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2′-Benzoyl-1′-(4-chlorophenyl)-5′,6′,7′,7a′-tetrahydrospiro[indan-2,3′(2′H)-1H-pyrrolizine]-1,3-dione

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The title compound, $C_{28}H_{22}ClNO_3$, has two crystallographically independent molecules in the asymmetric unit. The pyrrolidine ring (*A*) of the pyrrolizine system adopts an envelope conformation in both molecules, whereas the other five-membered ring (*B*) adopts an envelope conformation in one molecule and a twist conformation in the other. The molecular packing is stabilized by intermolecular C—H···O, C—H···π and π–π interactions.

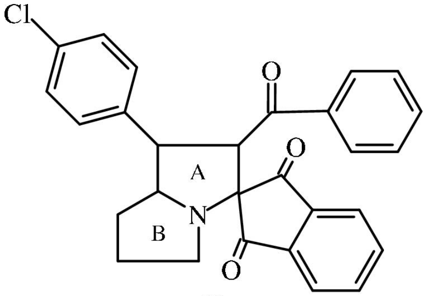
Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.002 Å
R factor = 0.046
wR factor = 0.143
Data-to-parameter ratio = 17.4

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

Comment

Pyrrolizidine alkaloids occur in more than 40 genera, and are responsible for heavy losses of livestock and poisoning in man due to their hepatotoxicity. These alkaloids are also reported to possess a number of other biological activities (Atal, 1978) and are used as DNA minor groove alkylating agents (Denny, 2001). In view of its importance, the X-ray analysis of the title compound, (I), has been undertaken and the results are presented here.



(I)

A displacement ellipsoid plot of (I) is shown in Fig. 1. The asymmetric unit of (I) contains two molecules (*A* and *B*) with similar bond lengths. In both molecules, the geometry of the pyrrolizidine system is comparable with that in related reported structures (Govind *et al.*, 2004*a*,*b*). The C—Cl bond lengths agree with reported values [C_{phenyl}—Cl = 1.739 (10) Å; Allen *et al.*, 1987).

The sum of the angles at N1 (328.2° in molecule *A* and 340.4° in molecule *B*) is in accordance with sp^3-hybridization.

In both molecules, the indanedione system is planar, with maximum deviations of 0.082 (1) and 0.089 (1) Å for atoms C4*A* and C4*B*, respectively. The keto O atoms O2 and O3 deviate from the mean plane through the ring by 0.164 (1) and 0.190 (1) Å, respectively, for molecule *A*, and 0.152 (1) and 0.221 (1) Å for molecule *B*. The chlorophenyl ring is planar, with maximum deviations of −0.050 (1) (molecule *A*) and 0.017 (1) Å (molecule *B*) for atom Cl1. The chlorophenyl ring and the benzoyl ring are oriented at angles of 67.2 (1) (molecule *A*) and 70.9 (1)° (molecule *B*) with respect to each other. The dihedral angle between the indanedione group and the chlorophenyl ring is 24.9 (1)° for molecule *A* and 46.2 (1)° for molecule *B*, whereas the dihedral angle with the benzoyl ring is 43.3 (1)° for molecule *A* and 24.7 (1)° for molecule *B*.

In both molecules, the pyrrolidine ring *A* of the pyrrolizidine system adopts an envelope conformation, with puckering parameters of q_2 = 0.710 (1) (molecule *A*) and 0.810 (3) Å (molecule *B*), and φ = −27.8 (1) (molecule *A*) and −47.9 (1)° (molecule *B*) (Cremer & Pople, 1975). For molecule *A*, atom C1*A* deviates by 0.563 (1) Å from the least-squares plane through the remaining four atoms, whereas for molecule *B*, atom C3*B* deviates by 0.615 (1) Å from the least-squares plane. The other five-membered ring (N1/C1/C5–C7) of the pyrrolizidine system adopts an envelope conformation for molecule *A* [q_2 = 0.695 (3) Å and φ = 180.0 (2)°] and a twist conformation for molecule *B* [q_2 = 0.440 (3) Å and φ = 73.4 (4)°]. For molecule *A*, atom N1*A* deviates by 0.542 (1) Å from the least-squares plane through the remaining four atoms.

The molecular packing is stabilized by intramolecular and intermolecular C—H···O interactions (Table 1 and Fig. 2). In addition, the molecular packing is stabilized by weak C—H···π and π–π intermolecular interactions. Intermolecular π–π interactions occur between the benzoyl rings (C15*B*–C20*B*) at (x, y, z) and (1 − x, −y, −z), with a centroid separation of 3.768 (1) Å. Inversion-related molecules are linked by weak C—H···π interactions, such that atom H18*B* is 2.89 Å from the centroid of the chlorophenyl ring (C8*B*–C13*B*) at (1 − x, −y, −z), with a C18*B*—H18*B*···centroid angle of 150° and a C18*B*···centroid distance of 3.724 (2) Å.

