3,3-Difluoro-5-nitro-1*H*-indol-2(3*H*)-one: sheets of $R_2^2(8)$ and $R_4^6(34)$ rings built from three-centre N—H⋯(O)$_2$ hydrogen bonds

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The title compound, C$_8$H$_4$F$_2$N$_2$O$_3$, crystallizes with $Z' = 2$ in the space group $P2_1/c$. The molecules are linked into sheets of $R_2^2(8)$ and $R_4^6(34)$ rings by two independent asymmetric three-centre N—H⋯(O)$_2$ hydrogen bonds [H⋯O = 2.15/2.57 Å in one system and 2.23/2.46 Å in the other; N⋯O = 2.8959 (17)/3.2972 (16) and 2.9561 (16)/3.1774 (15) Å; N—H⋯O = 142/140 and 140/139°; O⋯H⋯O = 77 and 79°].

Comment

Indoline-2,3-diones (isatins) are very versatile synthetic substrates, useful both in the synthesis of heterocyclic compounds and as raw materials for drugs (da Silva *et al.*, 2001). 3,3-Difluorooxindolones, prepared from indoline-2,3-diones by reaction with (diethylamino)sulfur trifluoride (Torres *et al.*, 1999), have been shown to be particularly valuable precursors of pharmaceutically active materials (Boechat & Pinto, 2000). We report here the molecular and supramolecular structure of the title compound, (I), a typical simply substituted 3,3-difluorooxindolone.

(I)
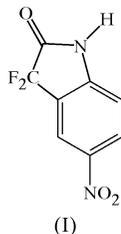
Compound (I) (Fig. 1) crystallizes in space group $P2_1/c$ with $Z' = 2$. The bond distances and angles within the two independent molecules are very similar (Table 1), but there are a number of unusual values consistently observed for the two

molecules. The distances Cn2—Cn3 (n = 1 or 2) are long for their type, where the mean value (Allen *et al.*, 1987) is 1.511 Å and the upper-quartile value 1.521 Å. In addition, there are indications of weak bond fixation within the aryl rings. Likewise, the interbond angles at both Cn2 and Cn3 show some unexpected values. In particular, the opposed pair of angles Fn31—Cn3—Fn32 and Cn2—Cn3—Cn3A (n = 1 or 2) are all significantly less than the idealized tetrahedral values; normally, the distortions in opposed pairs of angles are such that one angle is significantly larger and one is significantly smaller than the idealized value. While the bicyclic skeletons are essentially planar, the nitro groups are both twisted away from these planes. The nitro groups containing atoms N15 and N25 make dihedral angles with the adjacent rings of 13.2 (2) and 15.6 (2)°, respectively. The sense of these rotations, as shown by the key torsion angles (Table 1), indicates approximate twofold rotational symmetry for the selected asymmetric unit.

