5-Iodobenzofurazan 1-oxide: poly-morphs, pseudosymmetry and disorder

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5-Iodobenzofurazan 1-oxide (systematic name: 5-iodobenzo-1,2,5-oxadiazole 1-oxide), $C_6H_3IN_2O_2$, occurs in two polymorphic forms, both monoclinic in $P2_1/c$ with $Z' = 2$. The intermolecular interactions in the two polymorphs are quite different. In polymorph (I), there are strong intermolecular $I \cdots O$ interactions, with $I \cdots O$ distances of 3.114 (8) and 3.045 (8) Å. In polymorph (II), there are strong intermolecular $I \cdots N$ interactions, with $I \cdots N$ distances of 3.163 (4) and 3.175 (5) Å. In (I), there is about 15% disorder in one molecule and about 5% in the other. In both polymorphs, there are pseudosymmetric relationships between the crystallographically independent molecules.

Comment

The structure of 5-iodobenzofurazan 1-oxide was originally determined at room temperature (Gehrz & Britton, 1972). Diffractometer data were used, but no measurable data were found above $\theta = 18°$ (Mo $K\alpha$ radiation). The limited number of intensity measurements, combined with the dominance of the I atoms, led to large errors in the light-atom parameters. This structure, polymorph (I), has been redetermined to improve the accuracy. In the course of the redetermination a second polymorph, (II), was discovered, the structure of which is also reported.

(I)
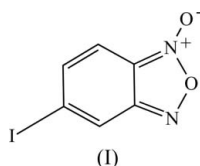
Both molecules in polymorph (I) are disordered (Fig. 1), but there is no disorder in polymorph (II) (Fig. 2). All of the bond distances and angles are normal.

Molecules of (I) form chains parallel to [010] held together by intermolecular $I \cdots O$ interactions (Fig. 3). Each chain involves one or other of the two independent molecules. The geometric data for these interactions are given in Table 1. The
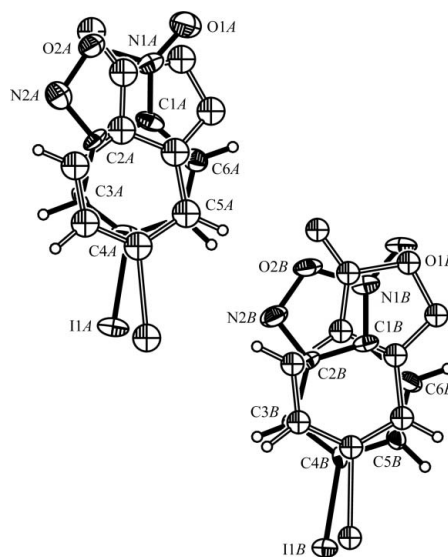
Figure 1
A view of polymorph (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The minor components of the disorder are shown with open bonds.

chains grow together in irregular sheets parallel to the $(10\bar{1})$ plane, with molecule A tilted by 11.2 (1)° and molecule B tilted by 10.8 (1)° with respect to the sheet; the molecules are 2.5 (1)° away from being parallel to one another. There are $H \cdots O$ interactions between adjacent chains. The geometric data for the H-atom interactions are given in Table 2; only contacts with distances less than the sum of the van der Waals radii (Bondi, 1964; Rowland & Taylor, 1996) are included. See Desiraju & Steiner (1999) for a discussion of C—H$\cdots X$ hydrogen bonds. The sheets stack so that columns occur parallel to the [001] direction, with each molecule A in contact
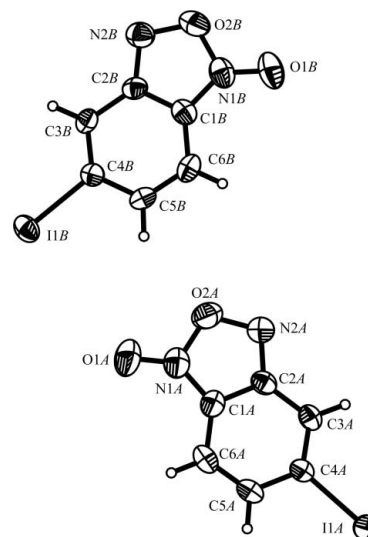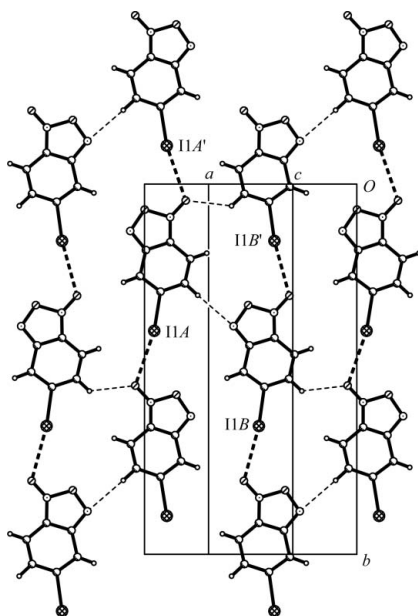
Figure 2
A view of polymorph (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
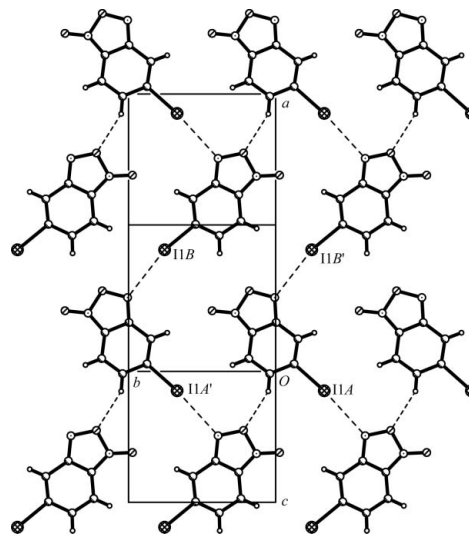
Figure 3
The packing of polymorph (I), showing one layer viewed normal to the (10$\bar{1}$) plane. Molecules in each vertical column are crystallographically equivalent. I···O and H···X contacts are shown as dashed lines. Atom I1A′ is related to atom I1A by the symmetry code $(2 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ and atom I1B′ is related to atom I1B by the symmetry code $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$.

