

A quasi-planar polyaromatic compound containing an azo and a Schiff base linkage

Ray J. Butcher,^{a*} Tushar S. Basu Baul,^b Keisham Surjit Singh^b and Frank E. Smith^c^aDepartment of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, ^bDepartment of Chemistry, North-Eastern Hill University, NEHU Permanent Campus, Umshing, Shillong 793 022, India, and ^cWeill Cornell Medical College in Qatar, PO Box 24144, Doha, Qatar

Correspondence e-mail: butcher@harker.nrl.navy.mil

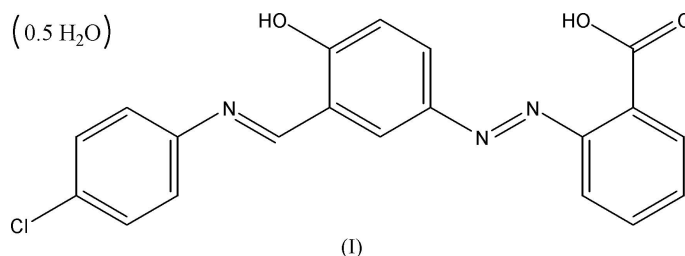
Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
 R factor = 0.076
 wR factor = 0.216
Data-to-parameter ratio = 13.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, 2-[(*E*)-3-[(*E*)-4-chlorophenylimino]-4-hydroxyphenyldiazenyl]benzoic acid hemihydrate, $\text{C}_{20}\text{H}_{14}\text{ClN}_3\text{O}_3 \cdot 0.5\text{H}_2\text{O}$, forms sheets, parallel to the (100) plane, that are linked by weak aromatic $\text{C}-\text{H} \cdots \text{O}$ interactions. These sheets are in turn linked by strong hydrogen bonds to interstitial water molecules.

Comment

Aromatic monoamines react with 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid to form products, such as the title compound, (I), which contain both azo and Schiff base (*i.e.* imino) linkages. Recently, a few tributyltin(IV) complexes containing similar azo and Schiff base components were obtained which exhibit interesting biological properties (Basu Baul *et al.*, 2004). Their structures were determined using spectroscopic techniques and single-crystal X-ray crystallography. A similar azo-Schiff base organic compound, namely *N-p*-methoxybenzylidene-*p*-phenylazoaniline, is a mesogen and exhibits a nematic liquid-crystal phase; its X-ray structure has also been determined recently (Revannasiddaiah *et al.*, 1997). In addition, structures of two similar molecules containing *meta* azo and imine substituents, also exhibiting liquid crystalline properties, have recently been determined (Baumeister *et al.*, 1990; Cariati *et al.*, 2004). The potential usefulness of such systems has prompted us to determine the structure of the title compound, (I).



The title compound (Fig. 1) crystallizes in the monoclinic space group $C2/c$ with $Z = 8$. Interstitial water molecules (one for each two of the title molecules) are located on four twofold axes that pass through the unit cell. The three-ring system assumes an extended conformation, with both outer rings slightly twisted with respect to the central aromatic ring. These quasi-planar molecules form sheets, parallel to the (100) plane (see Fig. 2), that are linked by weak aromatic $\text{C}-\text{H} \cdots \text{O}$ interactions. Adjacent sheets are linked by strong hydrogen bonds to interstitial water molecules (see Fig. 3). Bond lengths and angles within the molecule are unremarkable and similar to those found in related molecules (Baumeister *et al.*, 1990; Cariati *et al.*, 2004).

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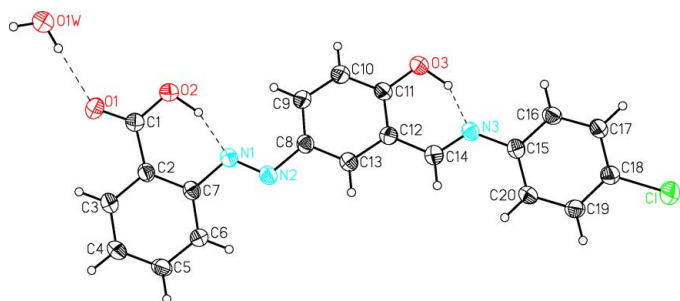


Figure 1
View of the molecule of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms have been omitted. Hydrogen bonds are shown as dashed lines.

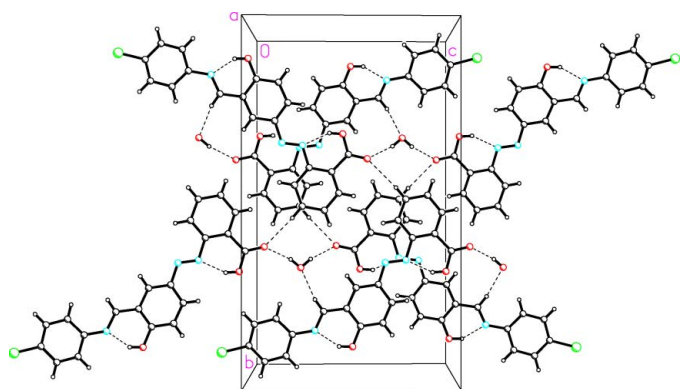


Figure 2
The molecular packing of (I), viewed down the *a* axis, perpendicular to the molecular sheets. Dashed lines indicate hydrogen bonds.