The two independent molecules of (I) are linked by paired N—H⋯O hydrogen bonds with carbonyl acceptors (Table 2), the dimensions of which differ sufficiently to preclude the possibility of any additional symmetry. These two interactions are each, in fact, one component of a planar but asymmetric three-centre N—H⋯(O)$_2$ system, in each of which the second
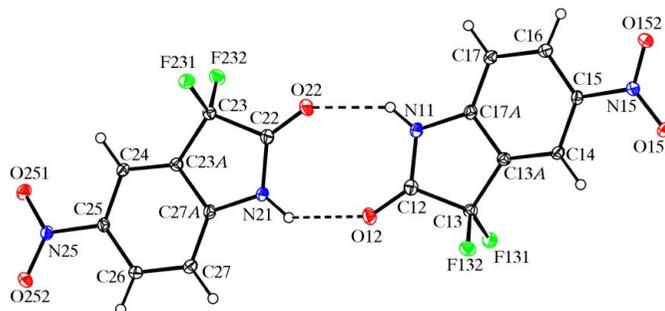
Figure 1
The two independent molecules in compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
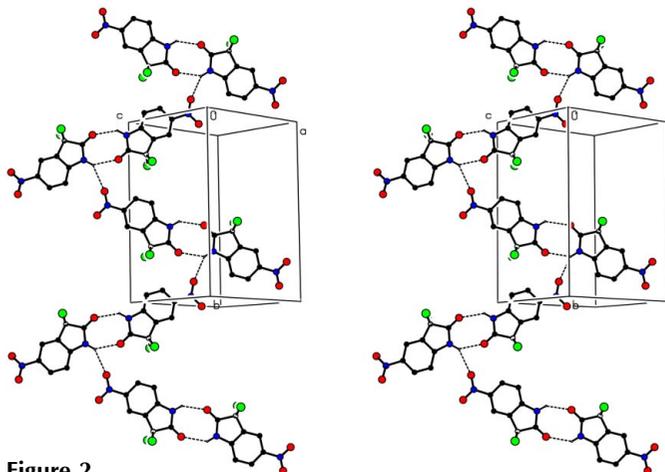
Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a chain of rings along ($\frac{1}{2}$, y, $\frac{1}{4}$). For the sake of clarity, H atoms bonded to C atoms have been omitted.

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acceptor is a nitro O atom, and these longer, and weaker, components link the bimolecular aggregates (Fig. 1) into continuous sheets.

Atom N11 in the type 1 molecule ($n = 1$) at (x, y, z) acts as hydrogen-bond donor to nitro atom O252 in the type 2 molecule ($n = 2$) at ($1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$), so forming a $C_1^2(9)[R_2^2(8)]$ chain of rings (Bernstein *et al.*, 1995) running parallel to the [010] direction and generated by the 2_1 screw axis along ($\frac{1}{2}$, y, $\frac{1}{4}$) (Fig. 2). Similarly, atom N21 at (x, y, z) acts as hydrogen-bond donor to O152 at ($-x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$), so producing a second $C_1^2(9)[R_2^2(8)]$ chain of rings, this time along (0, y, $\frac{3}{4}$) (Fig. 3). The combination of these two chain motifs generates a (101) sheet containing $R_2^2(8)$ and $R_4^6(34)$ rings (Fig. 4), in which each bimolecular aggregate is linked to four others. Hence, if these aggregates are regarded as the nodes of the resulting net, this is of the (4,4)-type (Batten & Robson, 1998). Two (101) sheets, related to one another by inversion, pass through each unit cell.

There are neither C—H···π(arene) hydrogen bonds nor aromatic π–π stacking interactions between the components of adjacent sheets. The only significant C—H···O hydrogen bonds (Table 2) all lie within a single (101) sheet. There are some short F···N contacts involving nitro N atoms between molecules in adjacent sheets, namely C15—N15···F232^i, with N15···F232^i = 2.915 (2) Å and C15—N15···F232^i = 109.6 (2)° [symmetry code: (i) $-x$, $1 - y$, $1 - z$], and C25—H25···F232^{ii}, with N25···F231^{ii} = 2.947 (2) Å and C25—N25···F231^{ii} = 91.2 (2)° [symmetry code: (ii) x, $\frac{3}{2} - y$, $z - \frac{1}{2}$], but the status of such dipolar contacts, in terms of their possible structural significance, has not yet been established.

Experimental

The title compound was obtained according to the procedure published by Torres *et al.* (1999) [m.p. 459–460 K; literature m.p. 461–462 K (Torres *et al.*, 1999)]. Crystals of (I) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in acetonitrile.

