Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

3-(4-Methoxyphenyl)-1′,6,6-trimethyl-4,5,6,7-tetrahydrospiro[1-benzofuran-2,3′(3*H*,2′*H*)-1*H*-indole]-2′,4-dione

D. Gayathri,[a] D. Velmurugan,[a]* K. Ravikumar,[b] G. Savitha[c] and P. T. Perumal[c]

[a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, [b]Laboratory of X-ray Crystallography, Indian Institute of Chemical Technology, Hyderabad 500 007, India, and [c]Organic Chemistry Division, Central Leather Research Institute, Adyar, Chennai 600 020, India

Correspondence e-mail: d_velu@yahoo.com

The title compound, $C_{24}H_{22}ClNO_3$, contains two independent molecules in the asymmetric unit. In one of the molecules, the furan ring is in a twist conformation, whereas in the other it adopts an envelope conformation. In both molecules, the cyclohexenone rings adopt envelope conformations. The crystal structure is stabilized by intermolecular C—H⋯O interactions.

Received 11 January 2007
Accepted 21 January 2007

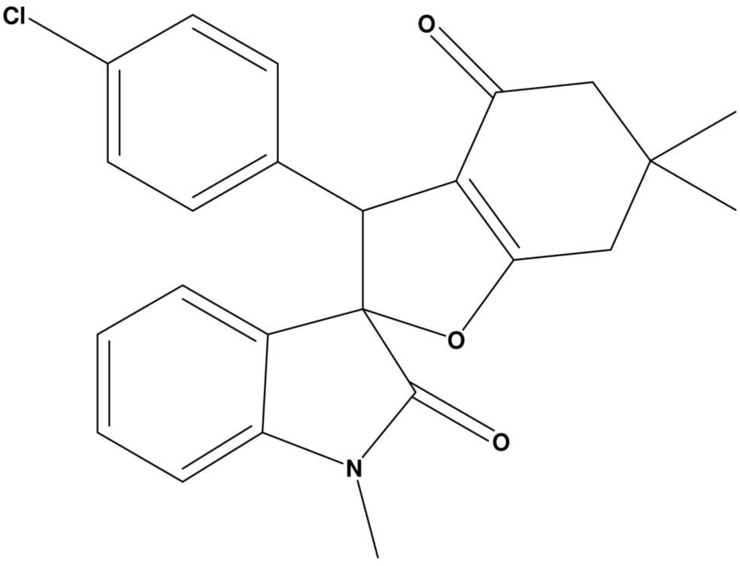
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.047
wR factor = 0.138
Data-to-parameter ratio = 18.7

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

Comment

Spiro compounds represent an important class of naturally occurring substances characterized by highly pronounced biological properties (Kobayashi *et al.*, 1991). The spiro-oxindole ring sytem is found in a number of alkaloids, such as horsifiline, spiro-tryprostatin and (+)-elacomine (Hilton *et al.*, 2000). Spiro-oxindole derivatives find wide biological application as antimicrobial and antitumour agents and as inhibitors of the human NKI receptor (Kornet & Thio, 1976). We report here the crystal structure of the title compound, (I).



(I)

The asymmetric unit of (I) contains two molecules, *A* (Cl1/N1/O1–O3/C1–C24) and *B* (Cl2/N2/O4–O6/C25–C48). The corresponding bond lengths and angles of these two molecules agree with each other and show normal values (Allen *et al.*, 1987), except at the spiro junctions. In both molecules *A* and *B*, the N atom exhibits sp^2 hybridization.

In molecule *A*, the dihydropyrrolone ring adopts an envelope conformation, with atom C1 at the flap [deviation 0.138 (1) Å], whereas in molecule *B* this ring is planar. The

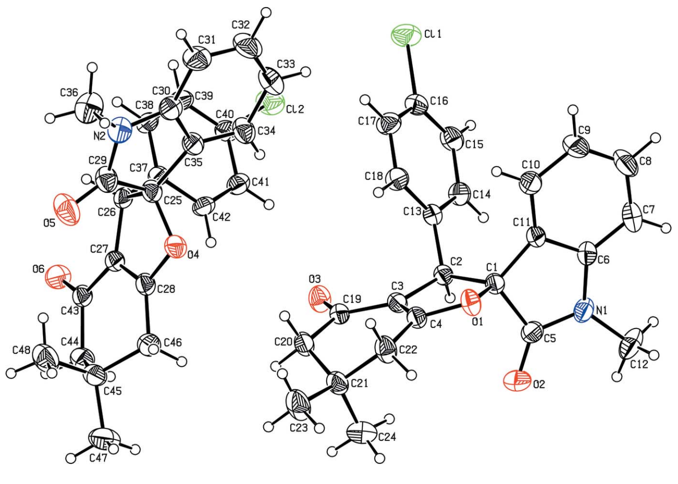


Figure 1
The asymmetric unit of (I), showing 30% probability displacement ellipsoids.

