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N-(2-Benzyloxyethyl)-4,7-dimethyl-6-(1,3-dithiolan-2-yl)-1,2,3,4,5,6-hexahydro-1,5-methano-2-azocino[4,3-*b*]-indol-2-one

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Key indicators

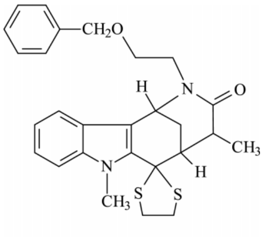
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.056
wR factor = 0.155
Data-to-parameter ratio = 8.7

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

The title compound, $C_{27}H_{30}N_2O_2S_2$, consists of a pentacyclic ring system containing a carbazolenine skeleton with an azocino group, two methyl groups and a dithiolane ring as substituents.

Comment

1,2,3,4-Tetrahydrocarbazole derivatives can be considered to be synthetic precursors of tetracyclic indole alkaloids, having tricyclic ring systems such as those in the *Strychnos* family of indole alkaloids (Bosch & Bonjoch, 1988). Tetrahydrocarbazole systems are present in the framework of a number of indole-type alkaloids of biological interest (Phillipson & Zenk, 1980; Saxton, 1983; Abraham, 1975).



(I)

The structures of tricyclic and pentacyclic ring systems, with dithiolane and other substituents of the tetrahydrocarbazole core, have been the subject of much interest in our laboratory. These include 1,2,3,4-tetrahydrocarbazole-1-spiro-2′-[1,3]dithiolane, (II) (Hökelek *et al.*, 1994), *N*-(2-methoxyethyl)-*N*-{2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2-(1,3)dithiolane]-4-yl}benzenesulfonamide, (III) (Patır *et al.*, 1997), spiro[carbazole-1(2*H*),2′-[1,3]-dithiolan]-4(3*H*)-one, (IV) (Hökelek *et al.*, 1998), 9-acetonyl-3-ethylidene-1,2,3,4-tetrahydrospiro-[carbazole-1,2′-[1,3]dithiolan]-4-one, (V) (Hökelek *et al.*, 1999), and *N*-(2,2-dimethoxyethyl)-*N*-{9-methoxymethyl-1,2,3,4-tetrahydro-spiro[carbazole-1,2′-[1,3]dithiolan]-4-yl}-benzamide, (VI) (Hökelek & Patır, 1999); also the pentacyclic compound 6-ethyl-4-(2-methoxyethyl)-2,6-methano-5-oxo-hexahydropyrrolo(2,3-*d*)carbazole-1-spiro-2′-(1,3)dithiolane, (VII) (Hökelek & Patır, 2002).

The hexahydro-1,5-methano[4,3-*b*]indole basic skeletal framework can be considered to be a synthetic precursor of pentacyclic indole alkaloids. These alkaloids share the *ABCDE* ring system as a common structural element, and include a large group of naturally occurring compounds, with highly complex structures (Rahman & Basha, 1983). They have pharmacological and extremely toxic properties.

Compound (I) (Fig. 1) consists of a pentacyclic system containing a carbazolenine skeleton with an azocino, two methyl groups and a dithiolane ring as substituents at posi-

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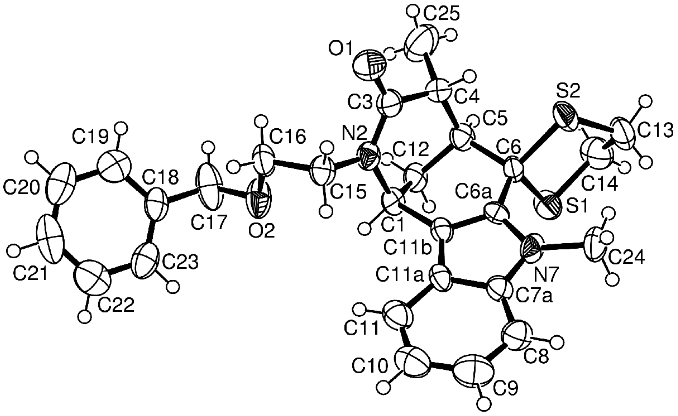

Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

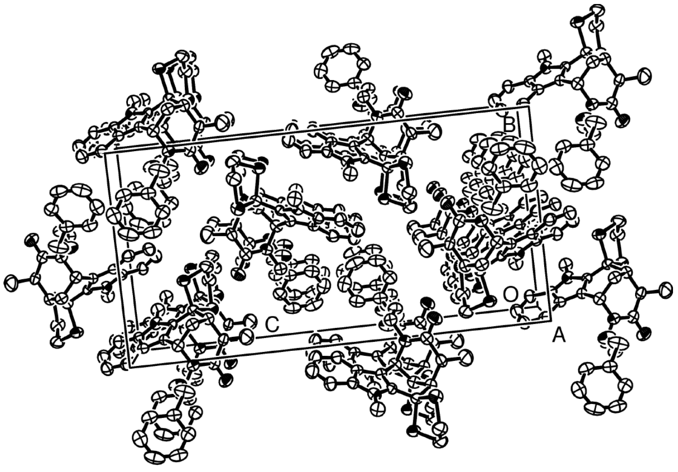

Figure 2
A packing diagram, viewed down the *a* axis. H atoms have been omitted.

tions N2, N7, C4 and C6, respectively. As can be seen from the packing diagram (Fig. 2), the molecules are stacked along the *a* axis. Dipole–dipole and van der Waals interactions are effective in the molecular packing.

The S atoms of the dithiolane ring have electron-releasing properties, but the N atom at position 7 and the O atom attached to C3 have electron-withdrawing properties, leading to some changes in the bond lengths and angles of the carbazolenine skeleton.

