

Table 1. Selected geometric parameters (Å, °)

P1—N1	1.583 (4)	P2—N1	1.585 (3)
P1—N2	1.578 (4)	P2—N2'	1.585 (4)
N1—P1—N2	121.5 (2)	P1—N1—P2	127.3 (2)
N1—P2—N2'	117.4 (2)	P1—N2—P2'	134.4 (2)
N3—P1—N1—P2	-138.1 (3)	N6—P2—N1—P1	-176.9 (3)
N4—P1—N1—P2	106.7 (4)	N5—P2—N1—P1	-65.1 (4)
N2—P1—N1—P2	-14.1 (5)		

Symmetry code: (i) $-x, 1 - y, -z$.

The title structure was solved by the Patterson method. H-atom positions were calculated geometrically, with $U(\text{H}) = 1.3U_{\text{eq}}$ of the parent non-H atom. A riding model was used in the refinement. Due to the inconsistent values of some of the components of the displacement parameters of the C5 and C7 atoms, they were refined isotropically during the refinement process.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1358). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 1297–1299

Spiro[carbazole-1(2H),2'-[1,3]dithiolan]-4(3H)-one

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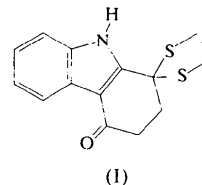
(Received 3 March 1998; accepted 3 April 1998)

Abstract

The title compound, C₁₄H₁₃NOS₂, consists of a carbazole skeleton and a pentacyclic dithiolane ring bonded at position 1. The heteroatoms in the molecule are responsible for the changes in the bond lengths and angles of the carbazole core.

Comment

The title compound is an intermediate in the synthesis of tetracyclic indole alkaloids (Patr, 1995; Patr *et al.*, 1996). It is used as a starting material for the preparation of 4-aminotetrahydrocarbazol-1-one derivatives (Patr & Götz, 1993; Patr *et al.*, 1997). The tricyclic 4-aminotetrahydrocarbazole and 2-chain-substituted 4-oxocarbazole derivatives allow formation of the dasycarpidone skeleton (Magnus *et al.*, 1992). Except for the 4-acetaminotetrahydrocarbazole derivative (Vogel *et al.*, 1982), 4-aminotetrahydrocarbazole has not been isolated in the free form, until now. Recently, starting from the title compound, (I), the stable tricyclic 4-aminotetrahydrocarbazole derivative was isolated in the free form (Patr, 1995; Patr & Götz, 1993). The structure determination of the title compound, (I), was undertaken in order to understand the effects of the dithiolane ring at position 1 on the geometry of the carbazole system and to compare the results obtained with those of 2,3-dihydro-9-(phenylsulfonyl)carbazole-4(1H)-one and 1,2,3,4-tetrahydrocarbazole-1-spiro-2'-[1,3]dithiolane (Hökelek *et al.*, 1994).



The title compound (Fig. 1) consists of a carbazole skeleton and a pentacyclic dithiolane ring spiro-bonded at position 1. The S atoms of the dithiolane

ring have electron-releasing properties, but the N atom at position 9 and the O atom at position 4 have electron-withdrawing properties, leading to some changes in the bond lengths and angles of the carbazole skeleton. The interatomic distances N9...H81 2.75 (3), S1...H9 2.93 (2), S1...H21 2.83 (2), S1...H22 2.95 (2), S2...H22 2.89 (2), O1...H31 2.53 (3) and O1...H32 2.76 (2) Å indicate that close contacts cause changes in the values of the bond lengths and angles of the carbazole skeleton.

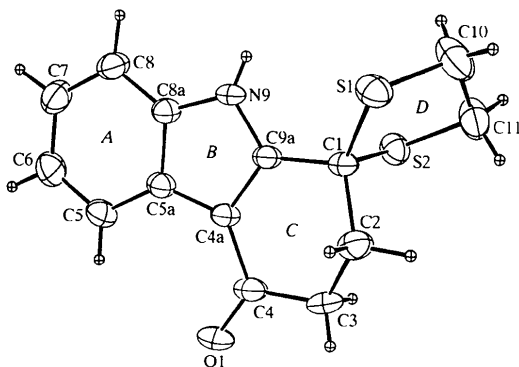


Fig. 1. An ORTEP (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

The absence of any protecting group at the N9 atom causes shortening of the C—N bonds [N9—C8a 1.382 (2) and N9—C9a 1.355 (3) Å] with respect to the corresponding ones [N9—C8a 1.423 (5) and N9—C9a 1.412 (5) Å] in 2,3-dihydro-9-(phenylsulfonyl)carbazole-4(1*H*)-one (Hökelek *et al.*, 1994). An examination of the deviations from the least-squares planes through the individual rings shows that rings A (C5a, C5—C8, C8a) and B (C4a, C5a, C8a, N9, C9a) are planar, and that rings C (C1—C4, C4a, C9a) and D (C1, S1, C10, C11, S2) are not planar, with maximum deviations for the C2 [−0.254 (2) Å] and C11 [0.587 (3) Å] atoms. These rings are also twisted with respect to each other. The dihedral angles between the best least-squares planes are A/B 1.7 (1), B/C 8.7 (1) and C/D 81.5 (1)°. Ring C has a sofa conformation with a local pseudo-mirror running along C2...C4a, while the conformation of ring D is half-chair with a local pseudo-twofold axis running along S1 and the midpoint of the S2—C11 bond.

Experimental

Compound (I) was prepared from the reaction of 3,4-dihydrospiro[1*H*-carbazole-1(2*H*),2′-[1,3]dithiolane] (3.0 g, 11.5 mmol) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (5.2 g, 22.9 mmol) in THF (50 ml) according to the literature

method of Patir & Götz (1993). The compound was crystallized from methanol [m.p. 521 K; yield: 2.9 g (92%)].