Experimental

A mixture of 4-chlorobenzylidineacetophenone (1 mmol), ninhydrin (1 mmol) and proline (1 mmol) was refluxed in aqueous methanol. After completion of the reaction, the reaction mixture was concentrated under reduced pressure and column chromatographed using a hexane and ethyl acetate mixture (9:1) to yield the title compound. The compound was recrystallized using methanol to afford diffraction quality crystals.

Crystal data

$C_{28}H_{22}ClNO_3$
M_r = 455.92
Triclinic, $P\bar{1}$
a = 8.2023 (5) Å
b = 11.7111 (7) Å
c = 25.4650 (15) Å
α = 102.102 (1)°
β = 90.014 (1)°
γ = 103.949 (1)°
V = 2317.9 (2) Å^3

Z = 4
D_x = 1.306 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9937 reflections
θ = 2.5–28.0°
μ = 0.20 mm^{-1}
T = 273 (2) K
Block, yellow
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: none
20028 measured reflections
10374 independent reflections

8360 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016
$\theta_{\rm max}$ = 28.0°
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 15$
$l = -32 \rightarrow 32$

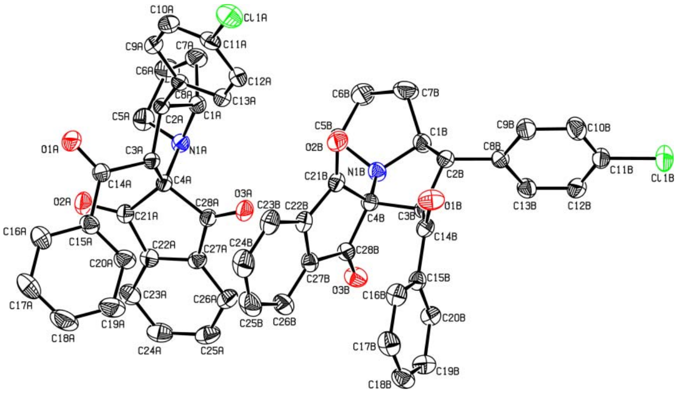


Figure 1
The molecular configuration and atom-numbering scheme for the asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

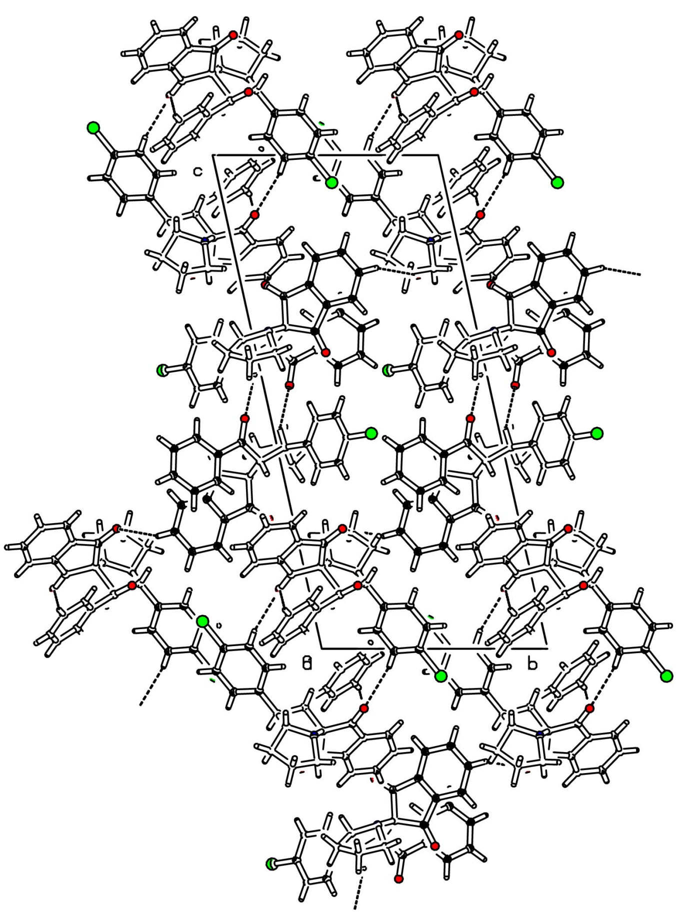


Figure 2
The molecular packing of (I), viewed down the *a* axis. Dashed lines indicate hydrogen bonding.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.143
S = 1.03
10374 reflections
595 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0907P)^2 + 0.2136P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.34 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.23 e Å^{-3}

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Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5*B*—H5*B*1···O2*B*	0.97	2.57	3.199 (2)	123
C2*A*—H2*A*···O1*A*$^{\rm i}$	0.98	2.60	3.490 (2)	152
C24*A*—H24*A*···O2*B*$^{\rm ii}$	0.93	2.51	3.372 (2)	154
C12*B*—H12*B*···O3*B*$^{\rm iii}$	0.93	2.48	3.285 (2)	144
C17*B*—H17*B*···O3*B*$^{\rm iv}$	0.93	2.43	3.347 (2)	167

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $x-1, y-1, z$; (iii) $-x, -y, -z$; (iv) $x+1, y, z$.

H atoms were positioned geometrically and were treated as riding on their parent C atoms, with C—H distances of 0.93–0.98 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

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: *ORTEP3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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