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A hydrogen-bonded chain of edge-fused rings in 5-nitroisatin

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.005 Å
R factor = 0.061
wR factor = 0.109
Data-to-parameter ratio = 14.7

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

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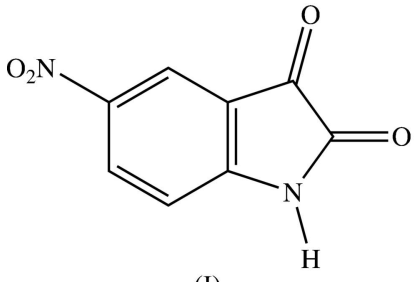
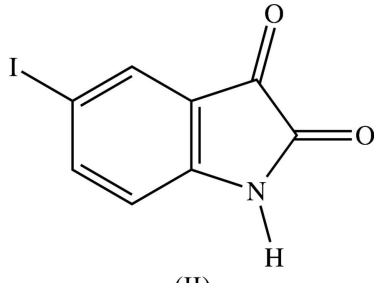
The title compound, $C_8H_4N_2O_4$, crystallizes with $Z' = 2$. The molecules are linked by a combination of N—H···O and C—H···O hydrogen bonds into chains of edge-fused $R_4^4(16)$ and $R_4^4(26)$ rings.

Comment

We report here the molecular and supramolecular structure of 5-nitroisatin (I), whose behaviour is briefly compared with that of 5-iodoisatin (II), which we reported recently (Garden *et al.*, 2006).



(I)



(II)

Compound (I) crystallizes with $Z' = 2$ in the space group $P\overline{1}$ (Fig. 1), and the two molecules have very similar dimensions. Both exhibit long bonds, C11—C12 and C21—C22, between the two carbonyl groups (Table 1), as typically found in isatins (Palenik *et al.*, 1990; Garden *et al.*, 2006), while the dihedral angles between the nitro groups and the adjacent aryl rings are 10.4 (2)° in molecule 1 and 7.4 (2)° in molecule 2.

The molecules are linked into chains of edge-fused rings by a combination of N—H···O and C—H···O hydrogen bonds (Table 2). The N—H···O hydrogen bonds link groups of four molecules, two of each type, into centrosymmetric $R_4^4(16)$ rings (Bernstein *et al.*, 1995) (Fig. 2), and these tetramolecular aggregates are linked by a single C—H···O hydrogen bond into a chain of edge-fused rings along [001], with $R_4^4(16)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, n + \frac{1}{2})$ (n = zero or integer) alternating with $R_4^4(26)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, n)$ (n = zero or integer) (Fig. 3).

These chain of rings are weakly linked by a sheared, parallel (type III, Allen *et al.*, 1998) carbonyl–carbonyl interaction. Atom O11 in the molecule at (x, y, z), which lies in the chain along $(\frac{1}{2}, \frac{1}{2}, z)$, makes a short dipolar contact with atom C22 in the molecule at $(-x, 1 - y, 1 - z)$, which is part of the chain along $(0, \frac{1}{2}, z)$; the key dimensions are O11···C22^{i} = 2.835 (4) Å, O11···O22^{i} = 3.266 (3) Å, C11—O11···C22^{i} = 145.8 (2)° and C11—O11···O22^{i} = 163.9 (2)° [symmetry code: (i) $-x, 1 - y, 1 - z$]. Propagation by inversion of this interaction links the chains into sheets parallel to (010).

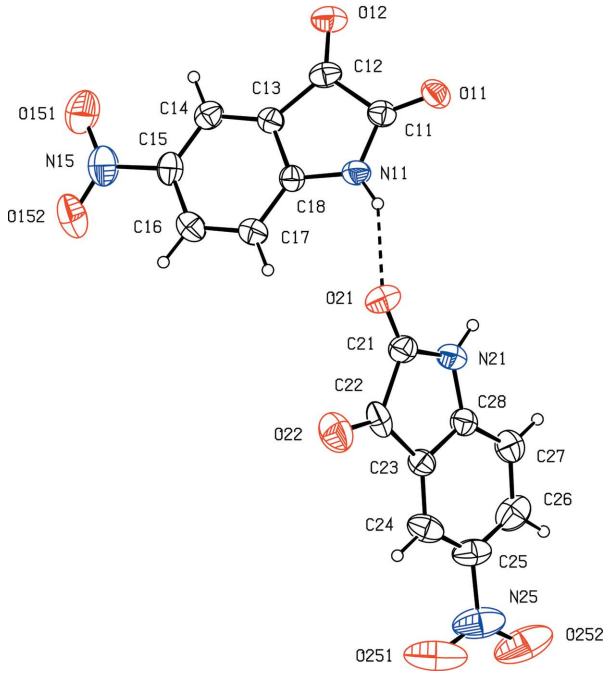


Figure 1
The two independent molecules of compound (I), showing the atom-labelling scheme and the hydrogen-bond (dashed line) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

