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4′-(4-Bromobenzoyl)-1′-methyldispiro-[indole-3(2H),2′-pyrrolidine-3′,3″(2″H)-indole]-2,2″-dione

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.114
Data-to-parameter ratio = 13.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{26}H_{20}BrN_3O_3$, the central pyrrolidine ring adopts an envelope conformation. In the crystal structure, the molecules exist as centrosymmetric N—H···O hydrogen-bonded dimers. The dimers are linked *via* C—H···O hydrogen bonds, forming a chain along the b axis.

Comment

Heterocyclic compounds, especially those with fused five- and six-membered rings, occupy an important place among organic compounds due to their varying biological activities. Substituted pyrrolidine compounds have gained much importance because they are the structural elements of many alkaloids. It has been found that they exhibit antifungal activity against various pathogens (Amal Raj *et al.*, 2003). Several unusual amino acids which contain a pyrrolidine ring have been investigated (Galeazi *et al.*, 1999). Optically active pyrrolidine derivatives have been used as intermediates in controlled asymmetric synthesis (Suzuki *et al.*, 1994). 1,3-Dipolar cyclo-addition reactions are considered to be the most important processes for the construction of spiro-compounds containing five-membered rings, due to the high regio- and stereo-selective properties of these reactions (Caramella & Grunanger, 1984). In view of the biological importance, and as a part of studies on pharmacologically active spiro-pyrrolidines, the crystal structure of the title compound, (I), was carried out to establish the conformation of the molecule.


(I)
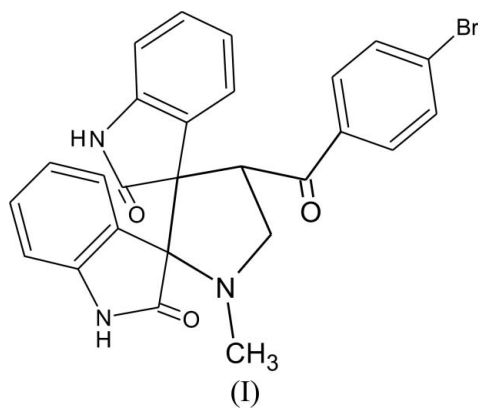
A *ZORTEP* (Zsolnai, 1997) plot of the molecule is shown in Fig.1. There are two spiro junctions in the molecule, which contain two oxindole ring systems. The N—C and C—C bond lengths (Table 1) in the pyrrolidine ring are slightly longer than the values reported for similar structures (Jeyabharathi *et al.*, 2001; Seshadri *et al.*, 2003; Abdul Ajees *et al.*, 2002). This may be due to the spiro fusion and steric forces caused by the bulky substituents on the pyrrolidine ring, at the C2, C10 and
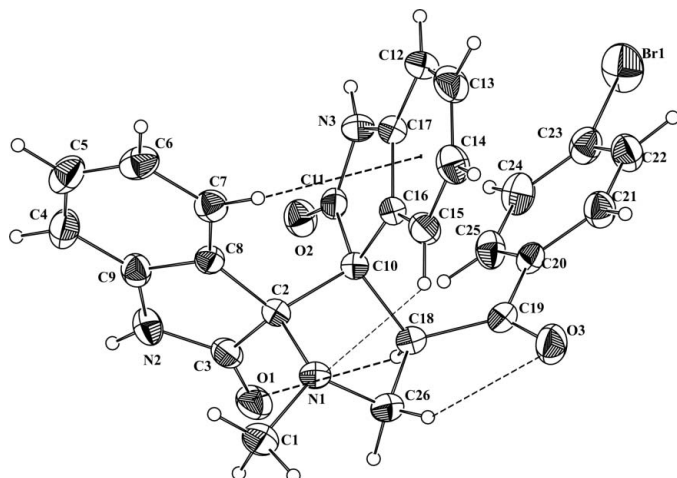
Figure 1
The structure of (I), showing 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.
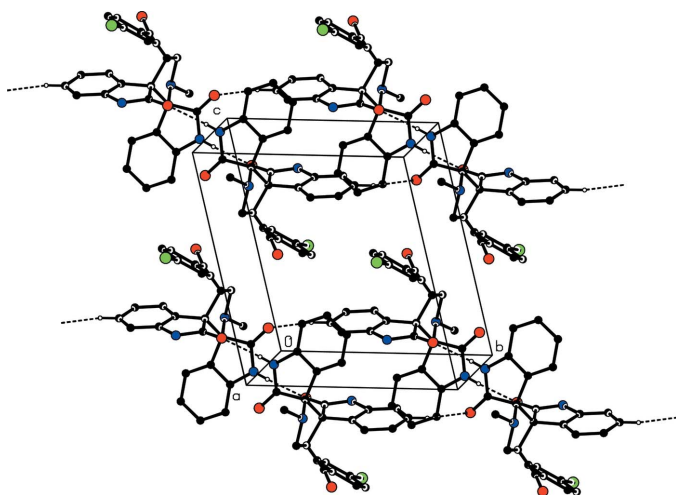
Figure 2
The crystal packing of (I), viewed approximately down the *a* axis. Dashed lines indicate hydrogen bonds. H atoms have been omitted.