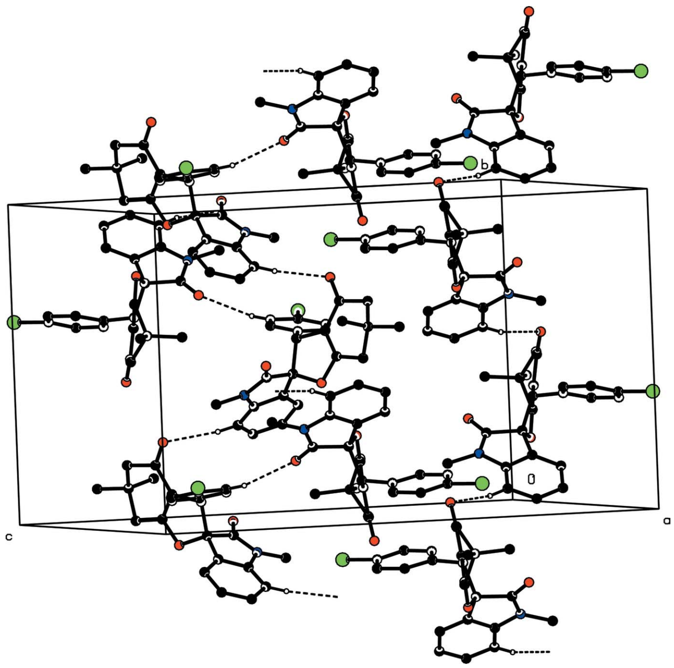


Figure 2
The crystal packing of (I). Dashed lines indicate hydrogen bonds and H atoms not involved in the interactions have been omitted.

puckering parameters (Cremer & Pople, 1975) and the smallest displacement asymmetry parameters (Nardelli, 1983) are q_2 = 0.084 (2) Å, φ = 247.0 (1)° and $\Delta_2(C_3)$ = 3.0 (2). In molecule *A*, the furan ring adopts a twist conformation, with a pseudo-twofold axis passing through atom C3 and the midpoint of the O1—C1 bond [q_2 = 0.130 (1) Å and φ = 206.4 (7)°]. In molecule *B*, the furan ring adopts an envelope conformation, with atom C25 deviating by 0.374 (2) Å from the mean plane of the rest of the atoms in that ring [q_2 = 0.234 (2) Å, φ = 38.6 (4)° and $\Delta_s(C_{25})$ = 1.1 (2)]. In both molecules *A* and *B*, the cyclohexenone rings adopt envelope conformations, with atoms C21 and C45 deviating by 0.649 (2) and 0.641 (2) Å, respectively, from the mean plane through the remaining atoms in the corresponding rings. The puckering parameters q_2, q_3, Q and θ, respectively, are 0.383 (2) Å, 0.261 (2) Å, 0.463 (2) Å and 55.7 (2)° for the C3/C4/C19–C22 ring, and 0.385 (2) Å, −0.247 (2) Å, 0.458 (2) Å and 122.7 (2)° for the C27/C28/C43–C46 ring. The dihedral angles between the two benzene rings in molecules *A* and *B* are 48.5 (1)° and 53.6 (1)°, respectively.

In the crystal structure of (I), molecules *A* are linked *via* C7—H7···O3^{i} hydrogen bonds, generating a zigzag *C*(9) chain (Bernstein *et al.*, 1995) running along the *b* axis. Similarly, molecules *B* are linked *via* C31—H31···O6^{iii} hydrogen bonds to form another *C*(9) chain running along the *b* axis. These chains are cross-linked by C15—H15···O5^{ii} hydrogen bonds (Fig. 2). (Symmetry codes are given in Table 2.)