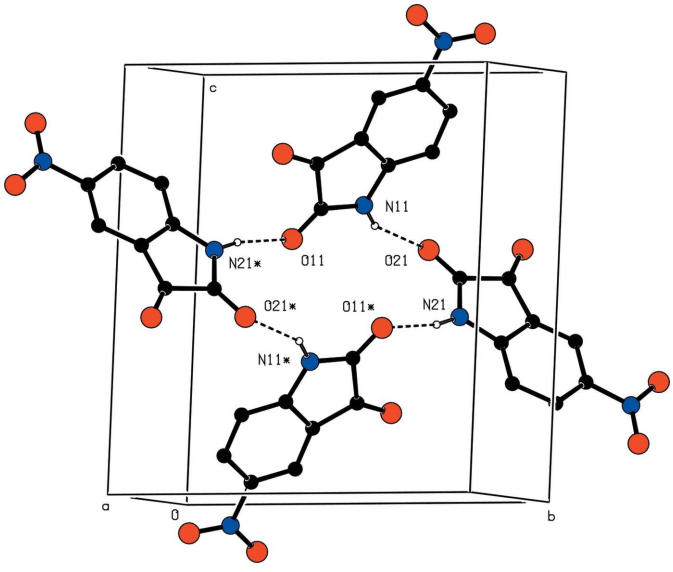


Figure 2
Part of the crystal structure of compound (I), showing the formation of a centrosymmetric tetramolecular aggregate built from N—H···O hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$, and hydrogen bonds are shown as dashed lines

In 5-iodoisatin, (II), by contrast, which crystallizes with $Z' = 1$, the molecules are linked by a combination of one N—H···O hydrogen bond, one C—H···O hydrogen bond and one iodo–carbonyl interaction into sheets containing alternating

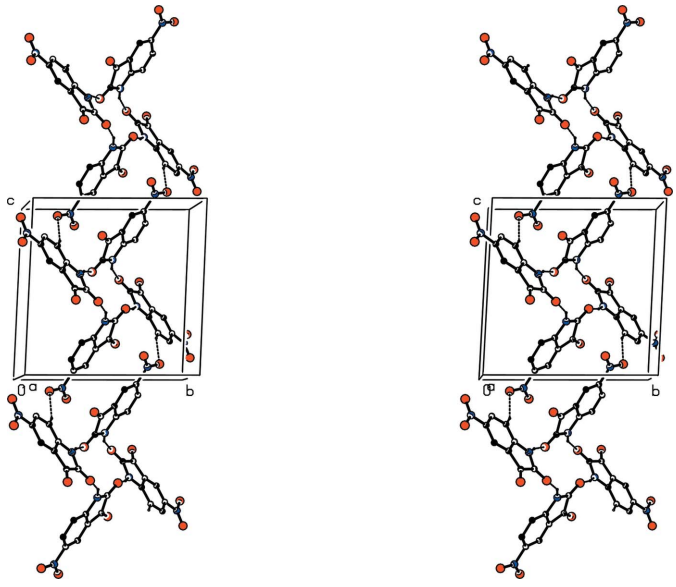


Figure 3
A stereoscopic view of part of the crystal structure of compound (I), showing the formation of a chain of edge-fused $R_4^4(16)$ and $R_4^4(26)$ rings along [001]. Hydrogen bonds are shown as dashed lines, and for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

columns of $R_2^2(9)$ and $R_4^3(16)$ rings, while in isatin itself, the molecules are linked by paired N—H···O hydrogen bonds into $R_2^2(8)$ dimers which are themselves linked into sheets by aromatic π–π stacking interactions (Garden *et al.*, 2006).

Experimental

A commercial sample (Aldrich) of 5-nitroisatin was recrystallized from ethanol.

Crystal data

$C_8H_4N_2O_4$
$M_r = 192.13$
Triclinic, $P\overline{1}$
$a = 5.5595$ (6) Å
$b = 12.0772$ (13) Å
$c = 12.2795$ (14) Å
$\alpha = 87.322$ (3)°
$\beta = 87.355$ (3)°
$\gamma = 83.049$ (3)°
$V = 816.85$ (16) Å^3
$Z = 4$
$D_x = 1.562$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 291$ (2) K
Thick plate, colourless
0.28 × 0.12 × 0.07 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.954$, $T_{max} = 0.991$
6130 measured reflections
4096 independent reflections
1331 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 28.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.109$
$S = 1.00$
4096 reflections
253 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C11—C12	1.558 (4)	C21—C22	1.552 (4)
C14—C15—N15—O151	−11.5 (5)	C24—C25—N25—O251	8.0 (6)
C14—C15—N15—O152	169.8 (3)	C24—C25—N25—O252	−173.5 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···O21	0.86	2.11	2.888 (3)	151
N21—H21···O11^{i}	0.86	2.03	2.875 (3)	168
C27—H27···O152^{ii}	0.93	2.43	3.272 (4)	151

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

All H atoms were located in difference maps and then treated as riding atoms, with C—H = 0.93 Å, N—H = 0.86 Å and U_{iso}(H) = $1.2U_{eq}$(C,*N*).

Data collection: *SMART* (Bruker, 2000); 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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