C18 positions. The sum of the angles around N1 [337.0°] is in accordance with sp^3 hybridization. The methyl group attached at N1 is in the equatorial position, evidenced by the C1—N1—C26—C18 torsion angle of 152.5 (3)°. The endocyclic angles around C8 and C16 are narrowed while those at C9 and C17 are widened from 120°. This may be caused by the fusion of the smaller pyrrole rings to the six-membered benzene rings of the oxindoles. A similar effect has also been observed by Sethusankar *et al.* (2002). The N2—C3 and C3—O1 bond lengths indicate electron delocalization over atoms N2, C3 and O2. A short Br1···O3 (*x* − 1, *y*, *z*) contact [3.240 (2) Å] is also present.

Torsion angles, a least-squares plane calculation, asymmetry parameters [ΔC_s(C2) = 0.062 (2); Nardelli, 1995] and puckering parameters [q_2 = 0.465 (3) Å and φ_2 = 46.3 (3)°; Cremer & Pople, 1975] indicate that the pyrrolidine ring adopts an envelope conformation. Atom C2 deviates from the N1/C10/

C18/C26 plane by 0.697 (2) Å. This causes the significant contraction of the angle N1—C2—C10 [100.0 (2)°].

The molecular structure is stabilized by intramolecular C—H···O, C—H···N and C—H···π interactions (Table 2). In the crystal structure, symmetry-related molecules form N—H···O hydrogen-bonded dimers, which are linked *via* C—H···O hydrogen bonds, forming a chain along the *b* axis (Fig. 2).

Experimental

A mixture of (*E*)-3-(4′-bromophenacylidene)oxindole (1 mmol), isatin (indole-2,3-dione) (1 mmol), and sarcosine (*N*-methylglycine) (1 mmol) was refluxed in aqueous methanol for 3 h. On completion of the reaction, the solvent was evaporated in a vacuum and the resulting crude product was purified by column chromatography using an *n*-hexane–ethyl acetate mixture (7:3) as eluent. The title compound was recrystallized from a methanol–chloroform mixture (2:1 *v/v*).

