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N-(2,2-Dimethoxyethyl)-*N*-{9-methoxymethyl-1,2,3,4-tetrahydrospiro[carbazole-1,2′-[1,3]dithiolan]-4-yl}benzamide

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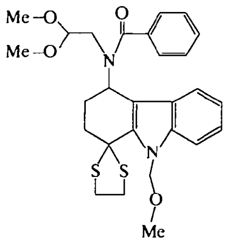
Abstract

The title compound, $C_{27}H_{32}N_2O_4S_2$, consists of a carbazole skeleton, a pentacyclic dithiolane ring spirobonded at position 1 and methoxymethyl- and amino-bonded carbazole chains, containing acetal and benzoyl groups, at positions 9 and 4, respectively. The methoxymethyl protecting group and the amino-functionalized acetal and benzoyl chains are responsible for changes in the bond angles of the carbazole core.

Comment

The structures of tetrahydrocarbazole derivatives having different substituents *e.g.* *N*-(2-methoxymethyl)-*N*-{2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2-[1,3]dithiolan]-4-yl}benzenesulfonamide (Patır *et al.*, 1997), 2,3-dihydro-9-(phenylsulfonyl)carbazole-4(1*H*)-one and 1,2,3,4-tetrahydrocarbazole-1-spiro-2′-[1,3]dithiolane (Hökelek *et al.*, 1994) have been the subject of much interest in our laboratory.

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 presence of an amino group on the C4 atom and a keto group on the C1 atom (according to carbazole numbering) allows the integration of ring *D* in tetracyclic indole alkaloids (Patır, 1995; Patır *et al.*, 1996). The title compound, (I), is used as a key intermediate in the synthesis of the dasycarpidone skeleton (Patır *et al.*, 1996). For the synthesis of the dasycarpidone skeleton, the protecting dithiolane group in the title compound is first removed to form 9-methoxymethyl-4-[benzoyl-(2,2-dimethoxyethyl)amino]-2,3,4,9-tetrahydro-1*H*-carbazole-1-one. Later, acetal and ether groups are cleaved to form [benzoyl-(1-oxo-2,3,4,9-tetrahydrocarbazole-1-one-4-yl)amino]acetaldehyde which has been converted to azocino[4,3-*b*]indole by a novel type of ring closure (Patır *et al.*, 1996).



(I)

The structure determination of the title compound was undertaken in order to understand the effects of the acetal, benzoyl and methoxymethyl groups at positions 4 and 9 on the geometry of the carbazole system, and to compare the obtained results with those of 2,3-dihydro-9-(phenylsulfonyl)carbazole-4(1*H*)-one, 1,2,3,4-tetrahydrocarbazole-1-spiro-2′-[1,3]dithiolane (Hökelek *et al.*, 1994), spiro[carbazole-1(2*H*),2′-[1,3]dithiolan]-4(3*H*)-one (Hökelek *et al.*, 1998) and 9-acetonyl-3-ethylidene-1,2,3,4-tetrahydrospiro[carbazole-1,2′-[1,3]-dithiolan]-4-one (Hökelek *et al.*, 1999) (sic).