Figure 4
The packing of polymorph (II), showing one layer viewed normal to the (001) plane. Molecules in each horizontal row are crystallographically equivalent. I···N and H···O contacts are shown as dashed lines. Atom I1A′ is related to atom I1A by the symmetry code $(x, 1 + y, z)$ and atom I1B′ is related to atom I1B by the symmetry code $(x, -1 + y, z)$.

with two other A molecules and each B molecule with two other B molecules. The A molecules are tilted by 16.3 (1)° and the B molecules by 16.9 (1)° with respect to the direction of the stacks. The perpendicular distances between molecules alternate between 3.59 (3) and 3.62 (3) Å in both stacks.

In the preceding discussion of the packing, only the major components of the disorder were considered. The disorder appears to arise from both kinds of chains shifting half a unit-cell length in the b direction. This seems a reasonable model, although all that can be said from the X-ray data is that there is disorder in the individual molecules.

Molecules of (II) form zigzag chains parallel to [100] (Fig. 4), held together by intermolecular I···N interactions. Each chain involves, alternately, the two kinds of independent molecules. The geometric data for these interactions are given in Table 1. The chains grow together in irregular sheets parallel to the (001) plane, with molecule A tilted by 18.6 (1)° and molecule B tilted by 19.3 (1)° with respect to the sheet; the two molecules are 27.7 (1)° away from being parallel to each other. There are H···O interactions between adjacent chains (Table 2). The sheets stack so that columns occur parallel to the [101] direction, with each molecule A in contact with one A molecule and one B molecule, and *vice versa*. The A molecules are tilted by 22.0 (1)° and the B molecules by 20.5 (1)° with respect to the direction of the stack. The perpendicular distances between molecules are: A···A = 3.736 (7) Å, A···B = 3.53 (3) Å and B···B = 3.770 (6) Å.

There are no I···I contacts in either structure shorter than 4.4 Å. The expected van der Waals distance (Bondi, 1964; Rowland & Taylor, 1996) is 3.96 Å.

The pseudosymmetry in (I) can be seen in Fig. 3. Molecule A is converted to molecule B by a pseudo-translation (all non-H atoms weighted equally)

$$x_B = -0.489\,(3) + x_A,$$
$$y_B = 0.258\,(1) + y_A,$$
$$z_B = -0.490\,(12) + z_A.$$

It can be converted to the other three molecules in Wyckoff position e of molecule B by a pseudo-center

$$x_B = 1.489\,(3) - x_A,$$
$$y_B = 0.742\,(1) - y_A,$$
$$z_B = 1.490\,(12) - z_A,$$

a pseudo-twofold screw axis

$$x_B = 1.489\,(3) - x_A,$$
$$y_B = 0.758\,(1) + y_A,$$
$$z_B = 0.990\,(12) - z_A$$

and a pseudo-a-glide

$$x_B = -0.489\,(3) + x_A,$$
$$y_B = 0.242\,(1) - y_A,$$
$$z_B = 0.010\,(12) + z_A.$$

Similar relationships hold for the other molecules in the Wyckoff position e of molecule A. As a measure of the precision of the pseudosymmetry, if molecules A and B are matched as well as possible using OFIT in *SHELXTL* (Sheldrick, 2008), the r.m.s. deviation between the atoms is 0.028 Å. If the translation above is used, the r.m.s. deviation is 0.079 Å, and if an idealized translation of $-a/2$, $b/4$, $-c/2$ is used, the r.m.s. deviation is 0.218 Å.

