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4-Ethyl-6,6-ethylenedithio-2-(2-methoxyethyl)-7-methoxymethylene-2,3,4,5,6,7-hexahydro-1,5-methano-1*H*-azocino[4,3-*b*]indol-3-one

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.063
wR factor = 0.181
Data-to-parameter ratio = 14.5

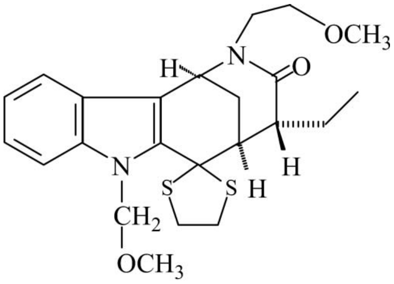
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{23}H_{30}N_2O_3S_2$, the dithiolane ring adopts an envelope conformation. In the crystal structure, the molecules are stacked along the *b* axis; dipole–dipole and van der Waals interactions are effective in the packing.

Comment

Tetrahydrocarbazole systems are present in the framework of a number of indole-type alkaloids of biological interest (Phillipson & Zenk, 1980; Saxton, 1983; Abraham, 1975). The structures of tri-, tetra- 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-tetrahydrospiro[carbazole-1,2′-(1,3-dithiolan)]-4-yl}-benzamide, (VI) (Hökelek & Patır, 1999); also the pentacyclic compounds 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) and *N*-(2-benzyloxy-ethyl)-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, (VIII) (Hökelek *et al.*, 2004).

Azocino[4,3-*b*]indole derivatives can be considered as synthetic precursors of pentacyclic indole alkaloids of the strychnos family, such as tubifoline, tubifolidine and 19,20-dihydroakummicine (Rahman & Basha, 1983). These alkaloids share the *ABCDE* ring system as a common structural element and include a large group of naturally occurring compounds such as strychnine, a convulsant poison. We present here the crystal structure of the title compound, (I).


(I)

doi:10.1107/S1600536806002601

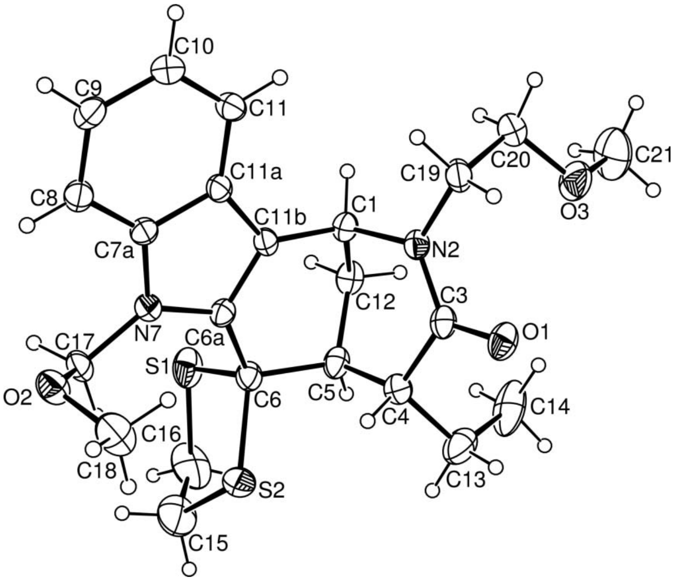


Figure 1
A drawing of the title molecular structure, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

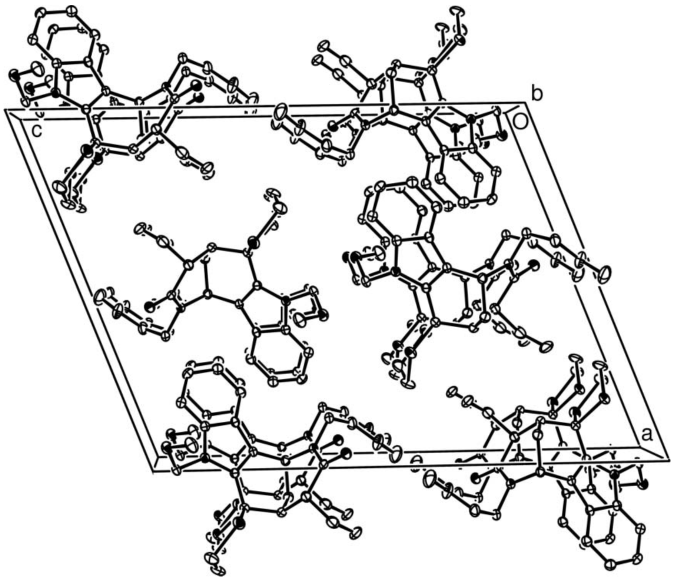


Figure 2
A packing diagram for (I), viewed down the *b* axis. H atoms have been omitted.

Compound (I) (Fig. 1) consists of a pentacyclic system containing an azocine skeleton, with methoxyethyl, ethyl and methoxymethylene groups and a dithiolane ring as substituents at positions N2, C4, N7 and C6, respectively.

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 azocino[4,3-*b*]indole skeleton.

An examination of the deviations from the least-squares planes through individual rings shows that rings *A* (C7a/C8–C11/C11a) and *B* (N7/C7a/C11a/C11b/C6a) are both planar. They are also nearly coplanar, with a dihedral angle of 0.74 (11)°. Rings *C* (C1/C11b/C6a/C6/C5/C12), *D* (C1/N2/C3–C5/C12) and *E* (C6/S1/S2/C13/C14) are, of course, not planar. Ring *E* has a local pseudo-mirror plane running through C16 and the midpoint of the C6—S2 bond (Table 1). The conformation of ring *E* is an envelope, with atom C16 at the flap position, 0.721 (6) Å from the mean plane through the other four atoms.