Crystal data

$C_{26}H_{20}BrN_3O_3$	$Z = 2$
$M_r = 502.36$	$D_x = 1.498$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.9029$ (11) Å	Cell parameters from 6845
$b = 10.2823$ (11) Å	reflections
$c = 11.6261$ (13) Å	$\theta = 1.5$–28.0°
$\alpha = 104.370$ (2)°	$\mu = 1.88$ mm^{-1}
$\beta = 94.036$ (2)°	$T = 293$ (2) K
$\gamma = 101.771$ (2)°	Block, colourless
$V = 1113.5$ (2) Å^3	$0.21 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4942 independent reflections
	3573 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.015$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 28.0°$
	$h = -12 \rightarrow 12$
$T_{min} = 0.694$, $T_{max} = 0.705$	$k = -13 \rightarrow 13$
7084 measured reflections	$l = -12 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$+ 0.4461P]$
$wR(F^2) = 0.114$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
4942 reflections	$\Delta\rho_{max} = 0.62$ e Å^{-3}
378 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

O2—C11	1.215 (3)	N1—C1	1.457 (3)
N3—C11	1.351 (3)	N1—C2	1.463 (3)
N3—C17	1.399 (3)	N1—C26	1.472 (3)
N2—C3	1.346 (3)	O3—C19	1.207 (3)
N2—C9	1.390 (3)	C3—O1	1.215 (3)
C1—N1—C2	116.0 (2)	C12—C17—C16	121.9 (2)
C1—N1—C26	113.9 (2)	C15—C16—C17	119.3 (2)
C2—N1—C26	107.1 (2)	C4—C9—C8	122.3 (3)
C7—C8—C9	119.2 (2)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C15—H15$\cdots$N1	0.93 (3)	2.60 (3)	3.103 (4)	114 (2)
C18—H18$\cdots$O1	0.92 (2)	2.43 (2)	2.935 (3)	115 (2)
C26—H26A$\cdots$O3	0.92 (3)	2.48 (3)	2.849 (4)	104 (2)
C7—H7$\cdots$Cg	0.91 (3)	2.92 (2)	3.561 (3)	128 (2)
N2—H2$\cdots$O2^i	0.80 (3)	2.11 (3)	2.905 (3)	174 (3)
C13—H13$\cdots$O1^{ii}	0.93 (3)	2.41 (3)	3.212 (4)	145 (3)

Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $x, y+1, z$. Cg is the C12—C17 ring centroid

H atoms were located in a difference Fourier map and refined isotropically. The range of C—H bond lengths is 0.86 (3)–1.01 (3) Å, and the N—H distance is 0.80 (3) Å.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

References

Abdul Ajees, A., Manikandan, S. & Raghunathan, R. (2002). *Acta Cryst.* E**58**, o802–o804.

Amal Raj, A., Raghunathan, R., Sridevi Kumari, M. R. & Raman, N. (2003). *Bioorg. Med. Chem.* **11**, 407–409.

Bruker (2001). *SMART* (Version 5.625) and *SAINT* (Version 6.28a). Bruker AXS Inc., Madison, Wisconsin, USA.

Caramella, P. & Grunanger, P. (1984). *1.3-Dipolar Cycloaddition Chemistry*, Vol. 1, edited by A. Padwa, pp. 291–312. New York: Wiley.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Galeazi, R., Gremia, S., Mobbili, G. & Orena, M. (1999). *Tetrahedron Asymmetry*, **10**, 587–605.

Jeyabharathi, A., Ponnuswamy, M. N., Amal Raj, R., Raghunathan, R., Razak, I. A., Usman, A., Chandrapromma, S. & Fun, H.-K. (2001). *Acta Cryst.* E**57**, o901–o903.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Seshadri, P. R., Selvanayagam, S., Velmurugan, D., Ravikumar, K., Sureshbabu, A. R. & Raghunathan, R. (2003). *Acta Cryst.* E**59**, o1458–o1460.

Sethusankar, K., Kannadasan, S., Velmurugan, D., Srinivasan, P. C., Shanmuga Sundara Raj, S. & Fun, H.-K. (2002). *Acta Cryst.* C**58**, o277–o279.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Suzuki, H., Aoyagi, S. & Kibayashi, C. (1994). *Tetrahedran Lett.* **35**, 6119–6122.

Zsolnai, L. (1997). *ZORTEP*. University of Heidelberg, Germany.