The pseudosymmetry in (II) can be seen in Fig. 4. Molecule A is converted to molecule B by a pseudo-a-glide

$$x_B = 0.506\,(4) + x_A,$$
$$y_B = 0.411\,(10) - y_A,$$
$$z_B = 0.015\,(7) + z_A.$$

It can be converted to the other three molecules in the Wyckoff position e of molecule B by a pseudo-center

$$x_B = 0.494\,(4) - x_A,$$
$$y_B = 0.911\,(10) - y_A,$$
$$z_B = 0.485\,(7) - z_A,$$

a pseudo-translation

$$x_B = 0.506\,(4) + x_A,$$
$$y_B = 0.089\,(10) + y_A,$$
$$z_B = 0.515\,(7) + z_A$$

and a pseudo-twofold axis

$$x_B = 0.494\,(4) - x_A,$$
$$y_B = 0.589\,(10) + y_A,$$
$$z_B = 0.985\,(7) - z_A.$$

Similar relationships hold for the other molecules in the Wyckoff position e of molecule A. Again, as a measure of the precision of the pseudosymmetry, if molecules A and B are matched as well as possible using OFIT in *SHELXTL*, the r.m.s. deviation between the atoms is 0.008 Å; if the translation above is used, the r.m.s. deviation is 0.123 Å. In this case, there is no idealized translation; although the a and c translations can both be idealized as $\frac{1}{2}$, the translation in y is not close to any rational fraction.

Polymorph (II) is isomorphous with the low-temperature form of 5-bromobenzofurazan 1-oxide (Pink & Britton, 2002). The pseudosymmetry relationships above are virtually identical to those for the bromo analog, except that the translation in y of 0.089 (10) in the iodo compound is 0.114 (7) in the bromo compound, marginally different.

Although both polymorphs have the same four supersymmetry relationships, namely translation, inversion, screw and glide, there are significant differences between the two. In (I), the two types of molecules in a layer are related alternately by a pseudo-translation and a pseudo-screw. In (II), the two types of molecules are all related by a pseudo-glide. Supersymmetry has been discussed extensively by Zorky and co-workers (see Zorky, 1996, and references therein).

Experimental

A sample of 4-iodo-2-nitroaniline, (1), from the chemical collection of W. E. Noland, was converted to 4-iodo-2-nitrophenyl azide, (2), according to the method of Deorha *et al.* (1962). Compound (2) was then converted to the title compound, (3). Compound (1) (2.00 g, 7.57 mmol) [m.p. 396.6 K, *cf.* 396.2 (Deorha *et al.*, 1962; Brenans, 1914a,b), 395–396 (Garden *et al.*, 2002), 395.2 (Bradfield *et al.*, 1928; Michael & Norton, 1878) and 394.6–395.2 K (Kavalek *et al.*, 1967,

1969)] was dissolved in boiling glacial acetic acid (50 ml) and then cooled to 298 K. A solution of $NaNO_2$ (0.575 g, 8.33 mmol) in concentrated H_2SO_4 (20 ml) was stirred into the acetic acid solution and the mixture was poured over crushed ice (150 g). An aqueous solution of NaN_3 (0.227 M) was added slowly until the evolution of N_2 ceased, giving a light-yellow precipitate, which was crystallized from ^{i}PrOH–H_2O (~1:1 v/v) giving (2) as light-yellow needles (2.10 g, 7.24 mmol, 96%) [m.p. 345.5 K, *cf.* 345.2 (Deorha *et al.*, 1962)]. Compound (2) (1.00 g, 3.45 mmol) was dissolved in toluene (50 ml) and the solution was refluxed until the evolution of N_2 ceased. The solvent was removed in a rotating evaporator, leaving (3) as a light-yellow precipitate (0.90 g, 3.4 mmol, 100%). Crystallization from ^{i}PrOH–H_2O (~1:1 v/v) gave light-yellow needles (0.85 g, 3.2 mmol, 94%). IR (KBr, cm^{-1}): 3089, 1604, 1517, 1466, 1267, 1194, 1123, 1018, 785, 613, 574, 545; ^{1}H NMR (acetone-d_6): δ 8.20 (*bs*, 7H), 765 (*bs*, 6H), 7.45 (*bs*, 4H). Recrystallization from benzene gave polymorph (I), previously obtained by sublimation (Gehrz & Britton, 1972). Recrystallization from acetone, chloroform, carbon tetrachloride or ^{i}PrOH–H_2O (~1:1 v/v) gave polymorph (II). Polymorph (I) melts at 348.5–348.8 K, while polymorph (II) turns opaque at 346.8 K and melts at 348.5 K; presumably, the opacity at 346.8 K indicates the transition from (II) to (I).