Crystal data

$C_8H_4F_2N_2O_3$	$D_x = 1.797$ Mg m^{-3}
$M_r = 214.13$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3611
$a = 11.0529$ (4) Å	reflections
$b = 15.4381$ (6) Å	$\theta = 3.1$–27.5°
$c = 9.2768$ (4) Å	$\mu = 0.17$ mm^{-1}
$\beta = 90.951$ (2)°	$T = 120$ (2) K
$V = 1582.74$ (11) Å^3	Block, yellow
$Z = 8$	$0.04 \times 0.04 \times 0.03$ mm

Data collection

Bruker-Nonius KappaCCD diffractometer	3611 independent reflections
	2980 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.033$
Absorption correction: multi-scan, (*SADABS*; Sheldrick, 2003)	$\theta_{max} = 27.5°$
	$h = -11 \rightarrow 14$
$T_{min} = 0.980$, $T_{max} = 0.995$	$k = -19 \rightarrow 20$
18 600 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$+ 0.7598P]$
$wR(F^2) = 0.090$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
3611 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
271 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
H-atom parameters constrained	

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a chain of rings along (0, y, $\frac{3}{4}$). For the sake of clarity, H atoms bonded to C atoms have been omitted.
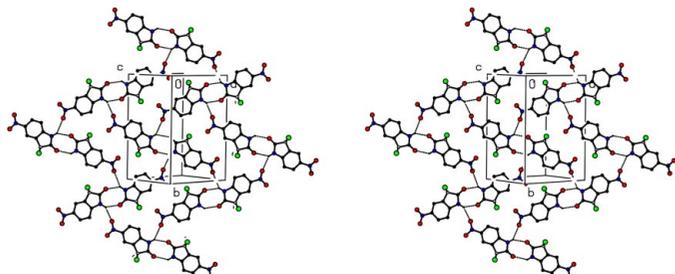
Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a (101) sheet of $R_2^2(8)$ and $R_4^6(34)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Table 1
Selected geometric parameters (Å, °).

N11—C12	1.3668 (19)	N21—C22	1.3602 (18)
C12—C13	1.5576 (19)	C22—C23	1.5562 (19)
C13—C13A	1.4886 (19)	C23—C23A	1.4863 (19)
C13A—C14	1.3744 (19)	C23A—C24	1.3761 (19)
C14—C15	1.3907 (19)	C24—C25	1.3925 (19)
C15—C16	1.3868 (19)	C25—C26	1.3899 (19)
C16—C17	1.3980 (19)	C26—C27	1.3963 (19)
C17—C17A	1.387 (2)	C27—C27A	1.388 (2)
C17A—N11	1.4064 (17)	C27A—N21	1.4109 (17)
C13A—C17A	1.4031 (19)	C23A—C27A	1.3999 (19)
C12—O12	1.2070 (17)	C22—O22	1.2085 (18)
C13—F131	1.3728 (16)	C23—F231	1.3641 (16)
C13—F132	1.3534 (16)	C23—F232	1.3620 (16)
C15—N15	1.4644 (17)	C25—N25	1.4662 (17)
N15—O151	1.2294 (15)	N25—O251	1.2327 (15)
N15—O152	1.2361 (15)	N25—O252	1.2301 (15)
N11—C12—C13	106.05 (11)	N21—C22—C23	106.46 (11)
N11—C12—O12	129.45 (13)	N21—C22—O22	129.78 (13)
O12—C12—C13	124.51 (13)	O22—C22—C23	123.75 (13)
F131—C13—F132	105.94 (11)	F231—C23—F232	106.00 (11)
C12—C13—C13A	103.80 (11)	C22—C23—C23A	103.84 (11)
C14—C15—N15—O151	13.26 (19)	C24—C25—N25—O251	15.37 (18)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N11—H11···O22	0.88	2.15	2.8959 (17)	142
N11—H11···O252[i]	0.88	2.57	3.2972 (16)	140
N21—H21···O12	0.88	2.23	2.9561 (16)	140
N21—H21···O152[ii]	0.88	2.46	3.1774 (15)	139
C14—H14···O251[iii]	0.95	2.52	3.3102 (18)	140
C17—H17···O252[i]	0.95	2.59	3.3708 (18)	140
C24—H24···O151[iv]	0.95	2.46	3.2766 (18)	144

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

The space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 Å and N—H distances of 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

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 *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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