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Key indicators

Single-crystal X-ray study
 $T = 193\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.057
 wR factor = 0.124
Data-to-parameter ratio = 15.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**6-Bromo-1'-ethyl-4-(1-ethyl-3,3-dimethyl-1*H*-indolin-2-ylidenemethyl)-3',3'-dimethylspiro[3,4-dihydro-2*H*-1-benzopyran-2,2'(3'*H*)-1'*H*-indoline], a dicondensed spiropyran**

The title molecule, $\text{C}_{33}\text{H}_{37}\text{N}_2\text{O}$, as a dicondensed spiropyran (DC), contains a benzopyran and two indoline ring systems. Each of the three systems is nearly planar. While both indolines are almost perpendicular to the benzopyran, they make a dihedral angle of $33.6(4)^\circ$ with each other. The two chiral C atoms have the same chirality (*RR* or *SS*).

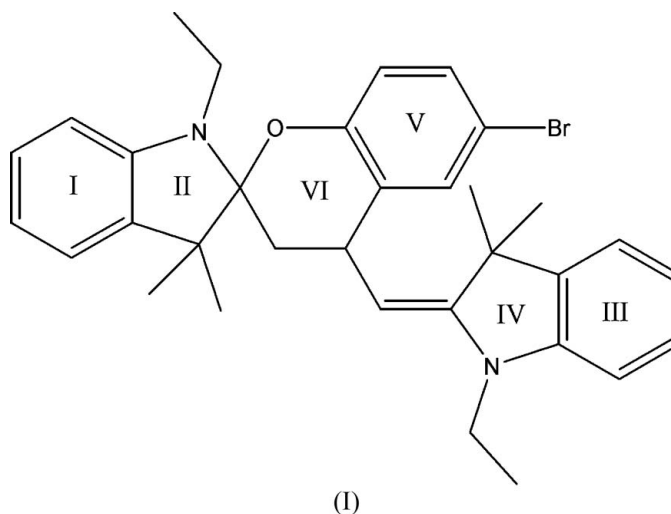
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Comment

As photochromic and thermochromic organic compounds, benzospiropyrans have received considerable attention (Berkovic *et al.*, 2000), due to their potential application in data recording, optical switching, displays and non-linear optics (Feringa *et al.*, 1993). Dicondensed spiropyrans (DC) were reported as side products in the synthesis of spiropyrans, and found use as additives in silver halide emulsions and components of thermal papers (Pommier *et al.*, 1975), but their structures were assigned differently (Koelsch & Workman, 1952; Hinnen *et al.*, 1968) and no crystal structure was found in the Cambridge Structural Database (Version 5.26; Allen, 2002). The unequivocal structure of (I) has therefore been established by X-ray single-crystal analysis and is reported here.



The title molecule contains six rings, and each pair of fused rings (I and II, III and IV, and V and VI) is nearly coplanar. The dihedral angles between rings I and II, III and IV, and V and VI are $7.2(2)$, $2.1(3)$ and $7.1(2)^\circ$, respectively. The dihedral angle between the first indoline (I and II) and the benzopyran (III and IV) is $98.7(3)^\circ$, that of the second indoline (V and VI) and benzopyran is $90.7(4)^\circ$, and that of the two indolines is $33.6(4)^\circ$. Atoms C7 and C9 have the same

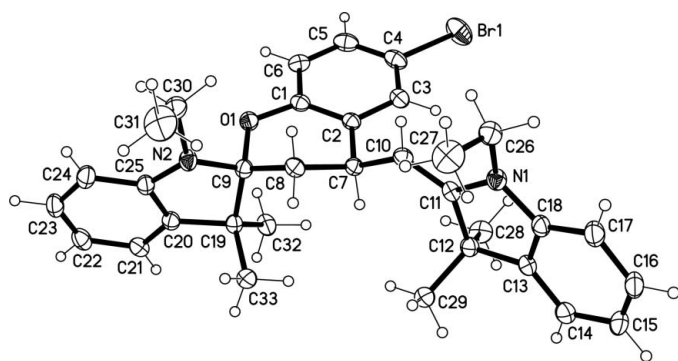


Figure 1
View of the molecular structure of the title compound, showing 30% probability displacement ellipsoids.

