N-(2-Hydroxy-3-iodo-5-nitrobenzylidene)-3-nitroaniline: conformational isomers linked into complex sheets by five C—H···O hydrogen bonds and a two-centre iodo–nitro interaction

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The title compound, $C_{13}H_8IN_3O_5$, crystallizes with $Z' = 2$ in the space group $P2_1/n$. The two independent molecules, which are both almost planar, are conformational isomers. The molecules are linked into complex sheets by a combination of five independent C—H···O hydrogen bonds and an almost linear two-centre iodo–nitro interaction.

Comment

We have recently reported the supramolecular structures of imines containing iodo and nitro groups, for example, N-(2-iodobenzylidene)-3-nitroaniline, $2\text{-}IC_6H_4CH{=}NC_6H_4NO_2\text{-}3'$ (Wardell *et al.*, 2002), and the various isomeric N-(nitrobenzylidene)iodoanilines, $O_2NC_6H_4CH{=}NC_6H_4I$ (Glidewell *et al.*, 2002), several of which crystallize in two polymorphic forms (Ferguson *et al.*, 2005). We have now continued our studies in this area with the title compound, (I), an imine containing an additional nitro group as well as a hard hydrogen-bonding donor group.

Compound (I) crystallizes with $Z' = 2$ in the space group $P2_1/n$ (Fig. 1). In each of the independent molecules there is an intramolecular O—H···N hydrogen bond, forming an $S(6)$ motif (Bernstein *et al.*, 1995), and these interactions undoubtedly influence the molecular conformations. Both molecules are nearly planar. The overall conformation in each is defined by five torsion angles (Table 1), and it is striking that in molecule A the two nitro groups are on the same edge of the molecule, whereas in molecule B these substituents are on opposite edges (Fig. 1). The two molecules are thus conformational isomers, and this alone suffices to preclude any possible additional symmetry.

Within the molecules, the bond distances show some interesting patterns (Table 1), consequent upon the mutually

(I), molecule *A*   (I), molecule *B*

(I*a*)
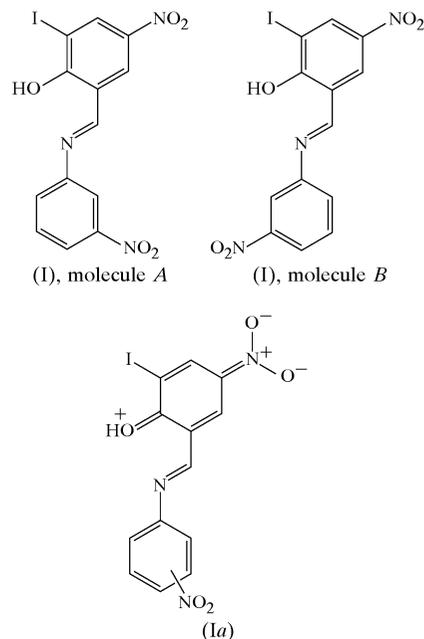
para arrangement in the iodinated rings of the electron-donor hydroxyl substituent and the electron-acceptor nitro group; in the non-iodinated rings, there is no possibility of any conjugative interactions. Thus, the C—O bonds are significantly shorter than is typical in simple phenols (mean value 1.362 Å; Allen *et al.*, 1987). Of the C—N bonds to the nitro groups, the
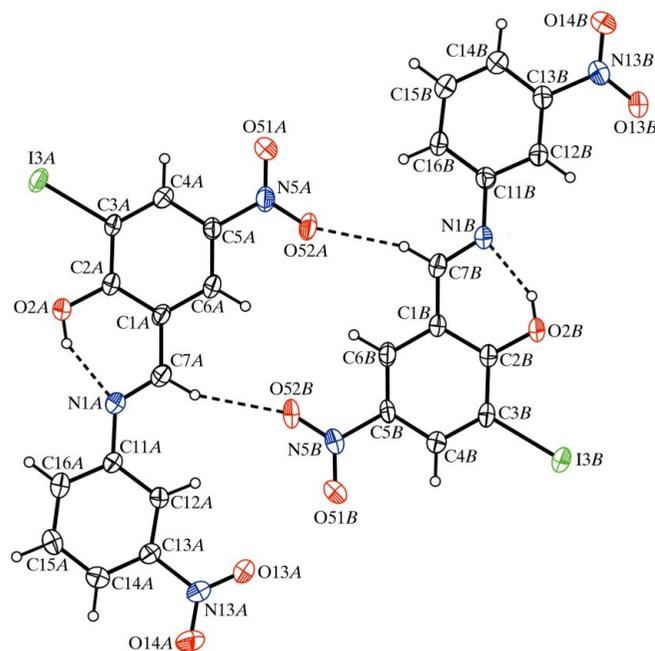

