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4-[(2-Chloro-4-nitrophenyl)diazenyl]phenol dimethylformamide solvate

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Key indicators

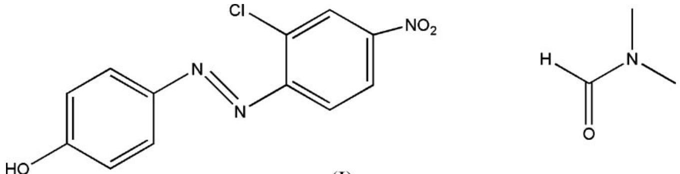
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.004 Å
R factor = 0.073
wR factor = 0.170
Data-to-parameter ratio = 13.6

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

The principal molecule of the title molecule, $C_{12}H_8ClN_3O_3 \cdot C_3H_7NO$, is essentially planar. The two benzene rings make a dihedral angle of only 6.9 (1)°. The nitro group is slightly twisted with respect to the benzene ring to which it is attached [3.7 (1)°]. The dimethylformamide solvent molecule and the azobenzene molecule are linked through a strong O—H···O hydrogen bond. In the crystal structure, the molecules are stacked through π–π interactions along [010]. Some weak C—H···O interactions stabilize the packing.

Comment

Aromatic azo compounds represent the dominant class of synthetic colorants (Zollinger, 1994, 2003); they are used extensively for dyeing and printing purposes, as well as for biochemical applications (Ojala *et al.*, 1996; Tsopelas & Sutton, 2002). Some azo dyes incorporating 'push–pull' donor–acceptor aryl rings exhibit non-linear optical properties (Barachevsky, 1998). The relationship between molecular structure, solid-state packing arrangements and dye/pigment performance characteristics has, over recent years, become an area of increasing investigation (Langhals *et al.*, 1991). As part of our search for organic functional materials, the title compound, (I), was synthesized.



(I)

The title azo molecule is essentially planar. The dihedral angle between the two benzene rings is only 6.9 (1)°. The nitro group is slightly twisted with respect to the benzene ring to which it is attached [3.7 (1)°].

The dimethylformamide solvent molecule and the azobenzene molecule are linked through a strong O—H···O hydrogen bond (Table 1). In the crystal structure, molecules are stacked through π–π interactions along [010] (Table 2). Some weak C—H···O interactions stabilize the packing (Table 1).

Experimental

A solution of $NaNO_2$ (2.17 g, in 8 ml water) was added dropwise to a mixture of 2-chloro-4-nitroaniline (5.18 g), HCl (36%, 9 ml) and water (9 ml) with vigorous stirring at 273–278 K. The disappearance of a suitable amount of $NaNO_2$ was determined using potassium

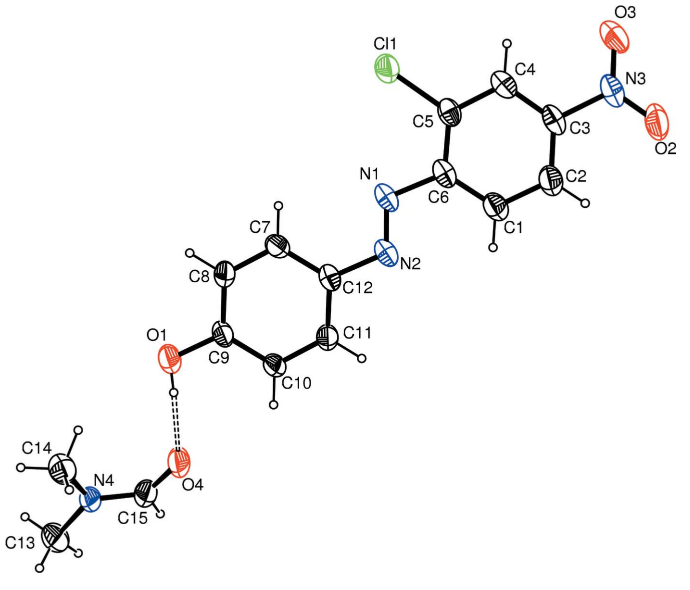


Figure 1
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The O—H···O hydrogen bond is shown with dashed lines.