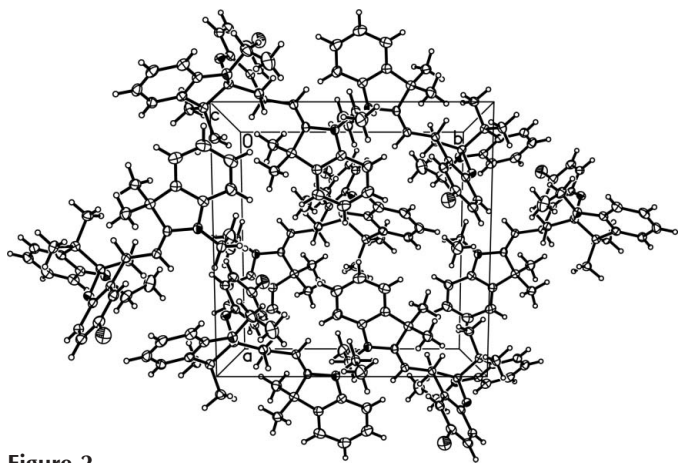


Figure 2
Packing diagram for (I), viewed down the *c* axis.

configuration (*RR* or *SS* in inversion-related molecules). The C7—C10—C11—N1 torsion angle is $-175.9(3)^\circ$, showing that the double bond C10=C11 adopts an *E* configuration. The torsion angles H8A—C8—C7—H7, H8B—C8—C7—H7 and H7—C7—C10—H10 are 53, 169 and -176° , respectively. All of the above is consistent with the results of a recent paper (Keum *et al.*, 2005), in which the authors discussed the mechanism of DC formation using geometric data.

In the crystal structure, molecules interact through C—H $\cdots\pi$ interactions (Table 2; Madhavi *et al.*, 1997; Umezawa *et al.*, 1998) and pack in a parallel manner along [010] (Fig. 2 and Table 2).

Experimental

A solution of 5-bromosalicylaldehyde (0.5 g) and 1-ethyl-3,3-dimethyl-2-methyleneindoline (0.3 g, Fischer base) in 15 ml of ethanol was boiled for 3 h and cooled. The solid was removed and washed with 95% ethanol. Colourless crystals (m.p. 456–458 K) were grown by slow evaporation at ambient temperature (298 K) of a solution in chloroform and ethanol (1:2 *v/v*) for 3 d. IR (FT-IR spectrometer with KBr pellets, ν , cm^{-1}): 1488, 1106, 989, 923, 1384, 1606; ^1H NMR (Bruker AV-400 NMR spectrometer, 399.97 MHz, CDCl_3 , 298 K): δ 1.14 (*t*, 7H), 1.28 (*s*, 4H), 1.33 (*s*, 3H), 1.64 (*s*, 4H), 2.10 (*t*, 1H), 2.41 (*m*, 1H), 3.20 (*m*, 2H), 3.30 (*m*, 1H), 3.55 (*d*, 1H), 3.87 (*d*, 1H), 5.72 (*d*, 1H), 6.57 (*t*, 2H), 6.79 (*m*, 2H), 7.06 (*d*, 2H), 7.15 (*s*, 3H), 7.58 (*d*, 2H).