Polymorph (I)

Crystal data

$C_6H_3IN_2O_2$	$V = 1495.1\,(7)$ Å^3
$M_r = 262.00$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.344\,(3)$ Å	$\mu = 4.23$ mm^{-1}
$b = 19.804\,(6)$ Å	$T = 174\,(2)$ K
$c = 7.489\,(2)$ Å	$0.35 \times 0.08 \times 0.04$ mm
$\beta = 102.950\,(10)°$	

Data collection

Siemens SMART 1K CCD area-detector diffractometer	15378 measured reflections
	2929 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)	2078 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.071$
$T_{min} = 0.68$, $T_{max} = 0.84$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	58 restraints
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 0.99$	$\Delta\rho_{max} = 0.77$ e Å^{-3}
2929 reflections	$\Delta\rho_{min} = -0.80$ e Å^{-3}
270 parameters	

Table 1
Geometry of the $C-I\cdots X-Y$ contacts (Å, °).

The $I\cdots X$ distances should be compared with the van der Waals distances (Bondi, 1964; Rowland & Taylor, 1996) of $I\cdots O = 3.50$ Å and $I\cdots N = 3.53$ Å.

I	$X-Y$	$C-I\cdots X$	$I\cdots X$	$I\cdots X-Y$
Polymorph (I)				
I1A	O1A—N1A^i	169.5 (5)	3.114 (8)	116.9 (5)
I1B	O1B—N1B^{ii}	172.3 (5)	3.045 (8)	121.5 (5)
Polymorph (II)				
I1A	N2B—O2B^{iii}	174.0 (2)	3.163 (5)	119.2 (2)
I1B	N2A—O2A^{iv}	167.1 (2)	3.175 (5)	110.8 (2)

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

organic compounds

Table 2
Geometry of the the C—H···X—Y contacts (Å, °).

All C—H distances are 0.95 Å.

H	X—Y	C—H···X	H···X	H···X—Y	C···X
Polymorph (I)					
H5A	N2B—C2B	160	2.59	161	3.503 (10)
H5B	O1A—N1A^i	126	2.55	122	3.201 (10)
Polymorph(II)					
H5A	O2B—N1B^{ii}	138	2.52	110	3.282 (5)
H6A†	O1B—N1B^i	132	2.55	135	3.261 (5)

† This contact is between layers and is not shown in Fig. 4. Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-1+x, y, z$.

Polymorph (II)

Crystal data

$C_6H_3IN_2O_2$
$M_r = 262.00$
Monoclinic, $P2_1/c$
$a = 14.392 (4)$ Å
$b = 7.640 (2)$ Å
$c = 15.284 (4)$ Å
$\beta = 116.390 (10)°$

$V = 1505.4 (7)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 4.20$ mm^{-1}
$T = 174 (2)$ K
$0.50 \times 0.10 \times 0.05$ mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{min} = 0.63$, $T_{max} = 0.81$

17038 measured reflections
3437 independent reflections
2916 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.065$
$S = 1.09$
3437 reflections

200 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.29$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

The first crystal of polymorph (I), after refinement as an ordered structure, showed peaks in the final difference map of 10 and 5 e Å^{-3} near the I atom. To make sure this was real, a second data set was collected, with the same results. At this point, the two large peaks were considered as a disordered I atom. The ordered structure had $R = 0.095$ and $wR_2 = 0.169$. Considering only the I atom to be disordered reduced R to 0.052 and wR_2 to 0.093. After consideration of various models, the arrangement shown in Fig. 1 seemed most reasonable, and refinement with the geometry in the minor components

constrained to be the same as in the major components, with identical isotropic displacement parameters for the atoms of the minor components, led to $R = 0.049$ and $wR_2 = 0.087$. Occupancies for the major components were 0.849 (3) for molecule *A* and 0.944 (4) for molecule *B*. Similar refinement of the first data set led to corresponding occupancies of 0.829 (3) and 0.920 (4). A reasonable model for the disorder would be one in which entire chains of molecules (Fig. 3) are shifted one molecule along in the chain direction, although this cannot be determined from the diffraction data. The minor components of the disorder have been ignored in the discussion of the packing. H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

For both polymorphs, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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