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4-(2-Methoxy-4-nitrophenyldiazenyl)phenol monohydrate

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Key indicators

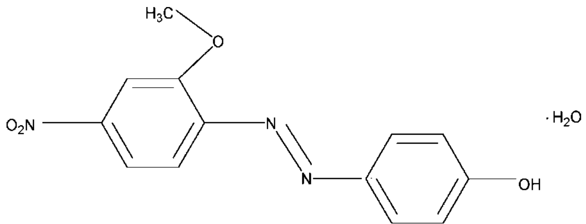
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.002 Å
R factor = 0.055
wR factor = 0.131
Data-to-parameter ratio = 15.0

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

The organic molecule of the title compound, $C_{13}H_{11}N_3O_4 \cdot H_2O$, is essentially planar. The two benzene rings make a dihedral angle of only 1.6 (1)° and the nitro group is rotated only 3.6 (1)° from the plane of its attached benzene ring. In the crystal structure, the planar molecules stack along [100] through π–π interactions, and these stacks interact laterally through strong and weak hydrogen bonds. The solvent water molecule is involved in all of the strong interactions through O—H···O(water), N···H—O(water) and O···H—O(water) hydrogen bonds.

Comment

Aromatic azo compounds represent the dominant class of synthetic colorants (Zollinger, 1994, 2003); they are used extensively for dyeing and printing purposes and are also useful in 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 investigation of the relationship between molecular structure, solid-state packing arrangements and dye/pigment performance characteristics has in recent years become an area of increasing interest (Langhals *et al.*, 1991). During our search for new organic functional materials, the title hydrate, (I), was synthesized.



(I)

The organic molecule is essentially planar. Fig. 1 shows the molecular structure with its atomic numbering scheme and Table 1 gives selected bond distances and angles. The dihedral angle between the two benzene rings is only 1.6 (1)°. With respect to the central azo linkage, the nitro-substituted benzene ring and the phenol ring are rotated in the same direction by 9.1 (1) and 8.5 (1)°, respectively. The nitro group is rotated with respect to its attached ring by only 3.6 (1)°.

The packing in this crystal structure is an assembly of extended stacks of parallel quasi-planar molecules that are cross-linked, stack-to-stack, by strong hydrogen bonds involving the water molecules (Fig. 2 and Table 2, lines 1–3) and weaker C—H···O hydrogen bonds (Table 2, lines 4–6). A typical stack in the array is formed by operations of inversion centers at $[0, 0, \frac{1}{2}]$ and $[\frac{1}{2}, 0, \frac{1}{2}]$, coupled with lattice translations

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along ±*a*. Alternate molecules in this stack are, of course, inverted, so that the terminal hydroxyl groups and nitro groups of adjacent molecules stack closely over one another. The alternating interplanar distances along the stack, which are not equivalent by symmetry, both happen to be 3.431 (2) Å if the mean plane is defined as that passing through the azobenzene portion of the molecule, *viz*. C1–C12 and N1–N2. These spacings are characteristic of aromatic molecules interacting through π-bonding. The shortest intermolecular C···C approaches are C4···C9($-x, -y, 1-z$) = 3.429 (3) Å and C2···C7($1-x, y, 1-z$) = 3.441 (3) Å.

Experimental

A solution of $NaNO_2$ (2.17 g, 8 ml of water) was added dropwise to a mixture of 2-methoxy-4-nitroaniline (5.04 g), HCl (36%, 9 ml) and water (9 ml) with vigorous stirring at 273–278 K. The appropriate amount of $NaNO_2$ was determined by KI–starch paper. The solution was then stirred for 30 min before filtration. The filtrate was added dropwise to a solution of phenol (2.82 g) in a mixture of NaOH (1.20 g) and water (10 ml) at 273–278 K, then stirred for 1 h and maintained at pH = 13. After acidification and filtration, the title compound was obtained; it was then washed with a copious amount of water and a little ethanol, and recrystallized five times from ethanol. Orange crystals were grown from toluene by slow evaporation at room temperature for three weeks (m.p. 499 K). Elemental analysis (Perkin–Elmer 240 C elemental analyzer) calculated for $C_{13}H_{13}N_3O_4$: C 56.73, H 4.73, N 15.27%; found: C 56.29, H 4.03, N 15.06%. IR (FT–IR spectrometer with KBr pellets, cm^{-1}): 3395, 3103, 1586, 1521, 1506, 1429 (*m*, N=N), 1342, 1282, 1259, 1142, 1090, 1018, 847, 804, 729. ^{1}H NMR: 1.646 (*s*, 2H, H_2O), 4.108 (*s*, 3H, CH_3), 5.502 (*s*, H, OH), 6.956 (*s*, H4*A*), 6.978 (*s*, H2), 7.676–7.698 (*s*, H1*A*), 7.908–7.943 (4H, Ph).

