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Key indicators

Single-crystal X-ray study

$T = 296\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ Å}$

R factor = 0.037

wR factor = 0.091

Data-to-parameter ratio = 18.2

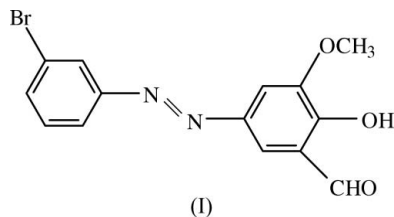
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

(*E*)-5-[(3-Bromophenyl)diazenyl]-2-hydroxy-3-methoxybenzaldehyde

The title structure, $\text{C}_{14}\text{H}_{11}\text{BrN}_2\text{O}_3$, displays the characteristic features of azobenzene derivatives. The two aromatic rings are nearly coplanar, forming a dihedral angle of $8.71(12)^\circ$. There is a strong intramolecular $\text{O}-\text{H}\cdots\text{O}$ bond, and weak $\pi-\pi$ and $\text{C}-\text{H}\cdots\pi$ interactions stabilize the structure.

Comment

Azo compounds have been the most widely used class of dyes owing to their versatile applications in various fields, such as dyeing textile fibres, colouring different materials, plastics, biological medical studies, lasers, liquid crystalline displays, electrooptical devices and ink-jet printers in high-technology areas (Catino & Farris, 1985). In azo compounds, conversion from the *trans* to the *cis* form can lead to photochromism. Photochromic compounds are of great interest for the control and measurement of radiation intensity, optical computers and display systems (Dürr & Bouas-Laurent, 1990), and for potential applications in molecular electronic devices (Martin *et al.*, 1995).



An ORTEP-3 (Farrugia, 1997) view of the molecule of the title compound, (I), and the molecular packing are shown in Figs. 1 and 2, respectively. Selected bond distances and angles

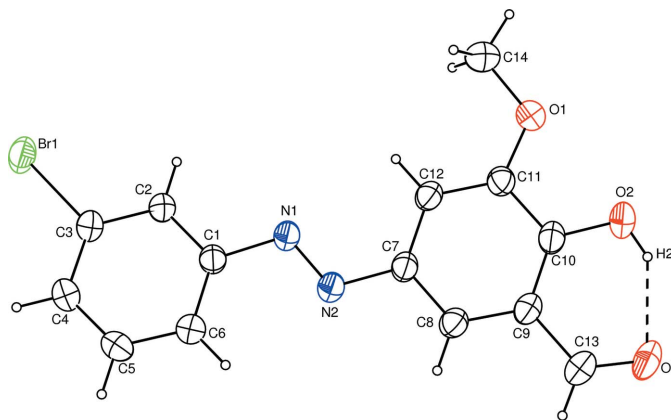


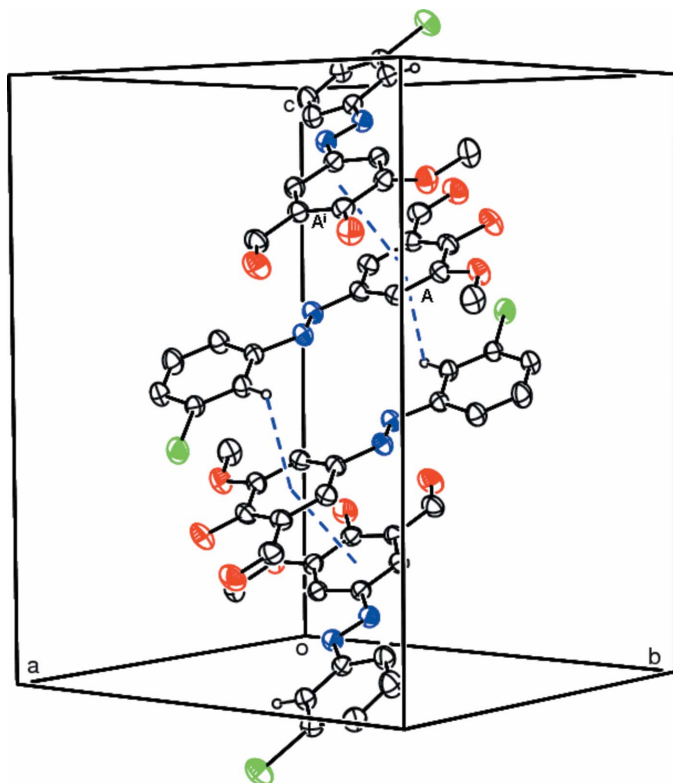
Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The $\text{O}-\text{H}\cdots\text{O}$ intramolecular hydrogen bond is indicated by a dashed line.

