

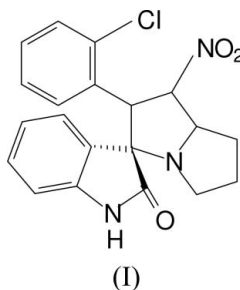
2'-(2-Chlorophenyl)-1'-nitro-2',3',4',5',6',7'-
hexahydro-1*H*-indole-3-spiro-3'-1'*H*-
pyrrolizin-2(3*H*)-oneG. Usha,^a S. Selvanayagam,^a
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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.042
wR factor = 0.127
Data-to-parameter ratio = 16.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The structure of the title cycloadduct, C₂₀H₁₈N₃O₃Cl, has been determined. The inversion-related molecules are held together by N—H···O hydrogen bonds, forming *R*₂²(8) rings. The overall conformation of the pyrrolizidine nucleus is folded about the bridging bond.

Comment

Nitro compounds are excellent precursors for aromatic amines and medicinally important compounds; they are also well known for their uses as explosives, dye intermediates and battery cathodes (Sivasamy *et al.*, 1988). Some of the indole alkaloids extracted from plants have been found to exhibit cytotoxic, antitumour and antiparasitic properties (Quetin-Leclercq, 1994). Pyrido[1,2-*a*]indole derivatives have been identified as potent inhibitors of human immunodeficiency virus type 1 (Taylor *et al.*, 1999). In view of the wide range of biological activities and industrial applications associated with the title adduct, (I), we have undertaken the X-ray analysis of the pyrrolizidine alkaloid.Bond lengths and bond angles of the pyrrolizidine group and the oxindole unit present no unexpected features and are in the same range as observed in reported structures (Govind *et al.*, 2004; Usha *et al.*, 2005). The C9=O1 double bond is slightly elongated [1.227 (2) Å] as a result of the hydrogen bonding. This is similar to what was found for the analogous bond in 1-naphthaleneacetic acid (Rajan, 1978), which forms hydrogen-bonded dimers.In the title adduct, each molecule forms a centrosymmetric dimer by N—H···O hydrogen bonds, generating *R*₂²(8) rings. Although atom Cl1 plays no role in hydrogen bonding, it participates in a fairly weak intramolecular contact (Table 2).The pyrrolizidine nucleus is composed of two five-membered rings. The N1/C2–C5 ring adopts a twist conformation, with a smallest asymmetry parameter (Nardelli, 1983) of $\Delta C_2(\text{C5}) = 0.009 (1)^\circ$. The asymmetry parameters [$\Delta_S(\text{C7}) = 0.044 (1)^\circ$ and $\Delta C_2(\text{C5}) = 0.040 (1)^\circ$] indicate the envelope conformation of the N1/C5–C8 ring. The overallReceived 9 September 2005
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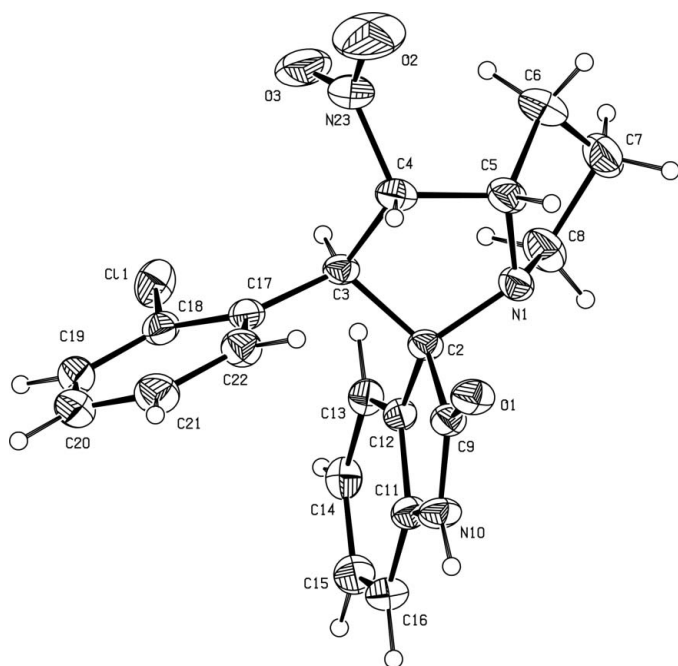


Figure 1
The molecular structure of the title compound, showing 30% probability displacement ellipsoids.

