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Ethyl 2,2″-dioxo-2′,3′,5′,6′,7′,7a′-hexahydroacenaphthene-1-spiro-3′-1′*H*-pyrrolizine-2′spiro-1″-acenaphthene-1-carboxylate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.061
wR factor = 0.177
Data-to-parameter ratio = 16.4

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

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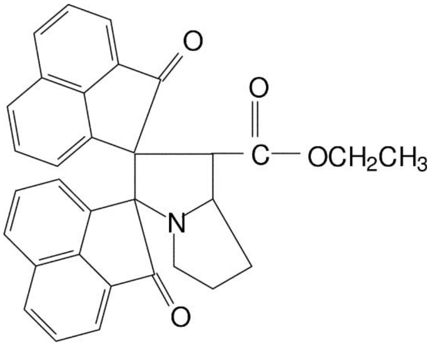
In the title compound, $C_{32}H_{25}NO_4$, the mean plane through the pyrrolizidine system is almost perpendicular [dihedral angle 88.9 (1)°] to that through one of the acenaphthene units, and the dihedral angle between the pyrrolizidine and the second acenaphthene system is 81.6 (1)°. In the pyrrolizidine system, one of the rings is in a half-chair conformation while the other is in an envelope conformation. The overall conformation is twisted about the fusion bond. The crystal structure is stabilized by a C—H···O intermolecular hydrogen bond.

Comment

Pyrrolizidine alkaloids represent a group of compounds present in a variety of plants throughout the world. Crogyrodine has been found to exhibit significant neuromuscular-blocking activity (Suri *et al.*, 1976). Polycyclic aromatic hydrocarbons are of particular interest because of their high toxicity (Jacob, 1996). Bis(*N*-imino)acenaphthene (Ar-BIAN) has been used as the spectator molecule in reaction sequences, modelling the copolymerization of CO and alkenes (Van Asselt *et al.*, 1994; Markies *et al.*, 1995). The structure of the title pyrrolizidine derivative, (I), is reported here (Fig. 1).



(I)

The three N—C distances in (I) differ from each other considerably. Generally, the bond distances and angles of the pyrrolizidine unit are distorted and this can be explained by the spiro character of the compound and the fused-ring system. In the pyrrolizidine unit, the ring-fusion distance [N1—C5 1.480 (3) Å] is in good agreement with values in similar structures (Hay *et al.*, 1982; Sussman & Wedak, 1973; Pérez-Salazar *et al.*, 1978). Bond lengths and angles around the quaternary atom C3 are distorted to some extent from ideal tetrahedral values. For example, the C2—C3 bond is longer than a typical C—C bond of 1.54 (2) Å. The angles around C3 vary from 101.0 (1) to 116.0 (2)°.

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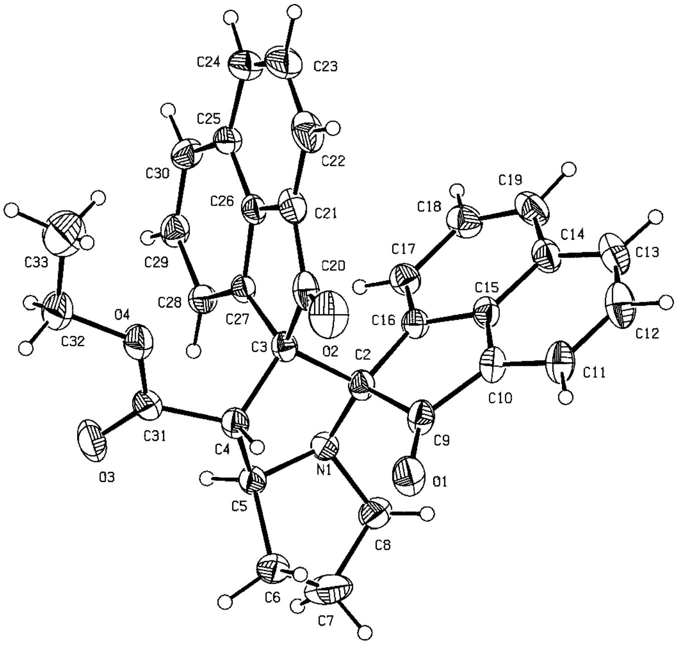

Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids.

The bond lengths and angles of the acenaphthene units of (I) are typical of such systems (Repo *et al.*, 1996; Edwards *et al.*, 1980; Selvanayagam *et al.*, 2004). Ketone atom O1 deviates by 0.230 (2) Å from the C2/C9/C10/C15/C16 plane and is observed as the acceptor in a weak intramolecular hydrogen bond from C6—H6*A*. On the other hand, ketone atom O2 is displaced from the C3/C27/C26/C21/C20 plane by 0.239 (2) Å and acts as an acceptor in a strong intermolecular hydrogen bond from C23—H23 (Table 2).

