Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Conformational dimorphism of the spiropyran 1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline]-6-carbaldehyde

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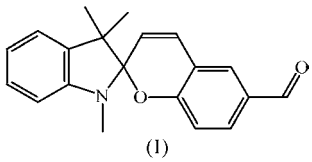
Received 13 May 2008
Accepted 29 May 2008
Online 14 June 2008

The title compound, $C_{20}H_{19}NO_2$, crystallizes from an acetone–heptane solution as two dimorphs in the space groups *C*2/*c* and *Cc*. Each dimorph has two molecules in the asymmetric unit. The four molecules adopt slightly different conformations expressed by the degree of bending around a vector connecting the O and C atoms attached to the bridgehead C atom of the pyran ring. Due to the fact that all four molecules are chemically identical, the difference in bending is attributed to packing forces. This is evident from the close contacts of neighbouring molecules perpendicular to the plane of the benzopyran moiety observed in the *Cc* structure and not in the *C*2/*c* structure. These observations provide a unique example that shows how packing forces can affect the conformation of a specific molecule.

Comment

The design and synthesis of spiropyran derivatives are of great interest in photochemistry (Iyengar & Biewer, 2002; Godzi *et al.*, 2001). For example, we have been interested in testing the photochemical behaviour of a single crystal composed of spiropyran as a guest molecule in inclusion compounds with light-stable host molecules. In the course of our studies, we found that the title compound, (I), crystallizes in two forms corresponding to different molecular conformations and crystal structures. Hence, they may be called conformational polymorphs, a subset of polymorphism in which molecules are folded into different three-dimensional conformations, which can then be packed into alternative crystal structures (Bernstein & Hagler, 1978).



(I)

Compound (I) crystallizes as colourless transparent plates in monoclinic space group *C*2/*c*, with two molecules, *A* and *B*, in the asymmetric unit (Fig. 1), and also as colourless transparent prisms in monoclinic space group *Cc*, with two molecules, *A* and *B*, in the asymmetric unit (Fig. 2). According to

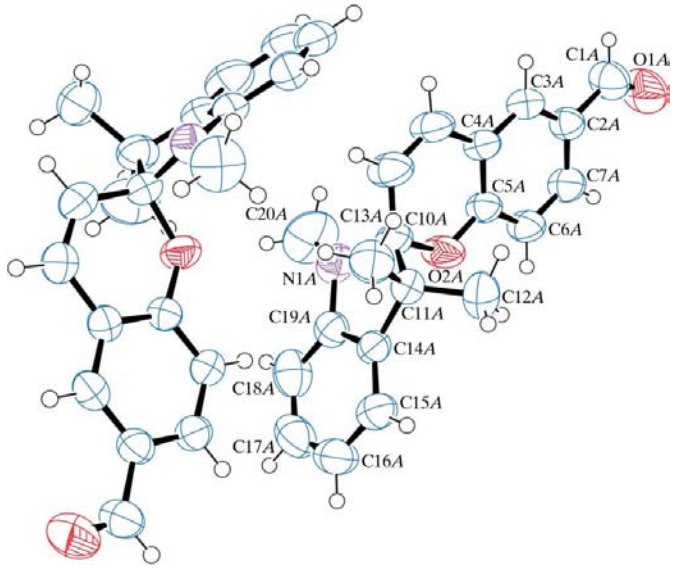


Figure 1
The two independent molecules of (I) in the *C*2/*c* dimorph; only the atoms of molecule *A* are labelled. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

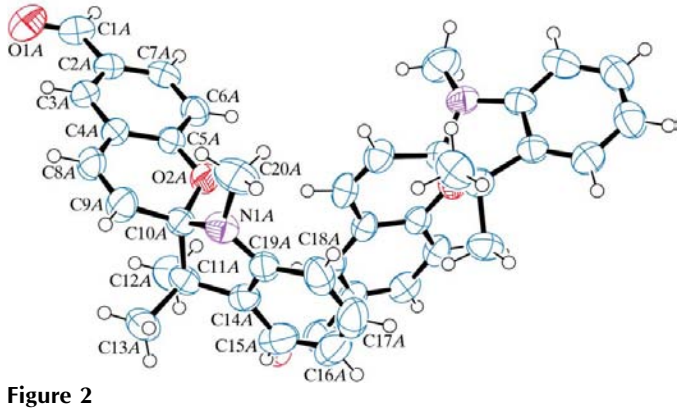


Figure 2
The two independent molecules of (I) in the *Cc* dimorph; only the atoms of molecule *A* are labelled. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

