is not planar. The two Schiff base moieties, *A* [C1, C2, C3, C4, C5, C6, O1, Cl1, C7, N1] and *B* [C8, C9, C10, C11, C12, C13, C14, O2] [both planar with a maximum deviation of 0.089 (2) Å], are inclined at an angle of 59.3 (1)° with respect to one another. The conformation of the Schiff base is of particular interest in the formation of metal complexes. The most interesting conformational feature of the present structure is the significant twist of *A* relative to *B*. The orientation of *A* with respect to *B* is defined by the torsion angle between them [C7—N1—C8—C9 152.4 (3)°]. Clearly, this conformation is not suitable for direct coordination to a metal ion.

In compound (I), a strong intramolecular hydrogen bond occurs between the O2 and N1 atoms [2.599 (3) Å], the H atom being essentially bonded to the O atom. The sum of the van der Waals radii of the O and N atoms (3.07 Å) is significantly longer than the intra-

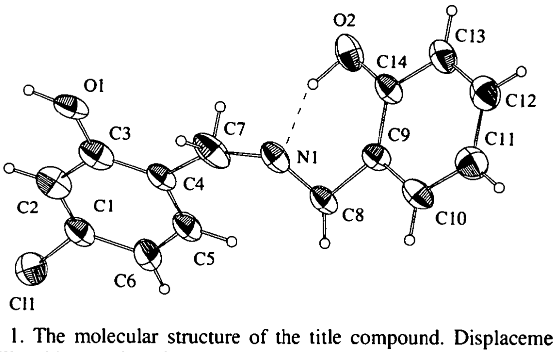


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

molecular O···N hydrogen-bond length (Bondi, 1964). The O1—C3 and O2—C14 bond distances of 1.339 (4) and 1.340 (4) Å, respectively, are consistent with O—C single bonds. The N1—C8 bond length of 1.297 (5) Å is typical for a C═N double bond.

Experimental

The title compound was synthesized according to well established methods (Vogel, 1966).

Crystal data

$C_{14}H_{12}ClNO_2$
$M_r = 261.70$
Orthorhombic
$Pca2_1$
$a = 6.246\ (3)$ Å
$b = 7.187\ (4)$ Å
$c = 31.334\ (2)$ Å
$V = 1406.6\ (10)$ Å^3
$Z = 4$
$D_x = 1.236$ Mg m^{-3}
$D_m = 1.239$ Mg m^{-3}
D_m measured pycnometrically using cyclohexane

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.35–13.05°$
$\mu = 0.265$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.50 × 0.15 × 0.05 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4347 measured reflections
1266 independent reflections
1152 observed reflections [$I > 2\sigma(I)$]

$R_{\text{int}} = 0.036$
$\theta_{\text{max}} = 24.97°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 36$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0402$
$wR(F^2) = 0.0969$
$S = 1.111$
1266 reflections
168 parameters
H atoms riding with fixed U's
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.025$

$\Delta\rho_{\text{max}} = 0.15$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.26$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.14 (9)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl1	0.1038	0.3897	0.6721	0.0562 (3)
O1	0.7858 (4)	0.1089 (3)	0.60939 (9)	0.0471 (6)
O2	0.8961 (4)	0.3842 (3)	0.44403 (8)	0.0475 (6)
N1	0.6479 (5)	0.1280 (3)	0.47532 (9)	0.0415 (6)
C1	0.2692 (6)	0.3185 (4)	0.63041 (10)	0.0428 (7)
C2	0.4680 (6)	0.2374 (4)	0.63748 (12)	0.0503 (8)
C3	0.5938 (6)	0.1856 (5)	0.60219 (12)	0.0504 (9)
C4	0.5203 (5)	0.2102 (4)	0.56143 (9)	0.0392 (7)
C5	0.3206 (5)	0.2898 (4)	0.55413 (11)	0.0430 (7)
C6	0.1938 (6)	0.3438 (5)	0.58810 (12)	0.0476 (8)
C7	0.6396 (7)	0.1658 (5)	0.52146 (14)	0.0565 (10)
C8	0.4963 (5)	0.1618 (4)	0.44811 (10)	0.0401 (7)
C9	0.6431 (5)	0.1851 (4)	0.41206 (10)	0.0384 (6)
C10	0.5719 (6)	0.0854 (4)	0.37618 (12)	0.0475 (8)
C11	0.6862 (6)	0.0900 (5)	0.33875 (13)	0.0521 (9)
C12	0.8750 (6)	0.1977 (5)	0.33639 (12)	0.0499 (9)
C13	0.9439 (6)	0.2949 (5)	0.37185 (10)	0.0489 (8)
C14	0.8278 (5)	0.2885 (4)	0.40995 (10)	0.0412 (7)