Figure 1
The two independent molecules of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular O—H···N hydrogen bonds and the two C—H···O hydrogen bonds within the selected asymmetric unit are indicated by dashed lines.

bonds C5A—N5A and C5B—N5B are both somewhat shorter than the mean value for simple aromatic nitro compounds (1.468 Å), whereas the bonds C13A—N13A and C13B—N13B are both considerably longer. The N—O bonds involving atoms N5A and N5B are shorter than those involving atoms N13A and N13B. Finally, there is some evidence of C—C bond fixation within the iodinated rings. These observations, taken together, provide some evidence in favour of polarized form (I*a*) (see scheme) as a modest contributor to the overall molecular electronic structure.

Within the selected asymmetric unit, the two molecules are linked by two C—H···O hydrogen bonds (Fig. 1 and Table 2), and this bimolecular aggregate can be regarded as the basic building block within the supramolecular structure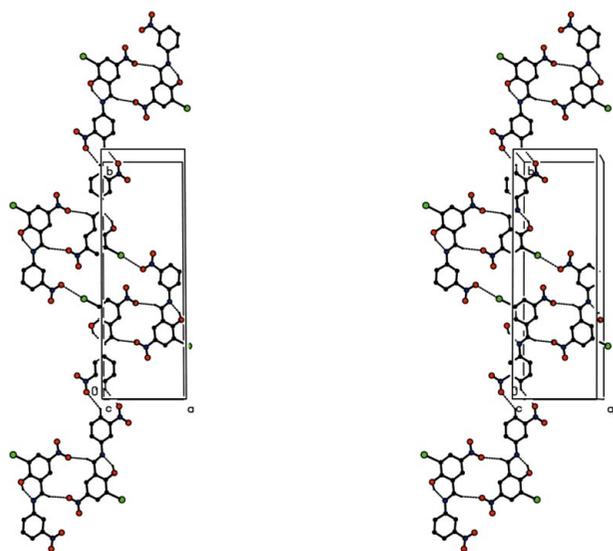. Three further C—H···O hydrogen bonds and a two-centre iodo–nitro interaction then link these aggregates into complex sheets, the formation of which can be readily analysed in terms of one-dimensional substructures.

In the principal substructure, atom C14B at (x, y, z) acts as hydrogen-bond donor to atom O14B at $(-x, -y, 1 - z)$, so generating by inversion a centrosymmetric $R_2^2(10)$ motif centred at $(0, 0, \frac{1}{2})$. At the same time, atom I3B at (x, y, z) forms a two-centre interaction with atom O13A at $(-x, 1 - y, 1 - z)$, with dimensions I···O = 3.173 (4) Å and C—I···O = 175.6 (2)°, so generating by inversion an $R_4^4(28)$ (Starbuck *et al.*, 1999) motif centred at $(0, \frac{1}{2}, \frac{1}{2})$. Propagation by inversion of these two interactions then generates a chain running parallel to the [010] direction containing $R_2^2(10)$ rings centred at $(0, n, \frac{1}{2})$ (n = zero or integer) and $R_4^4(28)$ rings centred at $(0, n + \frac{1}{2}, \frac{1}{2})$ (n = zero or integer), together with two types of $S(6)$ ring and an $R_2^2(14)$ ring (Fig. 2).

Two further C—H···O hydrogen bonds link the [010] chains into sheets. The type A molecules (Fig. 1) at (x, y, z) and $(-x, -y, 1 - z)$ form part of the chain along $(0, y, \frac{1}{2})$ (Fig. 2). The C14A atoms at (x, y, z) and $(-x, -y, 1 - z)$, act as hydrogen-bond donors to, respectively, atoms O51A at $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and $(-\frac{3}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z)$, which themselves lie in the [010] chains along $(\frac{3}{2}, y, 0)$ and $(-\frac{3}{2}, y, 1)$, respectively. Hence, the propagation of this hydrogen bond by the 2_1 screw axes along $[3(2m + 1)/4, y, (1 - 2m)/4]$ (m = zero or integer) links the [010] chains into a (103) sheet. The formation of this sheet is reinforced by the final C—H···O hydrogen bond, in which atom C16A at (x, y, z) acts as hydrogen-bond donor to atom O13B at $(\frac{3}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, so forming a $C_2^2(18)$-$C_2^2(18)[R_2^2(14)]$ chain of rings running parallel to the [30$\bar{1}$] direction and generated by the *n*-glide plane at $y = \frac{1}{4}$ (Fig. 3).

There are no direction-specific interactions between adjacent sheets. In particular, C—H···π(arene) hydrogen bonds and aromatic π–π stacking interactions are absent from the structure of (I).

Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a chain along [010] built from hydrogen bonds and iodo–nitro interactions, and containing five different rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.
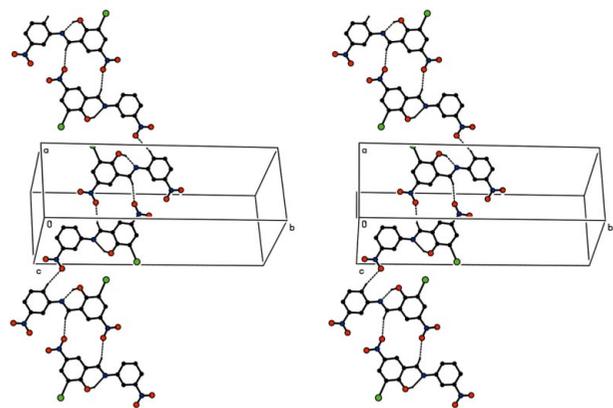

Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain of rings along [30$\bar{1}$]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

Experimental

A solution of 3-nitroaniline (1.38 g, 10 mmol) and 2-hydroxy-3-iodo-5-nitrobenzaldehyde (0.55 g, 10 mmol) (Garden *et al.*, 2004) in methanol (30 ml) was heated under reflux for 45 min. The mixture was then cooled and the solvent was removed under reduced pressure. Crystallization from ethanol of the resulting solid product gave crystals of (I) suitable for single-crystal X-ray diffraction.

Crystal data

$C_{13}H_8IN_3O_5$	$Z = 8$
$M_r = 413.12$	$D_x = 1.948$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.2957$ (4) Å	$\mu = 2.30$ mm^{-1}
$b = 27.5905$ (13) Å	$T = 291$ (2) K
$c = 11.0084$ (5) Å	Plate, colourless
$\beta = 93.830$ (2)°	$0.30 \times 0.22 \times 0.05$ mm
$V = 2817.1$ (2) Å^3	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	29048 measured reflections
	10158 independent reflections
φ and ω scans	4201 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$R_{int} = 0.068$
	$\theta_{max} = 32.5°$
$T_{min} = 0.545$, $T_{max} = 0.893$	

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.093$
$S = 0.87$
10158 reflections
399 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.72$ e Å⁻³
$\Delta\rho_{min} = -0.51$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

C1A—C2A	1.411 (5)	C1B—C2B	1.419 (5)
C2A—C3A	1.406 (5)	C2B—C3B	1.414 (5)
C3A—C4A	1.377 (5)	C3B—C4B	1.368 (5)
C4A—C5A	1.387 (5)	C4B—C5B	1.388 (5)
C5A—C6A	1.380 (5)	C5B—C6B	1.359 (5)
C6A—C1A	1.394 (5)	C6B—C1B	1.388 (5)
C2A—O2A	1.327 (4)	C2B—O2B	1.311 (4)
C5A—N5A	1.457 (5)	C5B—N5B	1.463 (5)
N5A—O51A	1.217 (4)	N5B—O51B	1.204 (4)
N5A—O52A	1.229 (4)	N5B—O52B	1.232 (4)
C13A—N13A	1.484 (5)	C13B—N13B	1.475 (5)
N13A—O13A	1.198 (5)	N13B—O13B	1.215 (5)
N13A—O14A	1.207 (4)	N13B—O14B	1.208 (4)
C12A—C13A—N13A—O13A	−7.1 (7)	C12B—C13B—N13B—O13B	5.5 (7)
C1A—C7A—N1A—C11A	−177.1 (4)	C1B—C7B—N1B—C11B	−179.4 (4)
N1A—C7A—C1A—C2A	0.4 (7)	N1B—C7B—C1B—C2B	1.1 (7)
C7A—N1A—C11A—C12A	−0.1 (7)	C7B—N1B—C11B—C12B	176.9 (4)
C4A—C5A—N5A—O51A	8.2 (6)	C4B—C5B—N5B—O51B	1.2 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2A—H2A···N1A	0.82	1.85	2.580 (4)	148
O2B—H2B···N1B	0.82	1.81	2.549 (4)	149
C7A—H7A···O52B	0.93	2.37	3.263 (5)	160
C7B—H7B···O52A	0.93	2.36	3.254 (5)	162
C14A—H14A···O51Aⁱ	0.93	2.53	3.372 (6)	151
C14B—H14B···O14Bⁱⁱ	0.93	2.51	3.279 (6)	141
C16A—H16A···O13Bⁱⁱⁱ	0.93	2.47	3.377 (5)	166

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, -y, -z+1$; (iii) $x+\frac{3}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

The space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C—H = 0.93 Å, O—H = 0.82 Å and U_{iso}(H) = $1.2U_{eq}$(C) or $1.5U_{eq}$(O).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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