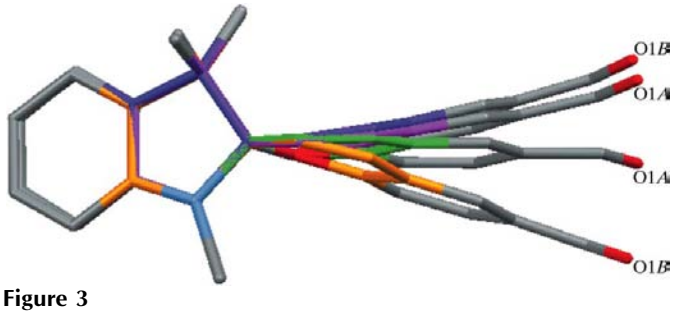


Figure 3
Overlap of the two dimorphs. The two upper aldehyde groups belong to the dimorph in *Cc* and the two lower groups to that in *C*2/*c*.

  doi: 10.1107/S0108270108016430

the density rule, the more tightly packed crystal with the higher density is the more stable (Kitaigorodsky, 1973; Burger & Ramberger, 1979). The density of the spiropyran in the *Cc* form (1.243 Mg m^{-3}) is slightly greater than that in the *C*2/*c* form (1.228 Mg m^{-3}), indicating that it is probably more stable in the acentric space group. However, no experimental effort has been devoted to confirming this assumption.

The four molecules adopt significantly different conformations, expressed by the bending of the benzopyran part of the molecule; Fig. 3 shows the overlap of the four molecules of spiropyran in the two space groups. The molecules were positioned in the overlap diagram in such a way that their indoline parts including tetrahedral C*sp*^{3} atoms overlap completely, but the bending of the pyran ring with the alde-

