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2-{(*E*)-3-[(*E*)-4-Bromophenyliminomethyl]-4-hydroxyphenyldiazenyl}benzoic acid toluene hemisolvate

Anthony Linden,[a]* Tushar S. Basu Baul[b] and Keisham S. Singh[b]

[a]Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland, and [b]Department of Chemistry, North-Eastern Hill University, NEHU Permanent Campus, Umshing, Shillong 793 022, India

Correspondence e-mail: alinden@oci.unizh.ch

Key indicators

Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.037
wR factor = 0.098
Data-to-parameter ratio = 15.5

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

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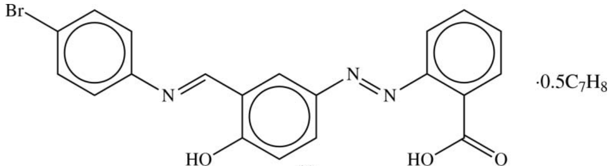
The polyaromatic title compound, $C_{20}H_{14}BrN_3O_3\cdot0.5C_7H_8$, has an extended and reasonably flat conformation. The hydroxy H atoms are involved in intramolecular hydrogen bonds only, while C—H···O and C—H···Br interactions link the molecules into two-dimensional networks.

Comment

Polyaromatic compounds containing an azo and a Schiff base linkage, such as the title compound, (I), are potential mesogens (Revannasiddaiah *et al.*, 1997). The coordination behaviour of such compounds towards organotin(IV) has also been investigated (Basu Baul *et al.*, 2004; Basu Baul, Singh, Holčapek, Jirásko, Linden *et al.*, 2005; Basu Baul, Singh, Holčapek, Jirásko, Rivarola & Linden, 2005; Basu Baul, Singh, Lyčka *et al.*, 2005; Linden *et al.*, 2005). In particular, complexes with tri-*n*-butyltin(IV) exhibit significant biological activity towards *Aedes aegypti* and *Anopheles stephensi* mosquito larvae (Basu Baul *et al.*, 2004; Basu Baul, Singh, Holčapek, Jirásko, Linden *et al.*, 2005) and sea urchin (*Paracentrotus lividus* and *Sphaerechinus granularis*) early development stages (Basu Baul, Rynjah *et al.*, 2005). The crystal structures of the 4-methylphenyl and 4-chlorophenyl analogues of (I) have already been reported (Basu Baul, Singh, Holčapek, Jirásko, Rivarola & Linden, 2005; Butcher *et al.*, 2005) and are now complemented by a description of the 4-bromo derivative, (I).



(I)

The asymmetric unit in (I) contains one molecule of the carboxylic acid plus one half of a toluene molecule which is disordered about a centre of inversion. The three-ring system of (I) has an extended and reasonably flat conformation (Fig. 1). The angles between the plane of the central ring and those of the benzoic acid and 4-bromophenyl rings are 6.01 (11) and 27.78 (11)°, respectively. The carboxylic acid group is coplanar with its parent benzene ring [O1—C1—C2—C7 = 179.60 (19)°]. The molecular conformation and dimensions are very similar to those of the 4-chlorophenyl and 4-methylphenyl analogues, with the exception that the 4-methylphenyl derivative crystallises in a zwitterionic form, where the phenolic H atom has migrated to the imine N atom. In (I), this H atom is clearly bonded to the phenolic O atom.

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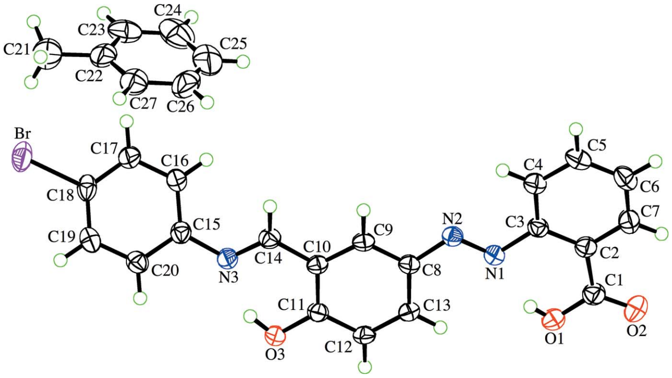

Figure 1

A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Only one orientation of the disordered toluene molecule is shown.

