(E)-1-(2,4-Dinitrophenyl)-2-{2-[2-(3-nitrophenoxy)ethoxy]benzylidene}hydrazine dimethylformamide solvate

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The molecule of the title compound, $C_{21}H_{17}N_5O_8 \cdot C_3H_7NO$, is non-planar. The central benzene ring makes dihedral angles of 86.87 (8) and 4.52 (6)° with the terminal benzene ring bonded to the ethoxy functionality and the *p*-nitrophenyl residue bonded to the hydrazine functionality, respectively. Intramolecular N—H⋯O and C—H⋯O hydrogen bonds help to stabilize the molecular conformation, while weak intermolecular C—H⋯O hydrogen bonds link adjacent molecules to form infinite chains in the crystal structure.

Comment

Metal complexes based on Schiff bases have been extensively studied, because of their significant biological activity (Kahwa *et al.*, 1986). Consequently, significant effort has been devoted to the synthesis of Schiff base derivatives to develop protein and enzyme mimics (Pires Santos *et al.*, 2001). As part of an investigation of their crystal structures, which will provide useful information for the coordination properties of Schiff bases functioning as ligands, we report the synthesis and structure of the title dinitrophenylhydrazine Schiff base derivative, (I).

(I)
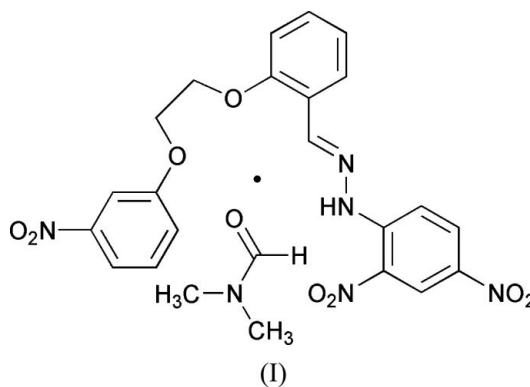
The central benzene ring of (I) (atoms C9–C14) is almost perpendicular to the terminal benzene ring bonded to the ethoxy functionality (C1–C6), with a dihedral angle of 86.87 (8)° (Fig. 1). The *p*-nitrophenyl residue (C16–C21/N5/O7/O8) bonded to the hydrazine functionality is planar, with an r.m.s. deviation of the fitted atoms of 0.010 Å. This plane makes dihedral angles of 87.56 (6) and 4.52 (6)° with the terminal benzene ring (C1–C6) and the central benzene ring (C9–C14), respectively. The O7—N5—C19—C18 and O8—N5—C19—C20 torsion angles are 179.3 (2) and 179.8 (2)°, respectively, confirming the coplanarity of the nitro group (N5/O7/O8) with the aromatic ring (C16–C21). The corresponding dihedral angle is indeed virtually zero, at 1.0 (3)°.
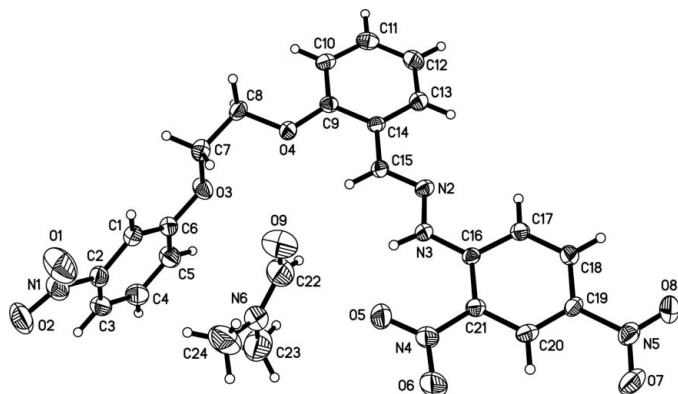
Figure 1
The structure of (I), with displacement ellipsoids drawn at the 30% probability level.

Figure 2
A packing diagram for (I), with hydrogen bonds drawn as dashed lines.

The other nitro group (N4/O5/O6) makes a dihedral angle of 2.26 (11)° with the same ring. All bond lengths and angles (Table 1) are within normal ranges (Allen *et al.*, 1987).

An intramolecular N3—H3···O5 hydrogen bond is found in (I) (Table 1), which helps to stabilize the conformation of the molecule. There is also a weak C15—H15···O9 hydrogen bond linking the main molecule and the solvent molecule. The crystal structure is stabilized by a couple of weak non-classical intermolecular C—H···O hydrogen bonds (Table 1), forming infinite chains (Fig. 2).

