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3-(4-Chlorobenzoyl)-7-(*N*,*N*-dimethylamino)-1-phenylindolizine and 3-(2,4-dichlorobenzoyl)-7-(*N*,*N*-dimethylamino)-1-phenylindolizine

R. Hema,[a] V. Parthasarathi,[a]* K. Sarkunam,[b] M. Nallu[b] and Anthony Linden[c]

[a]Department of Physics, Bharathidasan University, Tiruchirappalli 620 024, India, [b]Department of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India, and [c]Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland
Correspondence e-mail: vpsarati@yahoo.com

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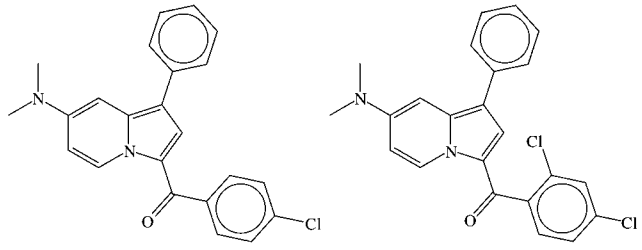
In both of the title compounds, $C_{23}H_{19}ClN_2O$, (I), and $C_{23}H_{18}Cl_2N_2O$, (II), the molecular packing is influenced by weak intermolecular C—H···O and C—H···π interactions, but despite the chemical similarity of the compounds, the packing in (II) is entirely different from that observed in (I).

Comment

The indolizines constitute the core structure of many naturally occurring alkaloids, *viz*. (−)-slaframine (Pourashraf *et al.*, 2000; Cossy *et al.*, 2002), (−)-dendroprimine (Diederich & Nubbemeyer, 1999), indalozin 167B (Chalard *et al.*, 1999) and coniceine (Park *et al.*, 2001). Heterocyclic compounds, such as indolizines, are important bioactive compounds that have a wide range of applications in biology, pharmacology and agrochemistry (Wu & Chen, 2003, and references therein). The synthesis of biologically active indolizines (Gubin *et al.*, 1992) continues to attract the attention of organic chemists (Bora *et al.*, 2003, and references therein), because these compounds are important as potential central nervous system depressants, calcium entry blockers, cardiovascular agents, spectral sensitizers and novel dyes (Katritzky *et al.*, 1999, and references therein). They are also used for the treatment of angina pectoris (Rosseels *et al.*, 1982) and as testosterone 5α-reductase inhibitors (Okada *et al.*, 1993). In view of these important attributes, we report here the crystal structures of the title compounds, (I) and (II). Full details of the syntheses of these compounds and their biological activities will be published elsewhere (Sarkunam & Nallu, 2003).

Perspective views of molecules of (I) and (II), with the atomic numbering schemes, are shown in Figs. 1 and 2, respectively. The corresponding bond lengths and angles in (I) and (II) are essentially equivalent and are comparable to those in related structures (Pritchard, 1988; Usman *et al.*, 2002). The indolizine rings of (I) and (II) can be superimposed on one another, with only a small r.m.s. deviation of the constituent atoms (0.011 Å). The carbonyl (C16═O16) bond lengths [1.243 (2) and 1.247 (2) Å for (I) and (II), respectively] are significantly longer than typical carbonyl bonds. This fact may be due to the involvement of atom O16 in intermolecular C—H···O interactions in both (I) and (II) (Tables 1 and 2). The dihedral angles between the plane of the indolizine ring and the planes of the phenyl and chlorobenzoyl moieties are 31.58 (4) and 60.93 (5)°, respectively, for (I), and 33.42 (4) and 72.47 (4)°, respectively, for (II). The angles between the planes of the phenyl and chlorobenzoyl rings are 70.94 (6) and 67.73 (4)° for (I) and (II), respectively.