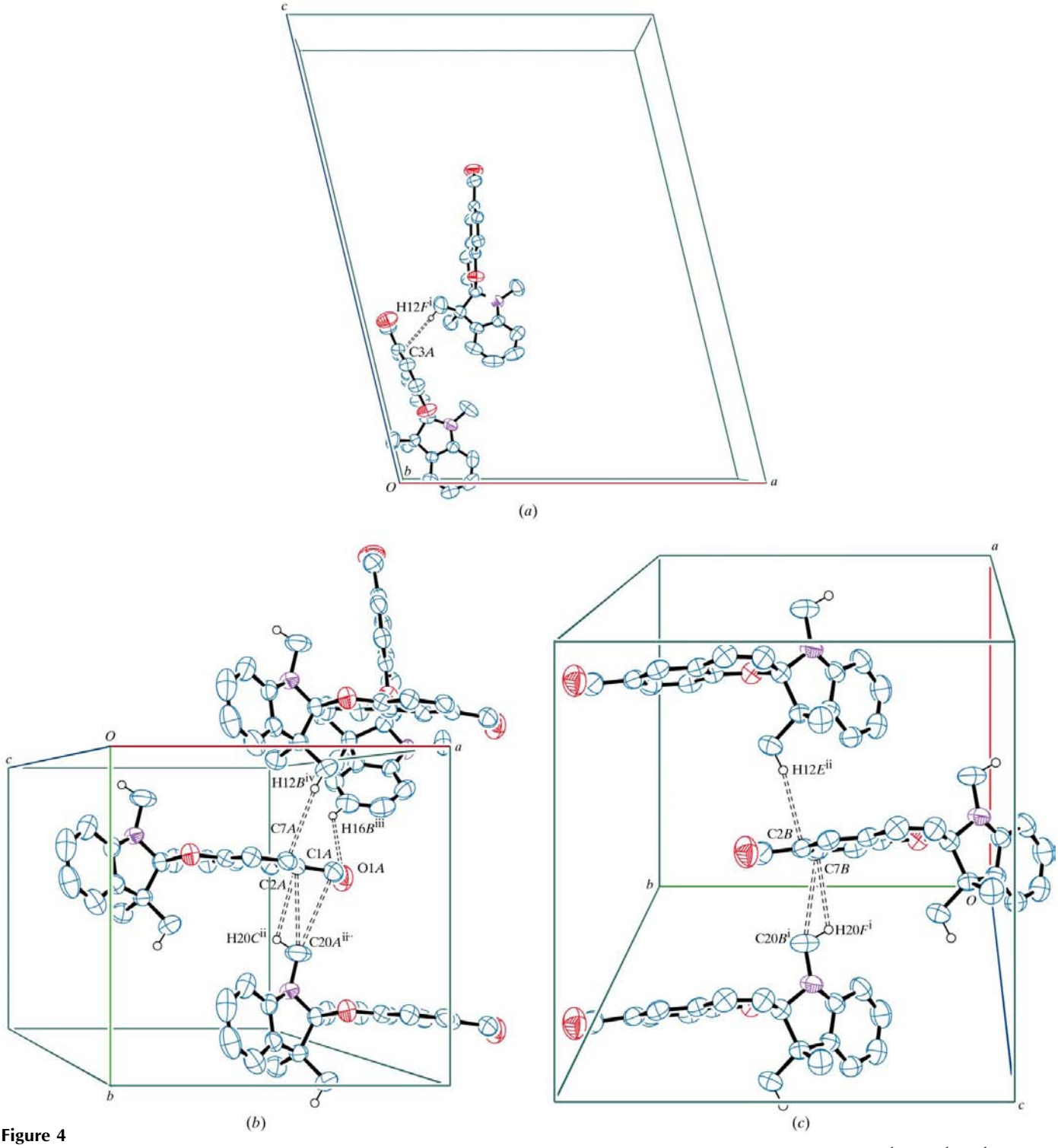


Figure 4
Short intermolecular contacts (dashed lines) directed towards the benzopyran plane in (*a*) space group *C*2/*c* [symmetry code: (i) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$], and (*b*) and (*c*) space group *Cc* [symmetry codes: (i) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (iii) $1 + x, -y, \frac{1}{2} + z$; (iv) $\frac{1}{2} + x, -\frac{1}{2} + y, z$].

hyde tail differs significantly in the four cases. The differences between the conformations of the four molecules may be attributed to the different degree of puckering of the pyran ring. Comparison of the angles α between the mean planes through atoms O2/C10/C9 and N1/C10/C11 shows that at the spiro atom, C10, the angles are close to the ideal of 90° (Table 1). At the five-membered heterocycle there is a bending around a vector connecting atoms N1···C11. This bending is expressed by the angles β between the mean planes through atoms N1/C10/C11 and N1/C19–C14/C11. The range of the angles β is too small to explain the differences in the conformation of the four molecules. The angle γ defines the angle between the mean planes through atoms O2/C10/C9 and O2/C5–C7/C2–C4/C8/C9. The γ angles are significantly different in the four molecules and determine the conformational variation. The bending angles in the two molecules that crystallize in space group *Cc* are different (17.2 and 20.0° in molecules *A* and *B*, respectively) and also different from those in the molecules which crystallize in space group *C*2/*c* (6.8 and −10.5° in molecules *A* and *B*, respectively), which have significantly smaller bending, albeit to opposite sides. The bending of the benzopyran group in space group *C*2/*c* is either towards the N1—C20 bond (molecule *B*) or towards the C11—C12 bond (molecule *A*), while in space group *Cc* the bending is towards the C11—C12 bond in both molecules.

A search of the Cambridge Structural Database (Version 5.29; Allen, 2002) revealed 85 molecules containing a similar benzopyran moiety. In all of them, two methyl groups are bonded to the spiro C atom (C10). It was found that the range of the γ angles is from 0.0° (ZEMHUU; Matsumoto *et al.*, 1995) to 42.2° (WUXGIF; Marek *et al.*, 2003). No correlations were found between the bending angle γ and the bond distances involving atom O2. Therefore, it is reasonable to assume that the bending does not result from electronic effects.

The differences between the conformations expressed by the degree of bending of the present molecules may be attributed to differences in packing rather than to differences in molecular properties. Close examination of the packing of the different dimorphs was carried out by calculating the intermolecular distances that are shorter than the sum of the van der Waals radii of the atoms involved. It was shown that in space group *Cc*, there are several close contacts between the atoms of a neighbouring molecule and atoms belonging to the benzopyran moiety in an almost perpendicular orientation, thus determining the degree of bending (Table 2; Figs. 4*b* and 4*c*). In space group *C*2/*c*, there is only one such contact (Table 2; Fig. 4*a*). The benzopyran ring is therefore blocked between neighbouring molecules in space group *Cc* and there is no such blocking in space group *C*2/*c*. Furthermore, the carbonyl atom O1 in the dimorph that crystallizes in *C*2/*c* is oriented in opposite directions in molecules *A* and *B*, while in space group *Cc* the carbonyl bonds are parallel (torsion angle C3—C2—C1—O1; Table 1). This difference in the orientation of the carbonyl O atom may also help to explain the existence of the dimorphic structures.