Crystal data

$\text{C}_{33}\text{H}_{37}\text{BrN}_2\text{O}$
 $M_r = 557.56$
Monoclinic, $P2_1/n$
 $a = 12.4808(15) \text{ \AA}$
 $b = 12.0528(15) \text{ \AA}$
 $c = 20.146(3) \text{ \AA}$
 $\beta = 107.031(4)^\circ$
 $V = 2897.7(7) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.278 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 9054 reflections
 $\theta = 3.1\text{--}25.3^\circ$
 $\mu = 1.45 \text{ mm}^{-1}$
 $T = 193(2) \text{ K}$
Block, colorless
 $0.32 \times 0.30 \times 0.19 \text{ mm}$

Data collection

Rigaku Mercury diffractometer
 ω scans
Absorption correction: multi-scan (Jacobson, 1998)
 $T_{\min} = 0.648$, $T_{\max} = 0.763$
28220 measured reflections
5291 independent reflections

4270 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$
 $\theta_{\text{max}} = 25.4^\circ$
 $h = -14 \rightarrow 15$
 $k = -13 \rightarrow 14$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.124$
 $S = 1.15$
5291 reflections
341 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 1.8582P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C1	1.366 (3)	N2—C9	1.446 (4)
O1—C9	1.474 (3)	N2—C30	1.455 (4)
N1—C18	1.388 (4)	C2—C7	1.520 (4)
N1—C11	1.401 (4)	C7—C10	1.492 (4)
N1—C26	1.449 (4)	C7—C8	1.529 (4)
N2—C25	1.394 (4)	C10—C11	1.337 (4)
C1—O1—C9	120.2 (2)	C9—C8—C7	115.0 (2)
C18—N1—C11	111.0 (2)	N2—C9—O1	105.1 (2)
C18—N1—C26	123.1 (2)	N2—C9—C8	112.2 (2)
C11—N1—C26	123.7 (2)	O1—C9—C8	109.3 (2)
C25—N2—C9	109.0 (2)	N2—C9—C19	103.0 (2)
C25—N2—C30	121.5 (2)	O1—C9—C19	108.3 (2)
C9—N2—C30	121.5 (2)	C8—C9—C19	118.0 (2)
C7—C10—C11—N1	$-175.9(3)$		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

Cg5 is the centre of ring V.

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
C31—H31B \cdots O1 ⁱ	0.98	3.19	3.960 (3)	136
C23—H23 \cdots Cg5 ⁱⁱ	0.95	2.82	3.629 (3)	143

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

H atoms were positioned geometrically. The C—H bond lengths are 0.98 \AA for primary C, 0.99 \AA for secondary C, 1.00 \AA for tertiary C and 0.95 \AA for aromatic sp^2 C atoms; the H atoms were treated as riding, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{carrier atom})$, with $x = 1.5$ for the primary C atoms and 1.2 for the other C atoms.

Data collection: *CRYSTALCLEAR* (Rigaku, 1999); cell refinement: *CRYSTALCLEAR*; data reduction: *CrystalStructure* (Rigaku, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Berkovic, G., Krongauz, V. & Weiss, V. (2000). *Chem. Rev.* **100**, 1741–1753.
- Feringa, B. L., Jager, W. F. & de Lange, B. (1993). *Tetrahedron*, **49**, 8267–8310.
- Hinnen, A., Audic, C. & Gautron, R. (1968). *Bull. Soc. Chim. Fr.* pp. 2066–2074.
- Jacobson, R. (1998). Private communication to Rigaku Corporation, Tokyo, Japan.
- Keum, S.-R., Ku, B.-S., Shin, J.-T., Ko, J. J. & Buncel, E. (2005). *Tetrahedron*, **61**, 6720–6725.
- Koelsch, C. F. & Workman, W. R. (1952). *J. Am. Chem. Soc.* **74**, 6288–6289.
- Madhavi, N. N. L., Desiraju, G. R., Katz, A. K., Carrell, H. L., & Nangia, A. (1997). *Chem. Commun.* pp. 1953–1954.
- Pommier, H., Samat, A., Metzger, J. & Guglielmetti, R. (1975). *J. Chim. Phys. Phys. Chim. Biol.* **72**, 589–594.
- Rigaku (1999). *CRYSTALCLEAR*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2000). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (1997a). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Umezawa, Y., Tsuboyama, S., Honda, K., Uzawa, J. & Nishio, M. (1998). *Bull. Chem. Soc. Jpn.* **71**, 1207–1213.