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Hydrogen-bonded chains of rings linked by iodo–carbonyl interactions in 5-iodoisatin and hydrogen-bonded sheets in 7-trifluoromethylisatin

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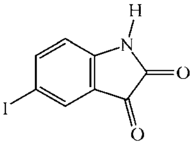
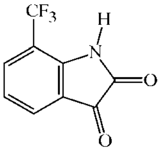
In 5-iodoisatin (5-iodo-1*H*-indole-2,3-dione), $C_8H_4INO_2$, the molecules are linked into chains of rings by N—H···O and C—H···O hydrogen bonds, and these chains are linked into sheets by iodo–carbonyl interactions. In 7-trifluoromethylisatin (7-trifluoromethyl-1*H*-indole-2,3-dione), $C_9H_4F_3NO_2$, the molecules are linked into sheets of centrosymmetric $R_2^2(8)$ and $R_6^6(34)$ rings by N—H···O and C—H···O hydrogen bonds.

Comment

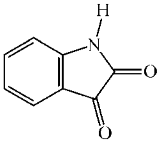
Isatin and its derivatives are versatile substrates, useful in the syntheses of a large variety of heterocyclic compounds, such as indoles and quinolines, and as raw materials for drug synthesis. Isatins have also been found in mammalian tissue and their function as a modulator of biochemical processes has been the subject of much discussion (da Silva *et al.*, 2001). We report here the molecular and supramolecular structures of two monosubstituted isatins, namely 5-iodoisatin, (I), and 7-trifluoromethylisatin, (II) (Figs. 1 and 2).



(I)



(II)



(III)

The bond distances in compounds (I) and (II) (Table 3) are, in general, similar to those in isatin itself [Cambridge Structural Database (CSD; Allen, 2002) refcode ISATIN03 (Palenik *et al.*, 1990)], although with a rather smaller range for the C—C bonds in the fragment C3a/C4–C7/C7a. In particular, the C2—C3 bond, which is longer than a typical single bond between two three-coordinate C atoms, is of similar length in each of (I) and (II) to that in isatin itself, compound (III) [1.555 (3) Å; Palenik *et al.*, 1990], where this long bond was ascribed to lone-pair–lone-pair repulsions involving two

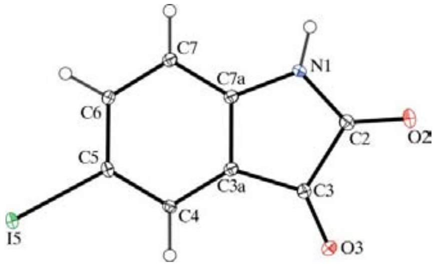


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

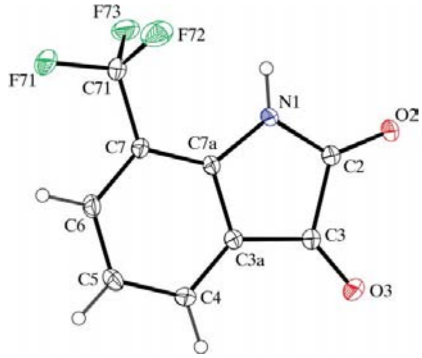


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

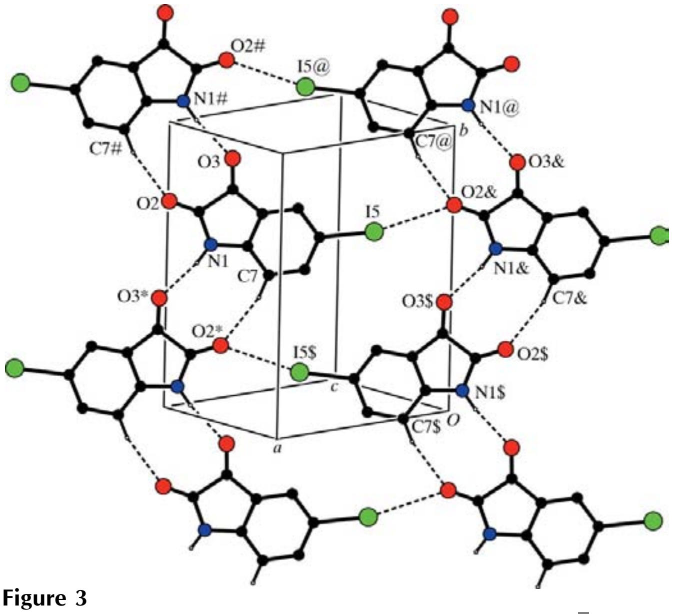


Figure 3
Part of the crystal structure of (I), showing the formation of a $(\bar{1}01)$ sheet built from alternating chains of $R_2^2(9)$ and $R_4^3(16)$ rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($), an ampersand (&) or an 'at' sign (@) are at the symmetry positions $(-x + 2, y - \frac{1}{2}, -z + \frac{3}{2})$, $(-x + 2, y + \frac{1}{2}, -z + \frac{3}{2})$, $(-x + 1, y - \frac{1}{2}, -z + \frac{1}{2})$, $(x - 1, y, z - 1)$ and $(-x + 1, y + \frac{1}{2}, -z + \frac{1}{2})$, respectively.

adjacent O atoms. This deduction was based on a survey of 1,2-diketone structures recorded in the CSD; the C(O)—C(O) distance was found to have a mean value of 1.542 (17) Å in *cis*-1,2-diketones but 1.476 (27) Å in *trans*-1,2-diketones. Similarly, long C—C bonds are typical of simple oxalate derivatives (Allen *et al.*, 1987).