Crystal data

$C_{13}H_{11}N_3O_4\cdot H_2O$
$M_r = 291.26$
Triclinic, $P\overline{1}$
$a = 7.2392$ (18) Å
$b = 8.6741$ (15) Å
$c = 11.066$ (3) Å
$\alpha = 75.286$ (11)°
$\beta = 88.505$ (15)°
$\gamma = 84.737$ (15)°
$V = 669.3$ (3) Å^3
$Z = 2$
$D_x = 1.445$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2640 reflections
$\theta = 3.4$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 193$ (2) K
Chip, orange
0.40 × 0.35 × 0.17 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min} = 0.956$, $T_{\max} = 0.981$
7473 measured reflections
2996 independent reflections
2568 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.131$
$S = 1.14$
2996 reflections
200 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.1914P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

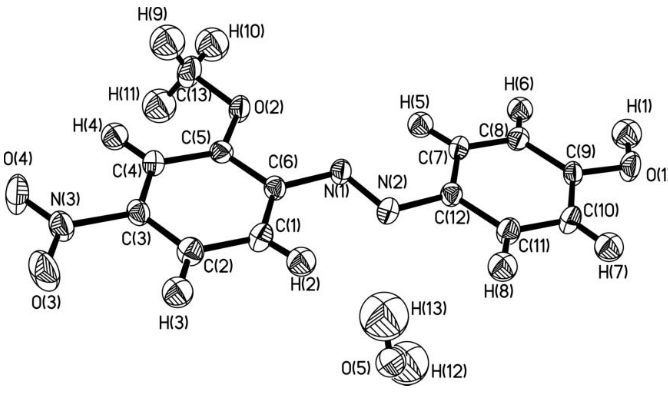

Figure 1
The molecular structure, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

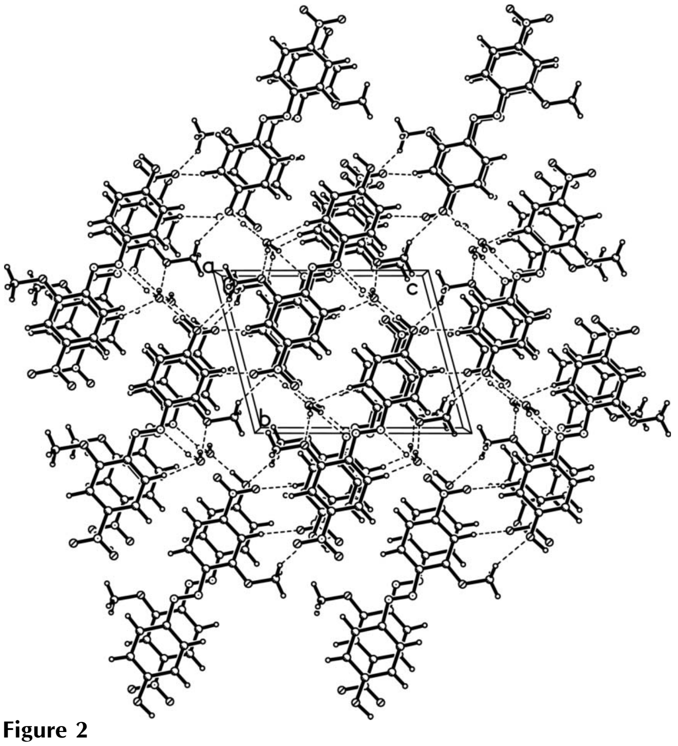

Figure 2
A packing diagram of the title compound, viewed down the *a* axis. Dashed lines indicate hydrogen bonds.

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.3551 (17)	N1—N2	1.2641 (17)
O2—C5	1.3561 (17)	N1—C6	1.4226 (18)
O2—C13	1.4320 (19)	N2—C12	1.4179 (18)
O3—N3	1.2224 (18)	N3—C3	1.4716 (19)
O4—N3	1.2230 (18)		
C5—O2—C13	117.86 (12)	O4—N3—C3	118.42 (13)
N2—N1—C6	114.24 (12)	O1—C9—C10	117.90 (13)
N1—N2—C12	114.35 (12)	O1—C9—C8	122.00 (14)
O3—N3—O4	123.41 (14)	C10—C9—C8	120.09 (13)
O3—N3—C3	118.18 (14)		
C6—N1—N2—C12	−179.94 (11)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O5—H5$B\cdots$O2^{i}	0.83 (3)	2.09 (3)	2.8757 (18)	160 (3)
O5—H5$A\cdots$N2^{ii}	0.87 (3)	2.11 (3)	2.9572 (19)	166 (3)
O1—H1$\cdots$O5^{iii}	0.84	1.84	2.6747 (18)	175
C8—H8$\cdots$O5^{iii}	0.95	2.68	3.346 (2)	128
C10—H10$\cdots$O4^{iv}	0.95	2.71	3.323 (2)	124
C13—H13$A\cdots$O1^{v}	0.98	2.54	3.439 (2)	153

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

H atoms were treated as riding, with C—H = 0.95 Å for aromatic C atoms, C—H = 0.98 Å for the methyl C atom, O—H = 0.84 Å for the phenol O atom and O—H = 0.83–0.87 Å for the water O atom. The $U_{\rm iso}$(H) values were set at $xU_{\rm eq}$(carrier atom), with x = 1.2 for aromatic C atoms, 1.5 for methyl C and phenol O atoms, and 1.89–2.25 for water O atom.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*).

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