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A novel bridged hexahydropyrrolo[2,3-*d*]carbazole

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.064
wR factor = 0.217
Data-to-parameter ratio = 15.8

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

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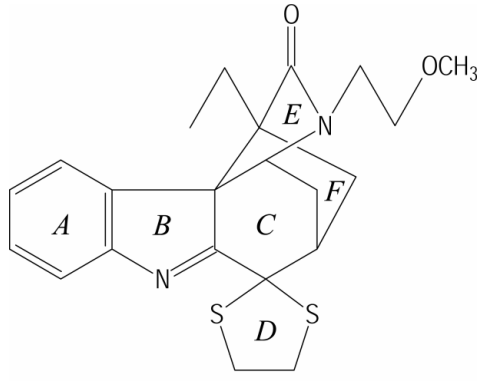
The title compound, $C_{22}H_{26}N_2O_2S_2$, consists of a pentacyclic system containing a carbazolenine skeleton with an ethyl group, a methoxyethyl group and a dithiolane ring as substituents. A few interatomic close contacts seem to influence the geometry of the carbazolenine core structure.

Comment

The structures of tricyclic ring systems such as those in the Strychnos family of indole alkaloids (Bosch & Bonjoch, 1988), 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).



(I)

The hexahydropyrrolo[2,3-*d*]carbazole skeleton can be considered to be a synthetic precursor of pentacyclic indole alkaloids. These alkaloids share the *ABCE* ring system (see Scheme) as a common structural element. Indole alkaloids include a large group of naturally occurring compounds, with highly complex structures, possessing the indole or dihydroindole (indoline) core. They include important biologically active compounds such as strychnine and the clinical anticancer agents vincristine and vinblastine (Rahman & Basha, 1983).

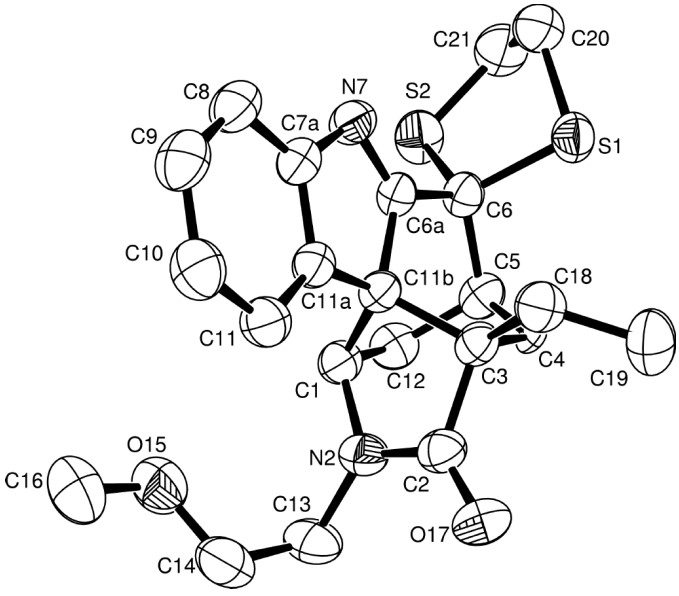


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of compound (I), with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

Compound (I) (Fig. 1) consists of a pentacyclic system containing a carbazolenine skeleton, with ethyl and methoxyethyl groups and a dithiolane ring as substituents at positions 3, N2 and 6, 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 C2 have electron-withdrawing properties, leading to some changes in the bond lengths and angles of the carbazolenine skeleton. The structure reveals a number of short contacts: S1···H4*A*(C4) 2.364 (1), S2···H12*B*(C12) 2.815 (1), O17···H13*A*(C13) 2.618 (3), O17···H19*C*(C19) 2.704 (3), O17···H21*B*(C21) (i) 2.424 (3), and O17···H16*B*(C16) (ii) 2.580 (3) Å [symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+1, -y+1, -z+1$]. Some significant changes in the geometry of the carbazolenine skeleton are evident when a few bond angles are compared with those in the structures of other tricyclic ring system containing the dithiolane substituent (Table 2).