In (I), the molecules are linked into chains of rings by a combination of N—H···O and C—H···O hydrogen bonds (Table 1), and these chains are linked into sheets by a short and almost linear iodo–carbonyl interaction. Atoms N1 and C7 in the molecule at (x, y, z) act as hydrogen-bond donors, respectively, to atoms O3 and O2 in the molecule at ($-x + 2$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$), so forming a $C(5)C(6)[R^2_2(9)]$ chain of rings (Bernstein *et al.*, 1995) running parallel to the [010] direction and generated by the 2_1 screw axis along (1, y, $\frac{3}{4}$) (Fig. 3). Atom I5 in the molecule at (x, y, z) makes a rather short contact with atom O2 in the molecule at ($x - 1$, y, $z - 1$) [I···O$^{\rm iv}$ = 3.226 (2) Å and C—I···O$^{\rm iv}$ = 167.2 (2)°; symmetry code: (iv) $x - 1$, y, $z - 1$], and this interaction links the [010] chains to form a ($\overline{1}01$) sheet of $R^2_2(9)$ and $R^3_4(16)$ (Bernstein *et al.*, 1995; Starbuck *et al.*, 1999) rings (Fig. 3).

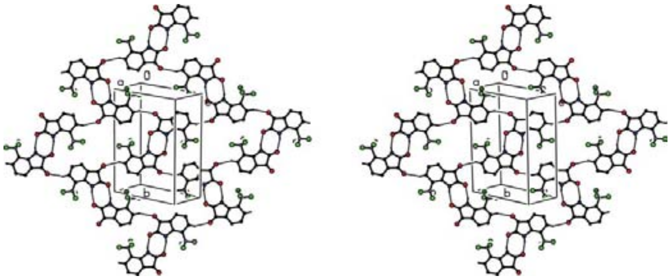


Figure 4
A stereoview of part of the crystal structure of (II), showing the formation of a (102) sheet built from alternating $R^2_2(8)$ and $R^6_6(34)$ rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

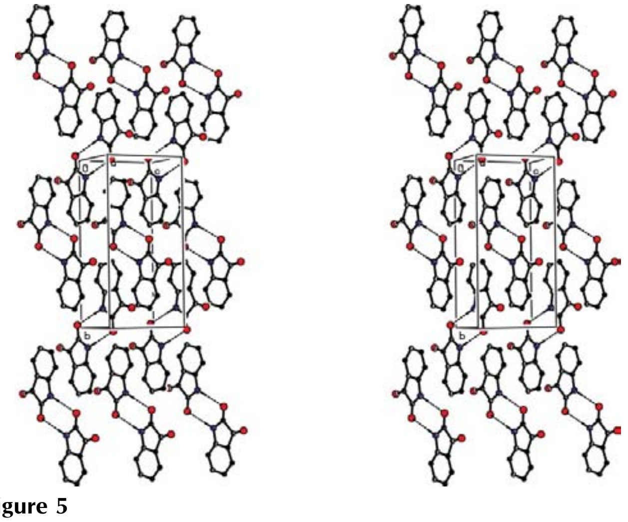


Figure 5
A stereoview of part of the crystal structure of (III), showing the formation of a (100) sheet of π-stacked $R^2_2(8)$ dimers. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. The original atomic coordinates (Palenik *et al.*, 1990) have been used.

The molecules of (II) are linked by paired N—H···O hydrogen bonds (Table 2) into centrosymmetric dimers, and these dimers are further linked by a single C—H···O hydrogen bond to form sheets. Amine atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O2 in the molecule at ($-x + 1$, $-y + 1$, $-z + 1$), so generating an $R^2_2(8)$ (Bernstein *et al.*, 1995) dimer centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (Fig. 4). In addition, atoms C6 in the molecules at (x, y, z) and ($-x + 1$, $-y + 1$, $-z + 1$) act as donors, respectively, to carbonyl atoms O3 in the molecules at ($x - 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$) and ($-x + 2$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$), which are components of the $R^2_2(8)$ dimers centred at ($-\frac{1}{2}$, 0, 1) and ($\frac{3}{2}$, 1, 0), respectively. In a similar way, atoms O3 in the molecules at (x, y, z) and ($-x + 1$, $-y + 1$, $-z + 1$) accept hydrogen bonds from atoms C6 in the molecules at ($x + 1$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$) and ($-x$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$), which are themselves components of the dimers centred at ($\frac{3}{2}$, 0, 0) and ($-\frac{1}{2}$, 1, 1), respectively. Propagation by the space group then generates a (102) sheet built from $R^2_2(8)$ and $R^6_6(34)$ rings, both centrosymmetric, alternating in a chess-board fashion (Fig. 4). However, there are no direction-specific interactions between adjacent sheets; in particular, C—H···π(arene) hydrogen bonds and aromatic π–π stacking interactions are both absent from the structure of (II).