Some angles in the carbazolenine skeleton are compared with those in the structures of other tricyclic ring systems containing the dithiolane substituent (Table 2). The bond lengths N7—C7a and N7—C6a agree well with those in compounds (V) and (VI) [1.370 (8), 1.377, 1.376; 1.392 (8), 1.396 and 1.391 Å, respectively]. In all three structures atom N7 is substituted.

An examination of the deviations from the least-squares planes through individual rings shows that rings *A* (C7a/C8/C9/C10/C11/C11a), *B* (N7/C7a/C11a/C11b/C6) and *F* (C18–C23) are planar. Rings *C* (C1/C11b/C6a/C6/C5/C12), *D* (C1/N2/C3/C4/C5/C12) and *E* (C6/S1/C14/C13/S2) are, of course, not planar.

The structure reveals a number of short contacts S1$\cdots$H5(C5) = 2.777 (2), S2$\cdots$H4(C4) = 2.483 (2), O1$\cdots$H15*A*(C15) = 2.379 (5), O1$\cdots$H25*B*(C25) = 2.585 (5), O1$^{i}\cdots$H13*A*(C13) = 2.486 (5) and O2$\cdots$H1(C1) = 2.651 (5) Å [symmetry code: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$].

Experimental

The title compound, (I), was prepared from sodium hydride (24.0 mg, 1.0 mmol) and *N*-(2-benzoyloxyethyl)-6-(1,3-dithiolan-2-yl)-1,2,3,4,-5,6-hexahydro-1,5-methano-2-azocino[4,3-*b*]indol-2-one (450.0 mg, 1.0 mmol) in THF (30 ml) and methyl iodide (1.0 ml). The mixture was heated at reflux for 4 h under a nitrogen atmosphere. The mixture was later cooled in an ice bath and methanol (5 ml) and water (20 ml) were added. After extraction with chloroform (30 ml), the organic layer was dried with $MgSO_4$ and the solvent was evaporated. The residue was crystallized from benzene:*n*-hexane (1:9) (yield 390.0 mg, 84%), m.p. 418.6 K.

Crystal data

$C_{27}H_{30}N_2O_2S_2$
M_r = 478.65
Orthorhombic, $P2_12_12_1$
a = 7.8787 (10) Å
b = 12.446 (2) Å
c = 24.501 (3) Å
V = 2402.5 (6) Å^3
Z = 4
D_x = 1.323 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–18°
μ = 0.25 mm^{-1}
T = 293 (2) K
Block, colourless
0.35 × 0.25 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: none
2790 measured reflections
2790 independent reflections
1470 reflections with $I > 2\sigma(I)$

θ_{max} = 26.3°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = -30 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.155$
S = 1.03
2543 reflections
292 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.843 (7)	C11a—C11	1.412 (7)
S2—C6	1.867 (6)	C11a—C7a	1.421 (7)
N2—C3	1.339 (8)	C7a—C8	1.390 (6)
N7—C7a	1.370 (8)	C5—C6	1.561 (7)
N7—C6a	1.392 (8)	C8—C9	1.359 (8)
C6a—C6	1.487 (8)	C11—C10	1.380 (8)
C11a—C11b	1.401 (8)	C9—C10	1.413 (7)
C3—N2—C1	122.5 (6)	C16—O2—C17	111.9 (6)
O1—C3—N2	121.0 (7)	N7—C7a—C8	129.7 (6)
C11b—C6a—N7	107.9 (5)	N7—C7a—C11a	107.4 (6)
C11b—C6a—C6	124.6 (6)	C8—C7a—C11a	122.8 (7)
N7—C6a—C6	127.2 (5)	C6a—C11b—C11a	109.0 (6)
C11b—C11a—C11	136.0 (7)	C6a—C11b—C1	121.8 (6)
C11b—C11a—C7a	106.5 (6)	C6a—C6—C5	110.6 (5)
C14—S1—C6—S2	−22.0 (4)	S2—C13—C14—S1	−51.0 (7)
C13—S2—C6—S1	−2.4 (4)	C6—S1—C14—C13	45.3 (6)
C6—S2—C13—C14	32.3 (6)		

Table 2

Comparison of the bond angles (°) in the carbazole core of (I) with the corresponding values in the related compounds (II), (III), (IV), (V) and (VI).

	(I)	(II)	(III)	(IV)	(V)	(VI)
C6—C6a—N7	127.2 (5)	125.0 (3)	124.1 (7)	126.4 (2)	127.5 (2)	126.7 (2)
C11b—C11a—C11	136.0 (7)	133.6 (4)	136.3 (8)	134.7 (2)	134.0 (3)	134.7 (2)
N7—C7a—C8	129.7 (6)	130.8 (4)	128.1 (9)	129.8 (2)	129.4 (3)	129.1 (2)
S1—C6—C6a	106.6 (4)	110.2 (3)	112.1 (5)	112.8 (1)	115.9 (1)	115.9 (2)
C6a—N7—C7a	109.2 (5)	108.6 (3)	108.1 (6)	109.6 (1)	108.1 (1)	108.1 (2)

Most of the reflections were weak probably due to the crystal quality. H atoms were positioned geometrically and refined with a riding model, with C—H in the range 0.93–0.98 Å. $U_{\rm iso}$ values were constrained to be 1.2 (1.3 for methyl groups) times $U_{\rm eq}$ of the carrier atom. The Flack (1983) parameter refined to a value of 0.7 (2), making the absolute configuration indeterminate.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); 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: *WinGX* (Farrugia, 1999).

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