Experimental

To a stirred mixture of 3-(4-chlorobenzylidene)-1-methyloxindole (1.11 mmol, 0.3 g, 1 equivalent), dimedone (1.11 mmol, 0.154 g, 1 equivalent) and $NaHCO_3$ (3.33 mmol, 0.277 g, 3 equivalents) in acetonitrile (10 ml), ceric ammonium nitrate (2.78 mmol, 1.52 g, 2.5 equivalents) dissolved in acetonitrile (5 ml) was added dropwise at 273 K under an N_2 atmosphere. The reaction mixture was stirred until the reaction was complete, as monitored by thin-layer chromatography. Water was added to the mixture, and the product was extracted into ethyl acetate (2× 20 ml) and then dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave a crude mixture of isomers, which was purified and separated by column chromatography on silica gel (100–200 mesh), with ethyl acetate–hexane (3:9) as eluent, to afford the isomers (1:1) in an overall yield of 0.294 g (65%). One of the isomers, which was obtained as a white crystalline solid, was recrystallized from ethyl acetate and used for the X-ray diffraction study.

Crystal data

$C_{24}H_{22}ClNO_3$
M_r = 407.88
Monoclinic, $P2_1/n$
a = 13.9638 (8) Å
b = 13.8490 (8) Å
c = 22.1754 (13) Å
β = 100.851 (1)°
V = 4211.7 (4) Å^3
Z = 8
D_x = 1.286 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.21 mm^{-1}
T = 293 (2) K
Block, colourless
0.26 × 0.25 × 0.23 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: none
47537 measured reflections
9908 independent reflections
7812 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022
$\theta_{\rm max}$ = 28.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.138
S = 1.02
9908 reflections
529 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 0.8149P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.28 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.27 e Å^{-3}

Acta Cryst. (2007). E**63**, o1034–o1036 Gayathri *et al.* • $C_{24}H_{22}ClNO_3$ **o1035**

Table 1
Selected bond lengths (Å).

C25—O4	1.461 (2)	C43—O6	1.223 (2)
C25—C35	1.503 (2)	C1—O1	1.455 (2)
C25—C29	1.550 (2)	C1—C11	1.493 (2)
C25—C26	1.571 (2)	C1—C5	1.542 (2)
C26—C37	1.510 (2)	C1—C2	1.580 (2)
C26—C27	1.511 (2)	C2—C3	1.506 (2)
C27—C28	1.335 (2)	C2—C13	1.512 (2)
C28—O4	1.357 (2)	C3—C4	1.330 (2)
C29—O5	1.212 (2)	C4—O1	1.353 (2)
C30—N2	1.402 (2)	C5—O2	1.213 (2)
C36—N2	1.455 (2)	C5—N1	1.353 (2)
C40—Cl2	1.740 (2)	C6—N1	1.407 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C7—H7$\cdots$O3^{i}	0.93	2.42	3.337 (3)	169
C15—H15$\cdots$O5^{ii}	0.93	2.47	3.295 (2)	148
C31—H31$\cdots$O6^{iii}	0.93	2.41	3.299 (3)	160

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

All H atoms were placed in idealized positions and refined using a riding model, with C—H = 0.93 (aromatic), 0.98 (CH), 0.97 (CH_2) or 0.96 Å (methyl), and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(C) for the methyl groups. A rotating-group model was used for the methyl groups.

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: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

DG thanks the CSIR, India, for the award of a Senior Research Fellowship. DV thanks the DST, India, for a Major Research Project. The Department of Science and Technology (DST-FIST) and the University Grants Commission (UGC-SAP), Government of India, are acknowledged by DV for providing facilities to the department.

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.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (2001). *SMART* (Version. 5.625/NT/2000) and *SAINT* (Version 6.28a). Bruker AXS Inc., Madison, Wisconsin, USA.

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

Hilton, S. T., Ho, T. C., Pljevaljicic, G. & Jones, K. (2000). *Org. Lett.* **2**, 17, 2639–2641.

Kobayashi, J., Tsuda, M., Agemi, K., Shigemori, H., Ishibashi, M., Sasaki, T. & Mikami, Y. (1991). *Tetrahedron*, **47**, 6617–6622.

Kornet, M. J. & Thio, A. P. (1976). *J. Med. Chem.* **19**, 892–898.

Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.

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

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

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

o1036 Gayathri *et al.* • $C_{24}H_{22}ClNO_3$ *Acta Cryst.* (2007). E**63**, o1034–o1036