It is of interest to compare the supramolecular aggregation in compounds (I) and (II) with that in (III); for this purpose we have used the atomic coordinates for ISATIN03 (Palenik *et al.*, 1990) retrieved from the CSD. The molecules are linked by paired N—H···O hydrogen bonds into centrosymmetric dimers, as first established by Goldschmidt & Llewellyn (1950). In addition, however, we find that these dimers are weakly linked into (100) sheets by a single aromatic π–π stacking interaction. The aryl rings of the molecules at (x, y, z) and (x, $-y + \frac{1}{2}$, $z \pm \frac{1}{2}$) are inclined to one another at only 0.7 (2)°; the separation of ring centroids is 3.857 (2) Å, with an interplanar spacing of *ca* 3.444 Å, corresponding to a ring offset of *ca* 1.736 Å. Propagation of this interaction links the hydrogen-bonded $R^2_2(8)$ dimers into a sheet (Fig. 5). If individual molecules are regarded as the nodes of the resulting net, this is of (6,3)-type, while if the dimers are regarded as the nodes then the net is of (4,4)-type (Batten & Robson, 1998).

Experimental

5-Iodoisatin was prepared by the reaction of aqueous $KICl_2$ with isatin (Garden *et al.*, 2001). 7-Trifluoromethylisatin was prepared following a modified Sandmeyer methodology (Garden *et al.*, 1997).

Compound (I)

Crystal data

$C_8H_4INO_2$
$M_r = 273.02$
Monoclinic, $P2_1/c$
$a = 9.3617$ (6) Å
$b = 11.0930$ (5) Å
$c = 7.6482$ (4) Å
$\beta = 101.146$ (2)°
$V = 779.28$ (7) Å^3

$Z = 4$
$D_x = 2.327$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 4.06$ mm^{-1}
$T = 120$ (2) K
Block, red
0.48 × 0.42 × 0.22 mm

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Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.142$, $T_{\max} = 0.408$
8625 measured reflections
1778 independent reflections
1623 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.031$
$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.051$
$S = 1.09$
1778 reflections
97 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 0.9452P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.74$ e Å^{-3}
$\Delta\rho_{\min} = -0.97$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O3$^{\text{i}}$	0.88	2.02	2.892 (3)	170
C7—H7$\cdots$O2$^{\text{i}}$	0.95	2.35	3.278 (3)	164

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

Compound (II)

Crystal data

$C_9H_4F_3NO_2$
$M_r = 215.13$
Monoclinic, $P2_1/c$
$a = 5.1704$ (2) Å
$b = 15.5609$ (11) Å
$c = 10.5780$ (7) Å
$\beta = 102.713$ (4)°
$V = 830.20$ (9) Å^3
$Z = 4$
$D_x = 1.721$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.17$ mm^{-1}
$T = 120$ (2) K
Plate, yellow
0.35 × 0.15 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.934$, $T_{\max} = 0.997$
9284 measured reflections
1893 independent reflections
1412 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.037$
$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.105$
$S = 1.04$
1893 reflections
137 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.3729P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O2$^{\text{ii}}$	0.88	2.06	2.913 (2)	164
C6—H6$\cdots$O3$^{\text{iii}}$	0.95	2.33	3.219 (2)	156

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

Table 3
Selected bond distances (Å) for compounds (I) and (II).

	(I)	(II)
N1—C2	1.356 (3)	1.360 (2)
C2—C3	1.565 (3)	1.562 (2)
C3—C3a	1.468 (3)	1.473 (2)
C3a—C7a	1.400 (3)	1.402 (2)
C7a—N1	1.405 (3)	1.408 (2)
C2—O2	1.210 (3)	1.219 (2)
C3—O3	1.208 (4)	1.205 (2)
C5—I5	2.101 (2)	
C7—C71		1.496 (2)

For each of (I) and (II), the space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C—H and N—H = 0.95 and 0.88 Å, respectively, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$

For both compounds, data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3019). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Garden, S. J., Torres, J. C., de Souza Melo, S. C., Lima, A. S., Pinto, A. C. & Lima, E. L. S. (2001). *Tetrahedron Lett.* **42**, 2089–2092.
Garden, S. J., Torres, J. C., Ferreira, A. A., Silva, R. B. & Pinto, A. C. (1997). *Tetrahedron Lett.* **38**, 1501–1504.
Goldschmidt, G. H. & Llewellyn, F. J. (1950). *Acta Cryst.* **3**, 294–299.
Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Palenik, G. J., Koziol, A. E., Katritzky, A. R. & Fan, W.-Q. (1990). *Chem. Commun.* pp. 715–716.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Silva, J. F. M. da, Garden, S. J. & Pinto, A. C. (2001). *J. Braz. Chem. Soc.* **12**, 273–286.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Starbuck, J., Norman, N. C. & Orpen, A. G. (1999). *New J. Chem.* **23**, 969–972.

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