Table 2. *Selected geometric parameters (Å, °)*

Cl1—C1	1.744 (3)	C4—C7	1.492 (5)
O1—C3	1.339 (4)	C5—C6	1.382 (5)
O2—C14	1.340 (4)	C8—C9	1.464 (4)
N1—C8	1.297 (5)	C9—C14	1.374 (4)
N1—C7	1.472 (5)	C9—C10	1.405 (5)
C1—C2	1.389 (5)	C10—C11	1.374 (5)
C1—C6	1.419 (5)	C11—C12	1.412 (5)
C2—C3	1.407 (5)	C12—C13	1.381 (5)
C3—C4	1.369 (5)	C13—C14	1.398 (4)
C4—C5	1.391 (5)		
C8—N1—C7	125.8 (3)	N1—C7—C4	151.8 (4)
C2—C1—Cl1	122.2 (3)	N1—C8—C9	94.1 (3)
C6—C1—Cl1	117.8 (3)	O2—C14—C9	120.4 (3)
O1—C3—C4	120.7 (3)	O2—C14—C13	119.9 (3)
O1—C3—C2	118.5 (4)		

The title structure was solved by direct phase determination. The parameters of the complete structure could be refined by full-matrix anisotropic least-squares methods. All phenyl rings were refined without any constraints. Values of distances and angles in the rings show no significant differences from those of an ideal benzene ring. All H-atom positions (except for the hydroxyl H atoms) were calculated using a riding model and were considered with fixed isotropic U's in all refinements. The hydroxyl H atoms were found in the difference Fourier maps calculated at the end of the refinement process as a small positive electron density.

Data collection: *SDP-Plus* (Frenz, 1985). Cell refinement: *SDP-Plus*. Data reduction: *SDP-Plus*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON*92 (Spek, 1992). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1276). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,5-Dihydroxy-1-nitroanthracene-9,10-dione

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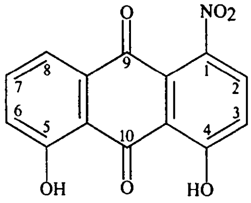
Abstract

In the search for new tautomeric systems among anthraquinone derivatives, we carried out an X-ray structural study of the title compound, 4,5-dihydroxy-1-nitro-9,10-anthraquinone, $C_{14}H_7NO_6$. The asymmetric unit contains two symmetry-independent molecules. Both anthraquinone tricyclic units (ATU) adopt a nearly planar conformation. The influence of the nitro group does not cause any fundamental changes in the distribution of the bond lengths in the intramolecular system of hydrogen bonds.

Comment

The bond dimensions in molecules 1 and 2 of the title compound, (I), are essentially the same; the r.m.s. difference of equivalent bond lengths is 0.006 Å. The main difference between the molecules seems to be due to some rotational disorder of the nitro group in molecule 1 [the 'effective' dihedral angle between the nitro group and the ATU is 85 (1)°], which leads to the splitting of the O9 and C9 atoms over two sets of sites above and below the molecular plane. This disorder manifests itself as a stretching of the displacement ellipsoids of O9, C9, O11 and O12. As a result, the ATU of molecule 1 becomes essentially planar [atom C5 has the maximum deviation from the least-squares plane of 0.038 (3) Å] and the bonds involving the C9 atom are 0.013–0.010 Å shorter than those in molecule 2. In molecule 2, the dihedral angle between the nitro group and the ATU is fixed at 73 (1)°, the displacement of atoms C9*A* and O9*A* from the tricyclic plane being 0.073 (3) and 0.244 (2) Å, respectively, thus minimizing the repulsion from the nitro group. The outer rings in molecules 1 and 2 are mutually inclined at angles of only 2.1 (5) and 0.7 (4)°, respectively, indicating the absence of any considerable steric hindrance between the *peri* substituents.



(I)

The bond lengths in both ATU's of this structure essentially do not differ from those observed in other structures containing the 1,8-dihydroxy-9,10-anthracenedione moiety reported in the literature; 1,8-dinitro-4,5-dihydroxyanthraquinone (Brown & Colclough, 1983), 7-methoxy-2-methyl-4,5-dihydroxyanthraquinone (Ulický, Kožišek & Ječný, 1991) and 1-acetyl-2,4,5,7-tetrahydroxyanthraquinone (Ulický, Kettmann, Soldánová & Betina, 1987). Only the mean disparity of the carbonyl bonds, C9=O9 and C10=O10, in the structure reported herein is noticeably less than in the former two structures; 0.039 (2) Å compared with 0.048 and 0.053 Å, respectively.

The average O4···O10 distance for the two molecules is 0.023 Å shorter than the mean O5···O10 contact distance, indicating some strengthening of the former hydrogen bond. The PM3 computations (results deposited) carried out with the *MOPAC*6.0 package (Stewart, 1990) have given nearly the same value for the O···O distance disproportion (0.025 Å). The energies of tautomerization into *ana*-quinonoid forms have also been calculated and the 4,9-tautomer appears to be only 1.5 kJ mol^{-1} more stable than the 5,9-tautomer. Thus, the nitro group, playing a σ-acceptor role, does not cause any fundamental changes in the electron-density distribution in the system of resonance-assisted hydrogen bonds.

Molecules 1 and 2 are arranged in pairs into 'head-to-tail' dimers (Fig. 1). The shortest intermolecular C···C distance in the dimer is 3.454 (4) Å and the shortest interdimer C···C spacing is 3.309 (4) Å. There are no intermolecular hydrogen bonds.

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