In (I), atom C6 is involved in a weak intermolecular C—H···O interaction with atom O16 of a centrosymmetrically related molecule, thus forming an $R_2^2(14)$ motif (Bernstein *et al.*, 1995). Atom C18 (*via* atom H18) acts as a donor in a weak intermolecular C—H···π interaction with the centroid (*Cg*1) of the six-membered ring of the indolizine moiety in an adjacent molecule at (x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$). Atom C13 (*via* atom H13) is involved in a weak intermolecular C—H···π interaction with the centroid (*Cg*2) of the chlorobenzoyl ring in the molecule at ($-x$, $-y$, $-z$) (Table 1).

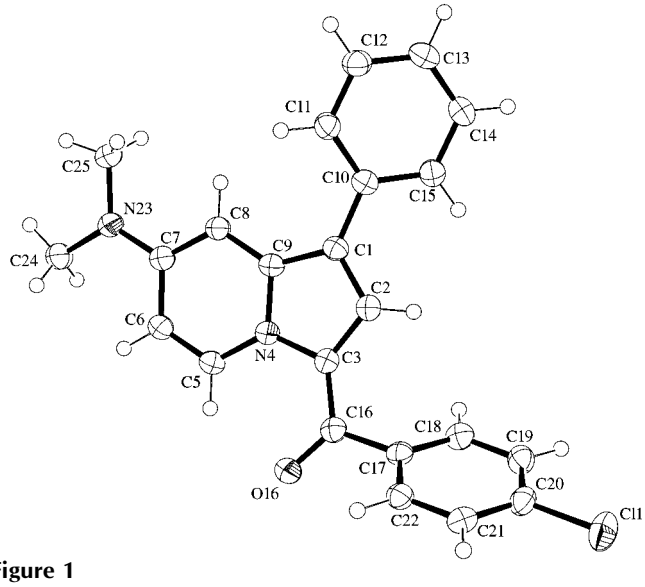


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii.

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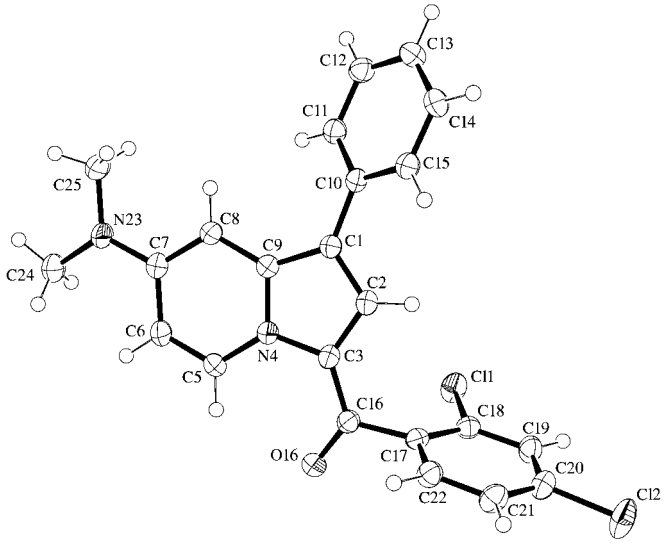

Figure 2
A view of the molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii.

Despite the similar chemical compositions of the title compounds, the packing of the molecules in the crystal structures of (I) and (II) is entirely different. In (II), atom C13 acts as a donor in a weak intermolecular C—H···O interaction with carbonyl atom O16 of an adjacent molecule. This interaction links the molecules into chains that run parallel to the *b* axis and have a graph-set motif of *C*(10). Atom C22 also acts as a donor in a weak intermolecular C—H···O interaction with atom O16 of a different adjacent molecule. This interaction produces a continuous chain that runs parallel to the *c* axis and has a graph-set motif of *C*(5) (Bernstein *et al.*, 1995). In addition, atom C19 (*via* atom H19) acts as a donor in a weak intermolecular C—H···π interaction with the centroid (*Cg*3) of the phenyl ring in the molecule at $(-1+x, y, z)$. Atom C24 (*via* atom H241) participates in a weak intermolecular C—H···π interaction with the centroid (*Cg*4) of the six-membered ring of the indolizine moiety in the molecule at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ (Table 2). It is of interest to note that the shortest intermolecular Cl1···Cl1 contact is 3.1818 (6) Å, which is smaller than the sum of the van der Waals radii of the corresponding atoms.