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**Figure 2**

Part of the crystal structure of (I). Dashed lines indicate stacking π - π and C-H $\cdots\pi$ interactions [symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, -z$]. H atoms not involved in these interactions have been omitted for clarity.

are given in Table 1. The aromatic rings are in a *trans* configuration with respect to the azo double bond.

The dihedral angle Θ_1 between the mean planes of the benzene ring (C1–C6) and the C1–N1=N2–C7 azo bridge is $10.95(21)^\circ$, and the angle Θ_2 between the C1–N1=N2–C7 azo group and the multiply substituted benzene ring (C7–C12) is $175.64(6)^\circ$. The angle Θ_3 between the planes of the two aromatic rings is $8.71(12)^\circ$. The N1–C1 and N2–C7 bond lengths of $1.435(3)$ Å and $1.415(3)$ Å, respectively, indicate single-bond character and the N=N bond length of $1.257(3)$ Å is indicative of significant double-bond character.

In the extended structure of (I), shown in Fig. 2, there are weak π - π and C-H $\cdots\pi$ interactions. An intermolecular π - π contact occurs between the two symmetry-related C7–C12 rings of neighbouring molecules. Ring A (C7–C12) is oriented in such a way that the perpendicular distance from A to Aⁱ is $3.500(13)$ Å [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. The distance between the ring centroids is $3.6594(14)$ Å. In the crystal structure of (I), there is also a weak C-H $\cdots\pi$ interaction between C2–H1 and the C7–C12 ring. The C-H \cdots CgA contact distance is 3.38 Å, where CgA is the centroid of ring A. The perpendicular distance between atom H1 and the plane of phenyl ring is 3.28 Å and the C-H \cdots CgA angle is 84° [symmetry code: (ii) $1 - x, 1 - y, -z$]. Compound (I) also has intramolecular O–H \cdots O hydrogen bonds (see Table 2 for details).

Experimental

A mixture of 3-bromoaniline (1.51 g, 8.8 mmol), water (50 ml) and concentrated hydrochloric acid (2.2 ml, 26.4 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 (0.85 g, 12.3 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. An *o*-vanillin (1.19 g, 8.8 mmol) solution (pH 9) was added gradually to the solution of cooled 3-bromobenzenediazonium 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 glacial acetic acid to obtain solid (*E*)-5-[(3-bromophenyl)diazenyl]-2-hydroxy-3-methoxybenzaldehyde. The product, (I), was recrystallized from acetic acid (yield 84%; m.p. 424–425 K).

Crystal data

C₁₄H₁₁BrN₂O₃
 $M_r = 335.16$
 Orthorhombic, *Pbcn*
 $a = 12.5131(6)$ Å
 $b = 13.2636(6)$ Å
 $c = 16.5594(7)$ Å
 $V = 2748.3(2)$ Å³
 $Z = 8$
 $D_x = 1.620$ Mg m^{−3}

Mo $K\alpha$ radiation
 Cell parameters from 23001 reflections
 $\theta = 2.2$ – 28.0°
 $\mu = 3.00$ mm^{−1}
 $T = 296$ K
 Prism, brown
 $0.50 \times 0.36 \times 0.13$ mm

Data collection

Stoe IPDS-2 diffractometer
 ω scans
 Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
 $T_{\min} = 0.275$, $T_{\max} = 0.692$
 28648 measured reflections
 3300 independent reflections

2374 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.108$
 $\theta_{\max} = 28.0^\circ$
 $h = -16 \rightarrow 16$
 $k = -17 \rightarrow 17$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.091$
 $S = 1.03$
 3300 reflections
 181 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 1.1485P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.29$ e Å^{−3}
 $\Delta\rho_{\min} = -0.41$ e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

C3–Br1	1.893 (3)	C10–O2	1.343 (3)
C1–N1	1.435 (3)	C13–O3	1.221 (3)
C7–N2	1.415 (3)	N1–N2	1.257 (3)
O3–C13–C9	124.3 (3)		
C13–C9–C10–O2	0.4 (4)	C1–N1–N2–C7	−177.6 (2)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
O2–H2 \cdots O3	0.82	1.92	2.632 (3)	145

All H atoms bound to carbon were refined using a riding model with C—H = 0.93 Å [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$] for aromatic and C—H = 0.96 Å [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{parent atom})$] for methyl C atoms. The H atom of the hydroxyl O atom was refined with O—H = 0.82 Å [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); 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, 1999).

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