Experimental

p-Chloroaniline in hot ethanol was condensed with with an equimolar amount of 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenylbenzoic acid (Basu Baul *et al.*, 1996) in hot toluene to yield the title compound, (I) (Basu Baul *et al.*, 2004), in 56% yield. Recrystallization from chloroform and dimethyl sulfoxide solution (3:1) gave orange crystals (m.p. 498–499 K). Analysis found: C 63.20, H 3.65, N 11.13%; calculated for $C_{20}H_{15}ClN_3O_3 \cdot 0.5H_2O$: C 63.25, H 3.72, N 11.06%.

Crystal data

$C_{20}H_{14}ClN_3O_3 \cdot 0.5H_2O$	$D_x = 1.422 \text{ Mg m}^{-3}$
$M_r = 388.80$	Cu $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 49 reflections
$a = 13.2451 (19) \text{ \AA}$	$\theta = 5.4\text{--}27.8^\circ$
$b = 21.668 (4) \text{ \AA}$	$\mu = 2.12 \text{ mm}^{-1}$
$c = 12.664 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 91.69 (2)^\circ$	Prism, red
$V = 3632.8 (10) \text{ \AA}^3$	$0.50 \times 0.35 \times 0.28 \text{ mm}$
$Z = 8$	

Data collection

Bruker <i>P4</i> diffractometer	$R_{int} = 0.037$
$2\theta/\omega$ scans	$\theta_{max} = 69.1^\circ$
Absorption correction: refined from ΔF (SHELXA; Sheldrick, 1998)	$h = 0 \rightarrow 16$
$T_{min} = 0.415$, $T_{max} = 0.552$	$k = 0 \rightarrow 26$
3534 measured reflections	$l = -15 \rightarrow 15$
3382 independent reflections	3 standard reflections
1707 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: 0.3%

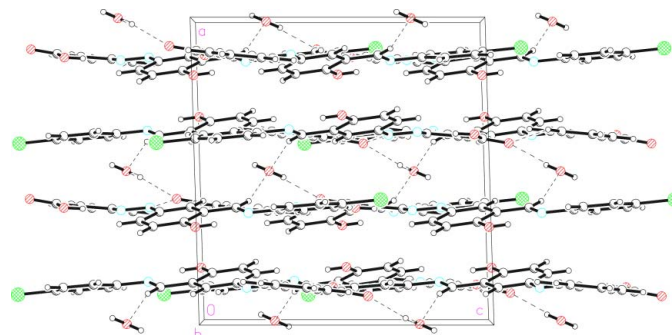


Figure 3
The molecular packing of (I), viewed down the *b* axis, showing how the aromatic sheets are linked by interstitial water molecules. Dashed lines indicate hydrogen bonds.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.076$
 $wR(F^2) = 0.216$
 $S = 1.06$
 3382 reflections
 254 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 7.4356P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.25 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cl—C18	1.730 (5)	N1—C7	1.426 (6)
O1—C1	1.207 (6)	N2—C8	1.411 (6)
O2—C1	1.311 (6)	N3—C14	1.287 (6)
O3—C11	1.333 (6)	N3—C15	1.407 (6)
N1—N2	1.269 (5)		
N2—N1—C7	114.2 (4)	C2—C7—N1	117.1 (4)
N1—N2—C8	114.3 (4)	C13—C8—N2	114.9 (4)
C14—N3—C15	123.0 (4)	C9—C8—N2	126.1 (4)
O1—C1—O2	118.6 (5)	N3—C14—C12	120.3 (5)
O1—C1—C2	122.1 (5)	C20—C15—N3	125.5 (4)
O2—C1—C2	119.2 (5)	C16—C15—N3	116.3 (4)
C6—C7—N1	122.6 (4)		
C7—N1—N2—C8	174.3 (4)	C15—N3—C14—C12	−179.2 (4)
N2—N1—C7—C2	168.7 (4)	C13—C12—C14—N3	177.9 (4)
N1—N2—C8—C13	177.0 (4)	C14—N3—C15—C16	−161.4 (5)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H2O \cdots N1	0.82	1.83	2.580 (5)	152
O3—H3O \cdots N3	0.82	1.81	2.544 (5)	148
O1W—H1W1 \cdots O1	0.852 (10)	2.05 (3)	2.875 (5)	164 (8)
C5—H5A \cdots O1 ⁱ	0.93	2.56	3.457 (7)	161
C14—H14A \cdots O1W ⁱⁱ	0.93	2.47	3.364 (7)	162
C19—H19A \cdots O2 ⁱⁱ	0.93	2.59	3.355 (6)	140

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

After location of the H atoms in a difference map, their positions were idealized. The H atoms were allowed to ride on their parent C atoms, with $C-H = 0.93 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$. Positional parameters for the water H were refined, but the $U_{iso}(H)$ value was fixed at $1.5U_{eq}(O)$.

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: SHELXTL (Sheldrick, 1997); program(s) used to solve structure: SHELXTL; program(s) used to refine

structure: *SHELXTL* ; molecular graphics: *SHELXTL* ; software used to prepare material for publication: *SHELXTL* .

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