Experimental

To a solution of 2-hydroxybenzaldehyde (6.1 g, 50 mmol) and potassium carbonate (13.8 g, 100 mmol) in acetonitrile (500 ml), 1-bromo-2-chloroethane (7.1 g, 50 mmol) was added dropwise over a period of 30 min and the mixture refluxed for 24 h under an N_2 atmosphere. 3-Nitrophenol (7.0 g, 50 mmol) dissolved in acetonitrile (100 ml) was then added dropwise over a period of 30 min and the mixture was refluxed for an additional 48 h under an N_2 atmosphere. The solvent was then removed and the resulting mixture poured into ice–water (500 ml). The white precipitate which formed was isolated and recrystallized from ethanol to give pure 2-[2-(3-nitrophenoxy)-ethoxy]benzaldehyde in 26% yield. An anhydrous ethanol solution of 2-[2-(3-nitrophenoxy)ethoxy]benzaldehyde (2.87 g, 10 mmol) was added to an anhydrous ethanol solution of 1-(2,4-dinitrophenyl)-hydrazine (1.98 g, 10 mmol) and the mixture stirred at 350 K for 5 h under N_2, whereupon an orange precipitate appeared. The product was isolated, recrystallized from acetonitrile and dried *in vacuo*, to give pure (I) in 88% yield. Orange single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of an *N,N*-dimethylformamide solution over a period of 20 d.

Crystal data

$C_{21}H_{17}N_5O_8 \cdot C_3H_7NO$	$D_x = 1.414$ Mg m^{-3}
$M_r = 540.49$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2554
$a = 6.9806$ (12) Å	reflections
$b = 25.764$ (4) Å	$\theta = 2.8$–25.9°
$c = 14.200$ (2) Å	$\mu = 0.11$ mm^{-1}
$\beta = 96.318$ (3)°	$T = 294$ (2) K
$V = 2538.4$ (7) Å^3	Block, orange
$Z = 4$	$0.28 \times 0.24 \times 0.20$ mm
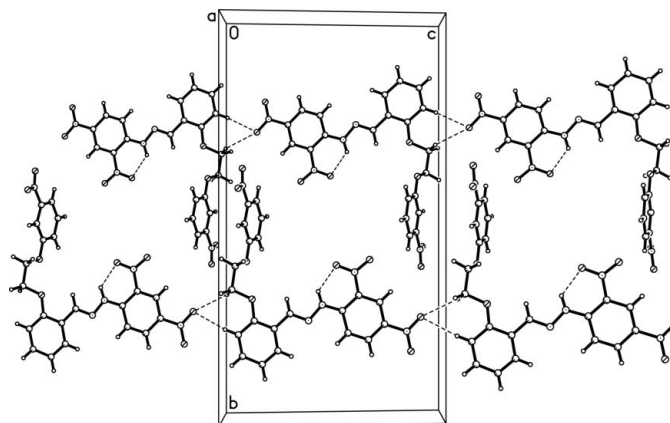
Data collection

Bruker SMART APEX CCD area-detector diffractometer	5198 independent reflections
	2638 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.049$
Absorption correction: multi-scan	$\theta_{max} = 26.4°$
(*SADABS*; Sheldrick, 1996)	$h = -8 \rightarrow 7$
$T_{min} = 0.920$, $T_{max} = 0.978$	$k = -32 \rightarrow 31$
14295 measured reflections	$l = -17 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.052$	$+ 0.0615P]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.005$
5198 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
354 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O5	0.86	2.01	2.623 (3)	127
C15—H15···O9	0.93	2.51	3.421 (3)	166
C8—H8A···O7^i	0.97	2.51	3.237 (3)	132
C10—H10···O7^i	0.93	2.61	3.520 (3)	168

Symmetry code: (i) $x + 1, y, z + 1$.

H atoms were included in calculated positions and refined using a riding-model approximation. Constrained C—H and N—H bond lengths and isotropic U parameters are as follows: 0.93 Å and U_{iso}(H) = $1.2U_{eq}$(C) for aromatic CH; 0.97 Å and U_{iso}(H) = $1.2U_{eq}$(C) for methylene CH$_2$; 0.96 Å and U_{iso}(H) = $1.5U_{eq}$(C) for methyl CH$_3$; 0.86 Å and U_{iso}(H) = $1.2U_{eq}$(N) for NH.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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