The dihedral angles between the acenaphthene rings (atoms C2/C9–C19 and C3/C20–C30) and the pyrrolizidine unit (atoms N1/C2–C8) are 88.9 (1) and 82.2 (1)°, respectively. The torsion angles show that the ring containing atoms N1/C2–C5 is in a half-chair conformation, with atom C2 displaced out of the plane of the other four by 0.609 (2) Å, while the ring of atoms N1/C5–C8 is in a near-perfect envelope conformation, with atom C7 displaced out of the plane of the other four atoms by 0.441 (4) Å. The overall conformation of the pyrrolizidine unit is folded and twisted about the fusion bond N1—C5, and this observation is consistent with the structure reported by Sawhney *et al.* (1983). The degree of twist about the N1—C5 bond is given by the torsion angles C8—N1—C5—C6 = 17.1 (2)° and C8—N1—C5—H5 = −99.4 (2)°.

The packing of the molecules of (I) in the crystal structure is stabilized by an intermolecular C—H···O-type hydrogen bond.

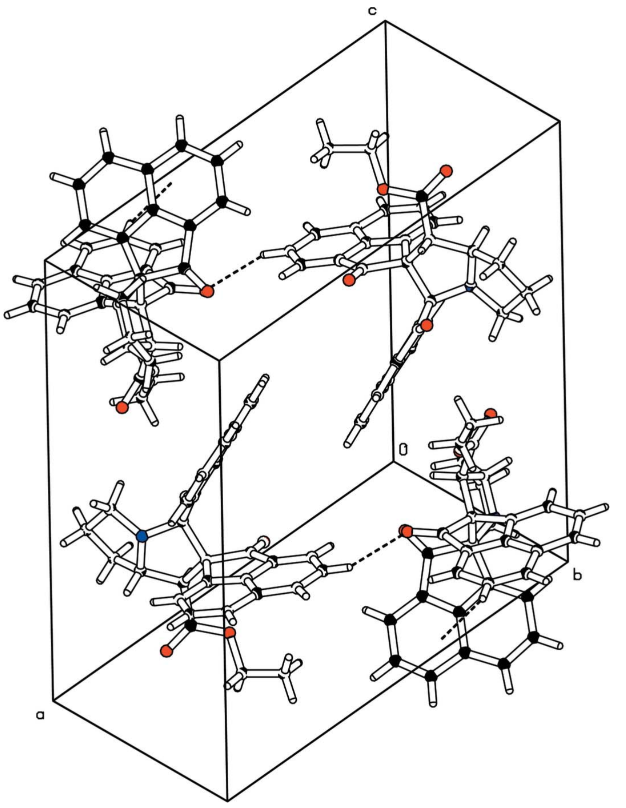

Figure 2
The packing of (I), viewed down the *a* axis. Hydrogen bonds are drawn as dashed lines.

Experimental

Acenaphthenequinone (1 mmol) and proline (1 mmol) were added to a refluxing solution of (2-oxo-2*H*-acenapthylen-1-ylidene)acetic acid ethyl ester (1 mmol) in methanol (10 ml). The mixture was refluxed for 7 h. The solvent was evaporated under reduced pressure and the residue was subjected to column chromotography using hexane–ethyl acetate (8:2), to afford (I) in 78% yield. Crystals suitable for X-ray diffraction were obtained by slow evaporation of dichloromethane–hexane mixture (2:1).

Crystal data

$C_{32}H_{25}NO_4$
$M_r = 487.53$
Monoclinic, $P2_1/c$
$a = 14.8348\ (12)$ Å
$b = 11.1902\ (9)$ Å
$c = 16.0909\ (13)$ Å
$\beta = 112.479\ (1)^\circ$
$V = 2468.2\ (3)$ Å^3
$Z = 4$

$D_x = 1.312$ Mg m^{-3}
Mo- $K\alpha$ radiation
Cell parameters from 4014 reflections
$\theta = 2.3$–26°
$\mu = 0.09$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.23 × 0.21 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: none
14755 measured reflections
5507 independent reflections

4065 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 28.0^\circ$
$h = -19 \rightarrow 18$
$k = -12 \rightarrow 14$
$l = -20 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.178$
$S = 1.00$
5507 reflections
335 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.5944P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.51$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.205 (2)	N1—C8	1.474 (3)
O2—C20	1.201 (2)	N1—C5	1.480 (2)
O3—C31	1.196 (2)	C2—C3	1.571 (3)
O4—C31	1.326 (2)	C9—C10	1.473 (3)
O4—C32	1.450 (3)	C20—C21	1.481 (3)
N1—C2	1.450 (2)	C32—C33	1.456 (5)
C2—N1—C8	118.6 (2)	C27—C3—C20	102.2 (2)
C2—N1—C5	110.0 (1)	C4—C3—C20	116.0 (2)
C8—N1—C5	108.8 (2)	C27—C3—C2	111.0 (1)
N1—C2—C3	100.5 (1)	C4—C3—C2	101.0 (1)
C27—C3—C4	114.9 (1)	C20—C3—C2	112.2 (1)
C8—N1—C5—C6	17.1 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*A*···O1	0.97	2.57	3.214 (3)	124
C23—H23···O2^{i}	0.93	2.35	3.162 (3)	146

Symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

H atoms were positioned geometrically and were treated as riding on their parent C atoms, with aromatic C—H distances of 0.93 Å, methyl C—H distances of 0.96 Å and methylene C—H distances of 0.97 Å, and with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C) for methyl H and $1.2U_{\rm eq}$ (C) for other H.

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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