Some angles in the carbazole skeleton are compared with those in the structures of other tri-, tetra- and pentacyclic ring systems containing the dithiolane substituent (Table 2). The bond length of N7—C7a [1.386 (5) Å] agrees well with the values in compounds (V), (VI) and (VIII) [1.377 (2), 1.376 (4) and 1.370 (8) Å, respectively]. Likewise, the bond length of N7—C6a [1.393 (4) Å] agrees well with the values in compounds (V), (VI) and (VIII) [1.396 (2), 1.391 (4) and 1.392 (8) Å, respectively]. In all four structures, atom N7 is substituted.

As can be seen from the packing diagram (Fig. 2), the molecules of (I) are stacked along the *b* axis. Dipole–dipole and van der Waals interactions are effective in the molecular packing. The structure reveals a number of short contacts: S2···H4(—C4) = 2.481, N7···H18b(—C18) = 2.591, O1···H19a(—C19) = 2.364, O2···H8(—C8) = 2.557 and O1^{i}···H9(—C9) = 2.454 Å [symmetry code: (i) $-x-\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$].

Experimental

The title compound, (I), was prepared from sodium hydride (0.1 g, 2.50 mmol) and 2-(2′-methoxyethyl)-2,3,4,5,6,7-hexahydro-1,5-methano-3-oxo-6,6-ethylene-dithio-7-(methoxymethylene)-1*H*-azocino[4,3-*b*]indole (0.4 g, 0.95 mmol) in tetrahydrofuran (20 ml) and iodoethane (0.39 g, 2.50 mmol). The mixture was stirred at 338 K for 12 h and then poured into sodium hydroxide solution (20 ml, 10%). After extraction with dichloromethane (100 ml), the organic layer was dried with $MgSO_4$ and the solvent was evaporated. The residue was crystallized from acetone–*n*-hexane (1:4) (yield 0.32 g, 75%; m.p. 409 K).

Crystal data

$C_{23}H_{30}N_2O_3S_2$
$M_r = 446.64$
Monoclinic, $P2_1/n$
$a = 15.897$ (3) Å
$b = 7.0394$ (14) Å
$c = 21.195$ (3) Å
$\beta = 111.164$ (13)°
$V = 2211.8$ (7) Å^3
$Z = 4$
$D_x = 1.341$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 3.2$–$34.6°$
$\mu = 2.40$ mm^{-1}
$T = 298$ (2) K
Rod, colourless
0.35 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non–profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.590$, $T_{max} = 0.697$
4215 measured reflections
4119 independent reflections
2322 reflections with $I > 2\sigma(I)$
$R_{int} = 0.089$
$\theta_{max} = 71.1°$
$h = -18 \rightarrow 19$
$k = -8 \rightarrow 0$
$l = -26 \rightarrow 0$
3 standard reflections every 120 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.181$
$S = 1.03$
3919 reflections
271 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0876P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.840 (4)	C7a—N7	1.386 (5)
S2—C6	1.868 (5)	C7a—C11a	1.414 (5)
N2—C3	1.346 (5)	C9—C8	1.382 (5)
C6—C5	1.555 (5)	C10—C11	1.362 (5)
C6a—N7	1.393 (4)	C10—C9	1.398 (6)
C6a—C6	1.491 (5)	C11a—C11	1.401 (5)
C7a—C8	1.374 (5)	C11a—C11b	1.429 (5)
C17—O2—C18	113.7 (4)	C8—C7a—N7	129.6 (4)
C3—N2—C1	121.4 (3)	C8—C7a—C11a	122.0 (4)
O1—C3—N2	122.6 (4)	N7—C7a—C11a	108.4 (3)
C6a—C6—C5	109.1 (3)	C11—C11a—C11b	135.1 (4)
C11b—C6a—N7	108.3 (3)	C7a—C11a—C11b	106.2 (3)
C11b—C6a—C6	123.6 (4)	C6a—C11b—C11a	108.3 (3)
N7—C6a—C6	127.8 (3)	C6a—C11b—C1	122.8 (3)
C6—S1—C16—C15	45.4 (5)	C6—S2—C15—C16	26.4 (5)
C16—S1—C6—S2	−25.6 (3)	S2—C15—C16—S1	−47.6 (5)
C15—S2—C6—S1	3.4 (3)		

Table 2
Comparison of the bond angles (°) in the carbazole core of (I) with the corresponding values in related compounds.

Compound	(I)	(II)	(III)	(IV)	(V)	(VI)	(VIII)
C6—C6a—N7	127.8 (3)	125.0 (3)	124.1 (7)	126.4 (2)	127.5 (2)	126.7 (2)	127.2 (5)
C11b—C11a—C11	135.1 (4)	133.6 (4)	136.3 (8)	134.7 (2)	134.0 (3)	134.7 (2)	136.0 (7)
N7—C7a—C8	129.6 (4)	130.8 (4)	128.1 (9)	129.8 (2)	129.4 (3)	129.1 (2)	129.7 (6)
S1—C6—C6a	107.4 (3)	110.2 (3)	112.1 (5)	112.8 (1)	115.9 (1)	115.9 (2)	106.6 (4)
C6a—N7—C7a	108.8 (3)	108.6 (3)	108.1 (6)	109.6 (1)	108.1 (1)	108.1 (2)	109.2 (5)

Most of the reflections were weak, probably due to the poor quality of the crystal. To improve the *R* factor, 200 reflections for which the difference between observed and calculated structure factors was 20–40% were suppressed in the refinement process. H atoms were positioned geometrically, with C—H = 0.93, 0.96, 0.97 or 0.98 Å for aromatic, methyl, methylene and methine H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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