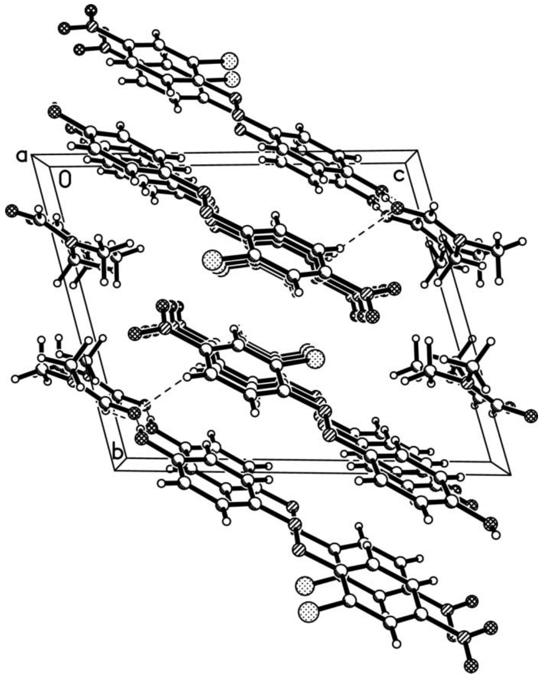


Figure 2
A packing diagram for the title compound, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

iodide–starch paper and the reaction mixture was stirred for a further 30 min before filtration. The filtrate was added dropwise to a solution of phenol (2.82 g), NaOH (1.20 g) and water (10 ml) at 273–278 K and the resulting solution stirred for 1 h, maintaining a pH of 13 (using a solution of Na_2NO_3 added dropwise). The precipitate was filtered off, washed with copious amounts of water and a small amount of ethanol, and recrystallized five times from tetrahydropyran. Red crystals were grown from dimethylformamide by slow evaporation at room temperature over a period of two months (m.p. 495 K). Elemental analysis (Perkin–Elmer 240 C elemental analyzer) calculated for $C_{12}H_8ClN_3O_3$: C 51.89, H 2.88, N 15.14%; found: C 51.95, H 2.85, N 15.34%. IR (FT–IR spectrometer with KBr pellets, cm^{-1}): 3480 (*s*), 1606 (*m*), 1504 (*s*), 1423 (*m*), 1342 (*s*, –N=N–), 1282 (*s*), 1178 (*m*), 1144 (*m*), 890 (*m*), 841 (*m*). ^{1}H NMR (Bruker AV-400 NMR spectrometer, 399.97 MHz for H and 100.57 MHz for C atoms): δ 10.781 (1H), 8.490–8.496 (1H), 8.276–8.305 (1H), 7.767–7.790 (1H) 7.898–7.921 (2H), 6.998–7.020 (2H); ^{13}C NMR: 151.7 (C6), 133.2 (C5), 125.8 (C4), 147.8 (C3), 126.4 (C1), 118.1(C2), 145.8 (C12), 123.4 (C7,C11), 116.4 (C8, C10), 163.9 (C9).

Crystal data

$C_{12}H_8ClN_3O_3 \cdot C_3H_7NO$
$M_r = 350.76$
Triclinic, $P\bar{1}$
$a = 6.041$ (2) Å
$b = 10.875$ (4) Å
$c = 12.819$ (5) Å
$\alpha = 73.78$ (2)°
$\beta = 81.29$ (3)°
$\gamma = 82.77$ (3)°
$V = 796.2$ (5) Å^3
$Z = 2$
$D_x = 1.463$ Mg m$^{-3$}
Mo *K*α radiation
Cell parameters from 3019 reflections
$\theta = 3.3$–25.7°
$\mu = 0.27$ mm^{-1}
$T = 193$ (2) K
Chip, red
0.35 × 0.30 × 0.20 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.912$, $T_{max} = 0.948$
7891 measured reflections
2996 independent reflections
2601 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 25.7°$
$h = -7 \rightarrow 6$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.073$
$wR(F^2) = 0.170$
$S = 1.16$
2996 reflections
220 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 0.8335P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.043$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4	0.82	1.78	2.600 (3)	175
C14—H14*A*···O1	0.96	2.66	3.515 (4)	149
C2—H2···O4^{i}	0.93	2.59	3.424 (4)	150
C14—H14*B*···O3^{ii}	0.96	2.77	3.614 (5)	148
C14—H14*C*···O2^{iii}	0.96	2.72	3.441 (4)	133
C15—H15···O1^{iv}	0.93	2.57	3.359 (4)	143

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

Table 2
Table 2. 'π–π' Interactions in the title compound (Å,°).

$D_{p\cdots p}$	$D_{Cg\cdots Cg}$	θ	Sym. code
3.431	3.648	19.8	$(-x+1, -y+2, -z+1)$
3.417	3.878	28.2	$(-x+1, -y+1, -z+1)$

$D_{p\cdots p}$: the distance between the parallel molecular planes. $D_{cg\cdots cg}$: the distance between the centroids of the corresponding planes. θ: the angle formed by the vectors of the above *p*···*p* and *Cg*···*Cg* lines.

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All H atoms were found in difference Fourier syntheses but they were introduced in the refinement in calculated positions and treated as riding on their parent atoms [C—H = 0.93 and 0.96 Å, and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) and 1.5$U_{\rm eq}$(C) for aromatic and methyl H atoms, respectively; O—H = 0.82 Å, and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O)].

Data collection: *CrystalClear* (Rigaku/MSC, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); 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) and *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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