Experimental

The title compound was synthesized by the condensation reaction of 1,3,3-trimethyl-2-methyleneindoline and salicylaldehyde in boiling ethanol (Durr & Bouas-Laurent, 1990). After chromatographic purification, the product was recrystallized from an acetone–heptane solution (50:50 *v*/*v*) to give colourless crystals of (I) suitable for X-ray analysis.

Compound (I) in *C*2/*c*

Crystal data

$C_{20}H_{19}NO_2$
M_r = 305.36
Monoclinic, *C*2/*c*
a = 21.447 (4) Å
b = 11.226 (2) Å
c = 28.221 (6) Å
β = 103.57 (2)°
V = 6605 (2) Å^3
Z = 16
Mo *K*α radiation
μ = 0.08 mm^{-1}
T = 293 (2) K
0.05 × 0.04 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
15238 measured reflections
7218 independent reflections
3291 reflections with $I > 2\sigma(I)$
R_{int} = 0.071

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.169
S = 0.89
7218 reflections
421 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Compound (I) in *Cc*

Crystal data

$C_{20}H_{19}NO_2$
M_r = 305.36
Monoclinic, *Cc*
a = 11.699 (2) Å
b = 11.692 (2) Å
c = 24.406 (5) Å
β = 102.13 (3)°
V = 3263.8 (10) Å^3
Z = 8
Mo *K*α radiation
μ = 0.08 mm^{-1}
T = 293 (2) K
0.04 × 0.03 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
12585 measured reflections
5001 independent reflections
3405 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.091
S = 0.95
2878 reflections
422 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Table 1
Comparison of relevant torsion angles and angles between planes in the crystal structures of the two dimorphs of (I).

Angle (°)	*C*2/*c*		*Cc*	
	Mol. *A*	Mol. *B*	Mol. *A*	Mol. *B*
C9—C10—O2—O5	8.2 (3)	−12.7 (3)	−20.7 (4)	−23.1 (4)
C10—O2—C5—C4	−3.5 (3)	8.8 (3)	13.6 (5)	14.3 (4)
O2—C5—C4—C8	−2.3 (3)	−0.2 (3)	1.0 (5)	2.3 (5)
C5—C4—C8—C9	2.5 (4)	−4.0 (4)	−6.6 (5)	−7.5 (5)
C4—C8—C9—C10	3.1 (4)	−1.2 (4)	−2.6 (6)	−4.1 (6)
C8—C9—C10—O2	−8.1 (4)	8.9 (4)	15.3 (5)	18.4 (5)
C3—C2—C1—O1	−177.2 (3)	−4.8 (4)	−3.0 (6)	−1.2 (6)
α	89.7 (1)	87.3 (1)	89.6 (2)	89.3 (2)
β	26.5 (1)	23.0 (1)	26.4 (3)	28.2 (3)
γ	6.8 (3)	−10.5 (1)	17.2 (1)	20.0 (2)

Table 2
Comparison of short intermolecular distances in the crystal structures of the two dimorphs of (I).

Atom 1	Atom 2	Distance (Å)	Symmetry of atom 2
Dimorph in *C*2/*c*			
C3*A*	H12*F*	2.887	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
Dimorph in *Cc*			
C7*A*	H12*B*	2.875	$\frac{1}{2} + x, -\frac{1}{2} + y, z$
C1*A*	C20*A*	3.372	$\frac{1}{2} + x, \frac{1}{2} + y, z$
C2*A*	C20*A*	3.300	$\frac{1}{2} + x, \frac{1}{2} + y, z$
C2*A*	H20*C*	2.880	$\frac{1}{2} + x, \frac{1}{2} + y, z$
O1*A*	H16*B*	2.685	$1 + x, -y, \frac{1}{2} + z$
C7*B*	C20*B*	3.319	$-\frac{1}{2} + x, \frac{1}{2} + y, z$
C7*B*	H20*F*	2.863	$-\frac{1}{2} + x, \frac{1}{2} + y, z$
C2*B*	H12*F*	2.808	$\frac{1}{2} + x, \frac{1}{2} + y, z$

H atoms were placed at calculated positions [aromatic C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C); methyl C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C)] and included as riding atoms. The absolute structure in space group *Cc* could not be assigned based on Friedel pairs and the intensity data were merged.

For both compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *maXus* (Mackay *et al.*, 1998) for (I) in *C*2*c*; *SHELXS97* for (I) in *Cc*. For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3147). Services for accessing these data are described at the back of the journal.

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