

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 $\text{N—H}\cdots(\text{O})_2$ hydrogen bonds

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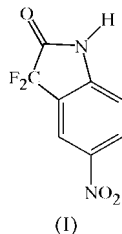
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The title compound, $\text{C}_8\text{H}_4\text{F}_2\text{N}_2\text{O}_3$, crystallizes with $Z' = 2$ in the space group $P2_1/c$. The molecules are linked into sheets of $R_2^2(8)$ and $R_4^6(34)$ rings by two independent asymmetric three-centre $\text{N—H}\cdots(\text{O})_2$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



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 $\text{Cn}2\text{—Cn}3$ ($n = 1$ or 2) are long for their type, where the mean value (Allen *et al.*, 1987) is 1.511 \AA and the upper-quartile value 1.521 \AA . In addition, there are indications of weak bond fixation within the aryl rings. Likewise, the interbond angles at both $\text{Cn}2$ and $\text{Cn}3$ show some unexpected values. In particular, the opposed pair of angles $\text{Fn}31\text{—Cn}3\text{—Fn}32$ and $\text{Cn}2\text{—Cn}3\text{—Cn}3A$ ($n = 1$ 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 $\text{N}15$ and $\text{N}25$ make dihedral angles with the adjacent rings of $13.2(2)$ and $15.6(2)^\circ$, 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 $\text{N—H}\cdots\text{O}$ 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 $\text{N—H}\cdots(\text{O})_2$ system, in each of which the second

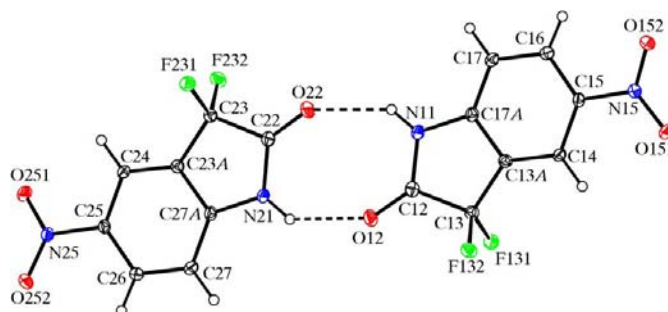


Figure 1

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.

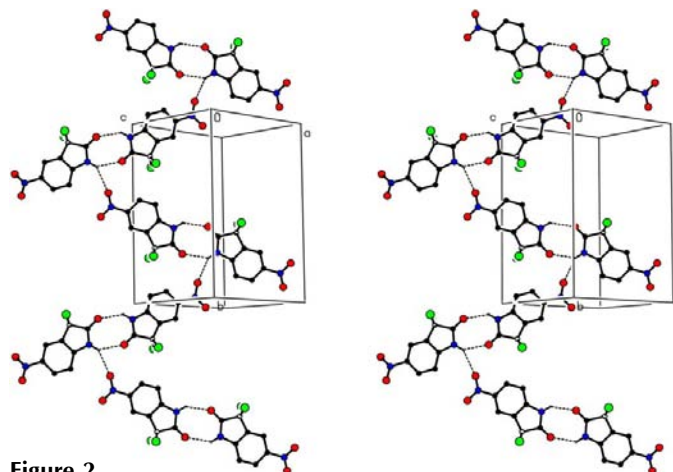


Figure 2

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.

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 $C_2^7(9)[R_2^2(8)]$ 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 $C_2^7(9)[R_2^2(8)]$ 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...F232ⁱ, with

N15...F232ⁱ = 2.915 (2) Å and C15—N15...F232ⁱ = 109.6 (2)° [symmetry code: (i) $-x, 1 - y, 1 - z$], and C25—H25...F232ⁱⁱ, with N25...F231ⁱⁱ = 2.947 (2) Å and C25—N25...F231ⁱⁱ = 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

C₈H₄F₂N₂O₃
M_r = 214.13
 Monoclinic, $P2_1/c$
a = 11.0529 (4) Å
b = 15.4381 (6) Å
c = 9.2768 (4) Å
 β = 90.951 (2)°
V = 1582.74 (11) Å³
Z = 8

D_x = 1.797 Mg m⁻³
 Mo K α radiation
 Cell parameters from 3611 reflections
 θ = 3.1–27.5°
 μ = 0.17 mm⁻¹
T = 120 (2) K
 Block, yellow
 0.04 × 0.04 × 0.03 mm

Data collection

Bruker-Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan, (SADABS; Sheldrick, 2003)
T_{min} = 0.980, *T_{max}* = 0.995
 18 600 measured reflections

3611 independent reflections
 2980 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
 θ_{max} = 27.5°
h = -11 → 14
k = -19 → 20
l = -12 → 12

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.090$
S = 1.04
 3611 reflections
 271 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.7598P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.24 \text{ e \AA}^{-3}$

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 (18) |
| 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) |

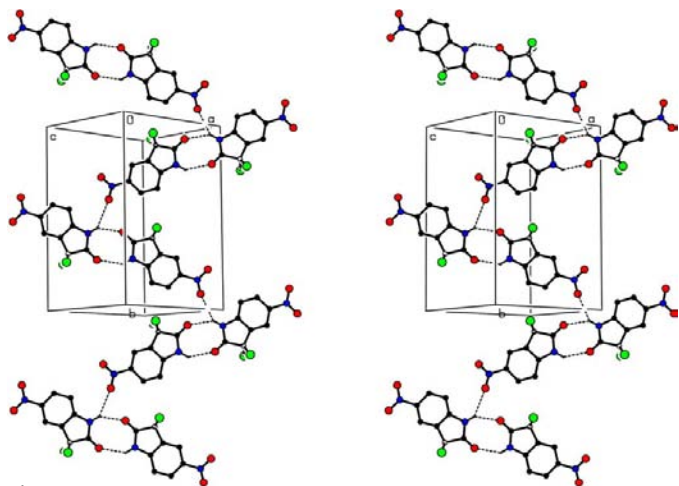


Figure 3

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.

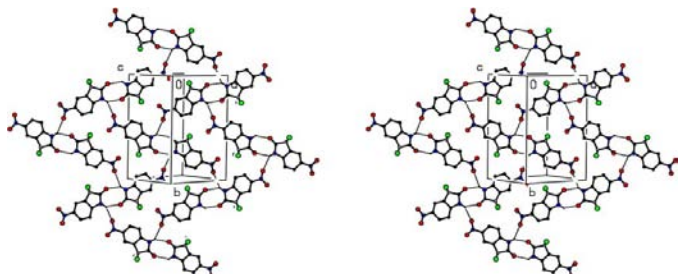


Figure 4

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 2
Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

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 *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: SK1799). Services for accessing these data are described at the back of the journal.

References

- 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.
- Boechat, N. & Pinto, A. C. (2000). US Patent No. 6 034 266.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- 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.
- 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**, 273–324.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Torres, J. C., Garden, S. J., Pinto, A. C., da Silva, F. S. Q. & Boechat, N. (1999). *Tetrahedron*, **55**, 1881–1892.