Experimental

A mixture of 4-(dimethylamino)pyridinium-1-(4-chlorophenacylide) (1.4 mmol), phenylacetylene (1.6 mmol) and potassium carbonate (1.6 mmol) in dimethylformamide (30 ml) was kept at room temperature overnight. The insoluble materials were removed by filtration and the filtrate was extracted with an ethyl acetate–dilute HCl mixture. The organic layer was evaporated and chromatographed to give (I), which was recrystallized from ethyl acetate (yield 0.29 g, 55%; m.p. 474–476 K). Compound (II) was prepared in an identical fashion but with 4-(dimethylamino)pyridinium-1-(2,4-dichlorophenacylide) as a starting material (yield 0.31 g, 63%; m.p. 516–518 K). Crystals suitable for X-ray diffraction were grown from ethyl acetate.

Compound (I)

Crystal data

$C_{23}H_{19}ClN_2O$
$M_r = 374.85$
Monoclinic, $P2_1/c$
$a = 10.4641$ (2) Å
$b = 16.3479$ (3) Å
$c = 11.0110$ (2) Å
$\beta = 102.4144$ (11)°
$V = 1839.57$ (6) Å^3
$Z = 4$
$D_x = 1.353$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 67 543 reflections
$\theta = 2.0$–27.5°
$\mu = 0.22$ mm^{-1}
$T = 160$ (2) K
Prism, yellow
0.25 × 0.13 × 0.13 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.842$, $T_{max} = 0.977$
41 157 measured reflections
4225 independent reflections
3353 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -21 \rightarrow 21$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.131$
$S = 1.06$
4225 reflections
247 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 0.614P]$ where $P = (F_o^2 + 2F_o^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.010 (3)

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

*Cg*1 and *Cg*2 are the centroids of the six-membered indolizine and phenyl rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O16^{i}	0.95	2.48	3.276 (2)	141
C13—H13···*Cg*2^{ii}	0.95	2.74	3.580 (2)	148
C18—H18···*Cg*1^{iii}	0.95	2.86	3.781 (2)	164

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

Compound (II)

Crystal data

$C_{23}H_{18}Cl_2N_2O$
$M_r = 409.29$
Monoclinic, $P2_1/c$
$a = 9.5888$ (2) Å
$b = 19.0878$ (4) Å
$c = 10.6508$ (2) Å
$\beta = 90.7580$ (13)°
$V = 1949.24$ (7) Å^3
$Z = 4$
$D_x = 1.395$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34 641 reflections
$\theta = 2.0$–27.5°
$\mu = 0.35$ mm^{-1}
$T = 160$ (2) K
Prism, yellow
0.25 × 0.23 × 0.20 mm

Table 2
Hydrogen-bonding geometry (Å, °) for (II).

*Cg*3 and *Cg*4 are the centroids of the phenyl and six-membered indolizine rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O16^{iv}	0.95	2.44	3.370 (2)	167
C22—H22···O16^{iii}	0.95	2.52	3.153 (2)	124
C19—H19···*Cg*3^{v}	0.95	2.68	3.568 (2)	156
C24—H241···*Cg*4^{vi}	0.98	2.86	3.600 (2)	132

Symmetry codes: (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $x-1, y, z$; (vi) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.842, T_{max} = 0.936
45 923 measured reflections
4465 independent reflections
3434 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 27.5°
$h = -12 \rightarrow 12$
$k = -24 \rightarrow 23$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.117
S = 1.04
4465 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 0.7326P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

For both compounds, methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å), with U_{iso}(H) values of $1.5U_{eq}$(C), but were allowed to rotate freely about the C—C bond. All remaining H atoms were placed in idealized positions (C—H = 0.95 Å) and constrained to ride on their parent atoms, with U_{iso}(H) values of $1.2U_{eq}$(C). For compound (II), reflections $\bar{1}31$, $\bar{2}21$ and 021 were partially obscured by the beam stop and were omitted.

For both compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1671). Services for accessing these data are described at the back of the journal.

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