An examination of the deviations from the least-squares planes through the individual rings shows that ring *A* (C7*A*/C8/C9/C10/C11/C11*A*) is planar, while ring *B* (N7/C7*A*/C11*A*/C11*B*/C6*A*) is nearly planar, with a maximum deviation for atom C6*A* [0.013 (3) Å]. Ring *D* (C6/S1/C20/C21/S2) is, of course, not planar. The rings are also twisted with respect to each other; thus, the dihedral angles between the mean least-squares planes are *A*/*B* = 0.9 (1), *A*/*D* = 87.7 (1), and *B*/*D* = 87.8 (1)°. The conformation of ring *D* is half-chair, with a local pseudo-twofold axis running through C20 and the midpoint of the S2—C6 bond.

Experimental

Compound (I) was prepared from sodium hydride (20.0 mg, 0.50 mmol) and *N*-(2-oxobutanyl)-*N*-(2-methoxyethyl)-{2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2′-[1,3]dithiolane]-4-yl}amine (100.0 mg, 0.23 mmol) in THF (50 and 10 ml, respectively). The mixture was stirred for 3 h under a nitrogen atmosphere. Later, it was 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 ethanol (yield 21.0 mg, 22%), m.p. 492 K.

Crystal data

$C_{22}H_{26}N_2O_2S_2$
M_r = 414.57
Monoclinic, $P2_1/n$
a = 8.683 (1) Å
b = 22.975 (2) Å
c = 9.973 (1) Å
β = 94.68 (1)°
V = 1982.9 (3) Å^3
Z = 4
D_x = 1.389 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.29 mm^{-1}
T = 293 (2) K
Prism, colorless
0.3 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Non-profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.933, T_{max} = 0.971
4283 measured reflections
4016 independent reflections
3067 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 26.3°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 28$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.217
S = 1.06
4016 reflections
254 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.122P)^2 + 2.1074P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.021
$\Delta\rho_{max}$ = 1.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.80 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S2—C6	1.833 (3)	N2—C2	1.332 (5)
S1—C6	1.832 (3)	C6*A*—C6	1.504 (4)
C11*A*—C11	1.387 (5)	C11—C10	1.392 (5)
C11*A*—C7*A*	1.399 (4)	C7*A*—C8	1.375 (5)
C11*A*—C11*B*	1.493 (4)	C6—C5	1.543 (5)
N7—C6*A*	1.287 (4)	C8—C9	1.386 (5)
N7—C7*A*	1.436 (4)	C10—C9	1.382 (6)
C11—C11*A*—C11*B*	133.4 (3)	C11*A*—C7*A*—N7	112.2 (3)
C7*A*—C11*A*—C11*B*	106.4 (3)	C4—C3—C18	109.4 (3)
C2—N2—C1	112.1 (3)	C18—C3—C2	115.8 (3)
C11*A*—C11*B*—C6*A*	100.4 (2)	C4—C3—C11*B*	107.6 (2)
C3—C11*B*—C1	98.0 (2)	C2—C3—C11B	100.6 (3)
O17—C2—N2	126.2 (3)	C5—C12—C1	109.2 (3)
N2—C2—C3	106.9 (3)	C6*A*—C6—C5	104.5 (3)
C20—S1—C6—S2	28.4 (2)	S1—C20—C21—S2	51.2 (3)
C21—S2—C6—S1	−4.4 (2)	C6—S2—C21—C20	−27.9 (3)
C6—S1—C20—C21	−48.8 (3)		

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).

Angle	(I)	(II)	(III)	(IV)	(V)	(VI)
C6—C6*A*—N7	128.9 (3)	125.0 (3)	124.1 (7)	126.4 (2)	127.5 (2)	126.7 (2)
C11*B*—C11*A*—C11	133.4 (2)	133.6 (4)	136.3 (8)	134.7 (2)	134.0 (3)	134.7 (2)
N7—C7*A*—C8	126.1 (3)	130.8 (4)	128.1 (9)	129.8 (2)	129.4 (3)	129.1 (2)
S1—C6—C6*A*	109.2 (2)	110.2 (3)	112.1 (5)	112.8 (1)	115.9 (1)	115.9 (2)
C6*A*—N7—C7*A*	105.2 (3)	108.6 (3)	108.1 (6)	109.6 (1)	108.1 (1)	108.1 (2)

The largest final difference electron-density peak, 1.35 e Å^{-3}, was located 0.22 Å from C4. The positions of the H atoms were calculated geometrically at distances of 0.95 (aromatic CH), 1.00 (CH), 0.99 (CH_2) and 0.98 Å (CH_3) from the parent C atoms, and a riding model was used during the refinement process.

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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