Crystal data

C₁₄H₁₃NOS₂
M_r = 275.38
 Monoclinic
*P*2₁/*c*
a = 7.537 (1) Å
b = 16.928 (1) Å
c = 10.292 (1) Å
 β = 106.044 (5)°
V = 1262.1 (2) Å³
Z = 4
D_x = 1.449 Mg m^{−3}
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 10–18°
 μ = 0.407 mm^{−1}
T = 298 K
 Block
 0.30 × 0.25 × 0.20 mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
 T_{\min} = 0.890, T_{\max} = 0.922
 2860 measured reflections
 2561 independent reflections

2404 reflections with $F > 2\sigma(F)$
 R_{int} = 0.063
 θ_{\max} = 26.3°
 h = 0 → 9
 k = 0 → 20
 l = −12 → 12
 3 standard reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

Refinement on *F*
 R = 0.040
 wR = 0.046
 S = 1.01
 2404 reflections
 215 parameters
 All H atoms refined
 $w = 1/[\sigma(F)^2 + (0.02F)^2 + 1.0]$

$(\Delta/\sigma)_{\max}$ = 0.01
 $\Delta\rho_{\max}$ = 0.41 e Å^{−3}
 $\Delta\rho_{\min}$ = −0.25 e Å^{−3}
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

S2—C11	1.792 (2)	C3—C4	1.503 (3)
S2—C1	1.835 (2)	C4—C4a	1.448 (3)
S1—C10	1.804 (3)	C4a—C9a	1.392 (2)
S1—C1	1.837 (2)	C4a—C5a	1.439 (3)
O1—C4	1.234 (2)		
C11—S2—C1	94.6 (1)	C2—C1—C9a	107.9 (1)
C10—S1—C1	98.4 (1)	C1—C2—C3	112.3 (2)
C9a—N9—C8a	109.6 (1)	C2—C3—C4	114.7 (2)
S2—C11—C10	107.5 (2)	C3—C4—C4a	115.9 (2)
S1—C10—C11	109.7 (2)	C4—C4a—C9a	122.0 (2)
S1—C1—S2	106.93 (8)	C1—C9a—C4a	124.3 (2)
S2—C1—C2	111.7 (2)		

The title structure was solved by direct methods. H-atom positions were located by difference synthesis and refined isotropically. The high value of R_{int} is probably due to the poor quality of the crystals.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Acta Cryst. (1998). **C54**, 1299–1301

An *N*-Substituted 6,7-Benzocoumarin-8,9-aziridine Derivative

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(Received 9 February 1998; accepted 6 March 1998)

Abstract

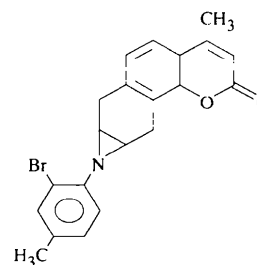
In the title compound, 8-(2-bromo-4-methylphenyl)-4-methyl-2,7,7a,8,8a,9-hexahydropyrano[2',3':1,2]naphth-[6,7]aziridin-2-one, C₂₁H₁₈BrNO₂, the tetrahydrobenzene ring adopts a flattened-boat conformation. The aziridine plane forms dihedral angles of 80.4 (1) and 59.1 (2)°

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with the tetrahydrobenzene and *N*-phenyl substituent ring planes, respectively. The crystal structure is stabilized by weak C—H···O intermolecular hydrogen bonds and π – π stacking interactions of the coumarin ring.

Comment

The title compound is a newly synthesized member of the aziridine family. The aziridine ring is a versatile building block for organic synthesis, not only because the ring opening of aziridines provides a convenient entry to the stereoselective preparation of functionalized amino compounds, but also because exocyclic *N*-substituents modulate the properties and reactivity of the three-membered ring (Pearson *et al.*, 1996; Tanner, 1994). Because of their high reactivity, aziridines serve as useful intermediates in the synthesis of several natural products, such as mitomycin, crinine and reframidine (Kametani & Honda, 1986). The structural study of the title compound, (I), was undertaken in order to elucidate the molecular conformation and packing arrangement.



(I)

The bond lengths and angles in the structure agree with those observed in aziridine and coumarin derivatives (Chinnakali *et al.*, 1997, 1998; Kumar *et al.*, 1997). The N atom has pyramidal bonding geometry. In the coumarin ring system, the pyran ring is planar, with a maximum deviation of 0.030 (3) Å for C2; the dihedral angle between the benzene and pyran rings is 1.85 (9)°. The tetrahydrobenzene ring adopts a flattened-boat conformation with C12 and C15 deviating from the plane of C7, C8, C13 and C14 by 0.117 (4) and 0.110 (3) Å, respectively. The asymmetry parameters are $\Delta C_s(C12) = 0.010(1)$ and $\Delta C_s(C7-C8) = 0.008(1)$ (Nardelli, 1983). The best plane through the tetrahydrobenzene ring makes a dihedral angle of 2.51 (8)° with the benzene ring. The aziridine plane forms dihedral angles of 80.4 (1) and 59.1 (2)°, respectively, with the best plane through the tetrahydrobenzene and substituent phenyl rings. In the crystal, the carbonyl O atom is involved in a weak C—H···O intermolecular hydrogen bond [C19···O11ⁱ 3.412 (4) Å and C19—H19···O11ⁱ 156 (2)°; symmetry code: (i) $x - \frac{1}{2}, -y - \frac{1}{2}, -z$]; the coumarin rings of the molecules are stacked 3.474 (3) Å apart, an optimum distance for π – π stacking interactions.