The carboxylic acid H atom forms an intramolecular hydrogen bond with the nearer N atom of the adjacent diazo group, while the phenolic H atom forms an intramolecular hydrogen bond with the adjacent imine N atom. Both of these interactions result in six-membered hydrogen-bonded rings.

The molecules of (I) pack in a way that facilitates several C—H···O and C—H···Br interactions (Table 1). These interactions link the solvent and substrate molecules together into two-dimensional networks, which lie parallel to the (101) plane (Fig. 2). The C—H···O angles are consistent with the most probable value of 160° for two-centre interactions (Jeffrey *et al.*, 1985).

Experimental

The title compound was prepared as described by Basu Baul *et al.* (2004). Orange crystals of (I) were obtained by slow evaporation of a solution of the compound in toluene (m.p. 487–489 K). Elemental analysis, found: C 60.04, H 3.78, N 8.97%; calculated for $C_{23.5}H_{18}BrN_3O_3$: C 60.01, H 3.85, N 8.93%.

Crystal data

$C_{20}H_{14}BrN_3O_3\cdot0.5C_7H_8$
$M_r = 470.32$
Triclinic, $P\overline{1}$
$a = 8.2708$ (3) Å
$b = 10.7547$ (3) Å
$c = 12.3929$ (3) Å
$\alpha = 88.1844$ (17)°
$\beta = 85.3535$ (16)°
$\gamma = 69.6152$ (13)°
$V = 1029.91$ (5) Å^3
$Z = 2$
$D_x = 1.516$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.03$ mm^{-1}
$T = 160$ (1) K
Tablet, orange
0.20 × 0.13 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.671$, $T_{max} = 0.795$ (expected range = 0.717–0.850)
23736 measured reflections
4718 independent reflections
3707 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 27.5°$

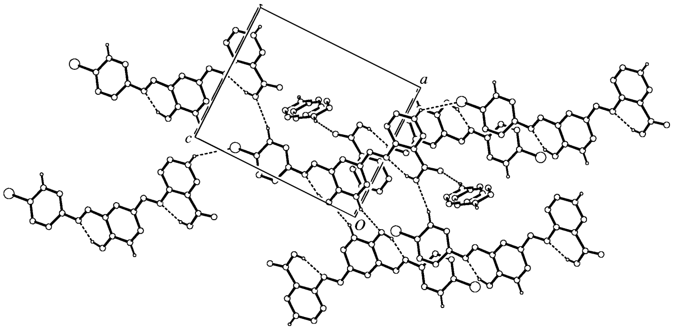

Figure 2

The crystal packing of (I), projected down the *b* axis and showing layers formed by the O—H···O, C—H···O and C—H···Br interactions (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.098$
$S = 1.03$
4718 reflections
304 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.3064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.73 (3)	1.92 (3)	2.593 (2)	154 (4)
O3—H3···N3	0.87 (3)	1.76 (3)	2.554 (2)	151 (3)
C6—H6···Br^{i}	0.95	2.92	3.630 (2)	133
C12—H12···O3^{ii}	0.95	2.53	3.388 (3)	151
C17—H17···O1^{iii}	0.95	2.49	3.419 (3)	166
C26—H26···O2^{iv}	0.95	2.50	3.374 (6)	153

Symmetry codes: (i) $x+1, y+1, z-1$; (ii) $-x+2, -y, -z$; (iii) $x-1, y, z+1$; (iv) $-x+2, -y+1, -z$.

The asymmetric unit contains one molecule of the carboxylic acid in a general position plus one half of a toluene molecule which is disordered about a centre of inversion, with the centre of gravity of the six-membered ring displaced slightly from the inversion centre. The atoms of one entire toluene molecule were defined with the site-occupation factors of the atoms set to 0.5. The atoms of the six-membered ring of the toluene molecule were constrained to an ideal hexagon, while neighbouring atoms within each orientation of the disordered toluene molecule were restrained to have similar atomic displacement parameters. The carboxylic acid and phenolic H atoms were placed in the positions indicated by a difference Fourier map and their positions were refined freely along with individual isotropic displacement parameters. The methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å) with $U_{iso}(H) = 1.5U_{eq}(C)$, but were allowed to rotate freely about the C—C bonds. All other H atoms were placed in geometrically idealised positions and constrained to ride on their parent C atom at a distance of 0.95 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994);

program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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