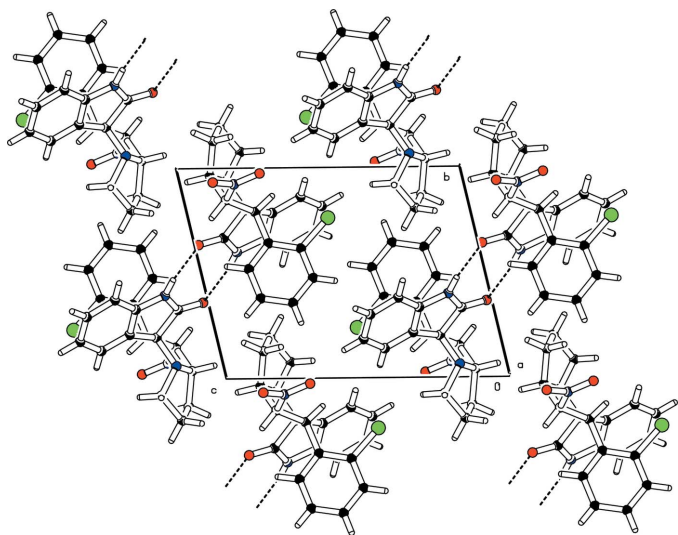


Figure 2
The crystal structure, showing the formation of hydrogen-bonded $R_2^2(8)$ rings. The view direction is along the a axis. Hydrogen bonds are shown as dashed lines.

conformation of the pyrrolidine nucleus is folded about the bridgehead bond, N1–C5. This observation is consistent with the structure reported by Usha *et al.* (2005).

Experimental

A mixture of 2-chloronitrostyrene (1 mmol), isatin (1 mmol) and proline (1 mmol) in methanol (20 ml) was refluxed until the disappearance of the starting materials. After the completion of the reaction, the reaction mixture was concentrated *in vacuo* and the residue was subjected to column chromatography with hexane–ethyl acetate (8:2), to give the pure cycloadduct. Crystals suitable for a

single-crystal X-ray structure determination were grown by slow evaporation of a methanol solution.

Crystal data

$C_{20}H_{18}ClN_3O_3$
 $M_r = 383.82$
Triclinic, $P\bar{1}$
 $a = 8.4698$ (5) Å
 $b = 9.3359$ (6) Å
 $c = 12.6058$ (8) Å
 $\alpha = 74.394$ (1)°
 $\beta = 72.025$ (1)°
 $\gamma = 79.334$ (1)°
 $V = 907.49$ (10) Å³

$Z = 2$
 $D_x = 1.405$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 5235 reflections
 $\theta = 2.2$ – 27.2 °
 $\mu = 0.24$ mm⁻¹
 $T = 293$ (2) K
Block, colourless
 $0.22 \times 0.21 \times 0.19$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
Absorption correction: none
7852 measured reflections
4067 independent reflections

3661 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.016$
 $\theta_{max} = 28.0$ °
 $h = -11 \rightarrow 11$
 $k = -12 \rightarrow 11$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.128$
 $S = 1.02$
4067 reflections
244 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 0.1853P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.31$ e Å⁻³
 $\Delta\rho_{min} = -0.23$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C11–C18	1.738 (2)	N1–C2	1.471 (2)
O1–C9	1.227 (2)	N1–C5	1.478 (2)
O2–N23	1.204 (2)	N10–C9	1.345 (2)
O3–N23	1.196 (2)	N10–C11	1.402 (2)
N1–C8	1.467 (2)	N23–C4	1.508 (2)
C8–N1–C2	118.2 (1)	C2–N1–C5	108.5 (1)
C8–N1–C5	108.8 (1)		
C5–N1–C2–C3	29.2 (1)	C3–C4–C5–N1	–12.9 (1)
N1–C2–C3–C4	–36.0 (1)	N1–C5–C6–C7	–19.4 (2)
C2–C3–C4–C5	29.4 (1)	C5–C6–C7–C8	37.0 (2)
C8–N1–C5–C6	–6.5 (2)	C5–N1–C8–C7	29.4 (2)
C2–N1–C5–C4	–10.4 (1)	C6–C7–C8–N1	–40.9 (2)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C3–H3 \cdots C11	0.98	2.55	3.108 (1)	116
N10–H10 \cdots O1 ⁱ	0.86	1.99	2.843 (1)	172

Symmetry code: (i) $-x + 1, -y + 1, -z$.

H atoms were positioned geometrically and were treated as riding on their parent atoms, with C–H distances of 0.93–0.98 Å, an N–H distance of 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(N,C)$.

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: ORTEP-3 (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PARST (Nardelli, 1995).

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