The title compound consists of a carbazole skeleton, a pentacyclic dithiolane ring spirobonded at position 1, methoxymethyl- and amino-bonded acetal and benzoyl chains at positions 9 and 4, respectively. The interatomic distances N2···H51 (C5) 2.708, N2···H41 (C4) 2.171, N9···H132 (C13) 2.586, S1···H112 (C11) 2.332, S1···H32 (C3) 2.990, S2···H122 (C12) 2.708 and S2···H112 (C11) 2.308 Å indicate the close contacts causing changes in the values of bond lengths and angles of the carbazole skeleton. On the other hand, the interatomic distances N2···H151 (C15) 2.004, N2···H141 (C14) 1.973, N2···H142 (C14) 1.999, O4···H151 (C15) 2.159, O4···H51 (C5) 2.917, O3···H32 (C3) 2.600, O3···H151 (C15) 2.067, O3···H141 (C14) 1.619 and O2···H173 (C17) 2.575 Å in the carbazole chain indicate the close contacts causing interactions between the acetal and benzoyl groups. These types of interactions are notably effective on the molecular conformation. The C—N bonds [N9—C8a 1.376 (4) and N9—C9a 1.391 (4) Å] are shorter than 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). On the other hand N9—C8a is nearly the same, but N9—C9a is longer than the corresponding values 1.382 (2) and 1.356 (3) Å in spiro[carbazole-1(2*H*),2′-[1,3]-dithiolan]-4(1*H*)-one (Hökelek *et al.*, 1998), while N9—C8a is shorter and N9—C9a is longer than the corresponding values 1.396 (2) and 1.377 (2) Å in 9-methoxymethyl-3-ethylidene-1,2,3,4-tetrahydrospiro[carbazole-1,2′-[1,3]dithiolan]-4-one (Hökelek *et al.*, 1999). The CH_2—O—CH_3 protecting group and carbazole chain on N9 and C4 atoms, respectively, cause notable conformational changes on the geometry of the carbazole core and spirobonded dithiolane ring leading to the increases in angles C4—C4a—C9a [124.2 (3)°] and S2—C1—C9a [115.9 (2)°] and decreases in C8a—N9—C9a [108.1 (2)°], C4—C4a—C5a [128.6 (2)°], C3—C4—C4a [109.0 (2)°] and C2—C3—C4 [109.9 (2)°] compared to the corresponding ones [122.0 (2), 112.8 (1), 109.6 (1), 130.9 (2), 115.9 (2) and 114.7 (2)°] in spiro-[carbazole-1(2*H*),2′-[1,3]dithiolan]-4(3*H*)-one (Hökelek *et al.*, 1998). An examination of the deviations from the least-squares planes through the individual rings shows that rings *A*, *B* and *E* are close to planar.

Rings *C* and *D* are not planar with maximum deviations at C3 [0.375 (3) Å] and C10 [0.506 (4) Å]. They are also twisted with respect to each other. The dihedral angles between the best least-squares planes are *A*^*B* = 1.9 (1), *A*^*C* = 6.2 (1), *A*^*D* = 87.8 (1), *A*^*E* = 69.0 (1), *B*^*C* = 4.4 (1), *B*^*D* = 86.2 (1), *B*^*E* = 69.1 (1), *C*^*D* = 81.8 (1), *C*^*E* = 70.9 (1) and *D*^*E* = 61.1 (1)°. Ring *C* has a sofa conformation with a local pseudo twofold axis running along the mid-points of the C2—C3 and C4a—C9a bonds, while the conformation of ring *D* is half-chair with a local pseudo twofold axis running along S2 and the mid-point of the S1—C10 bond.

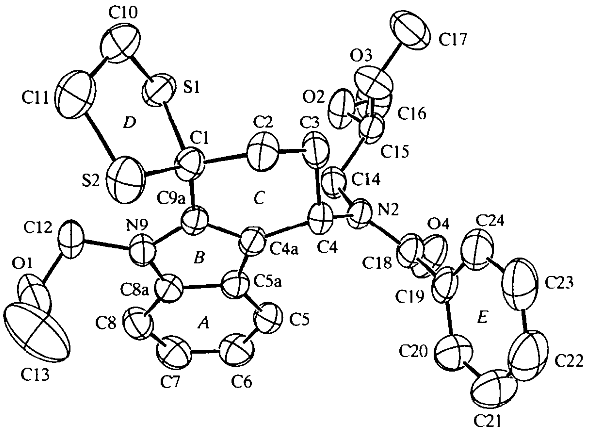


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound, (I), was prepared from the reaction of *N*-benzoyl-*N*-(2,2-dimethoxyethyl)-{2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2′-[1,3]dithiolan]-4-yl}amine (1 g, 2.13 mmol) and tetrabutylammonium hydrogen sulfate (0.1 g, 0.3 mmol) in 30 ml chloroform. Later, aqueous sodium hydroxide (50%) was added and stirred for 15 min. Methoxymethyl chloride (1 ml) was dropped into this mixture and stirred at 298 K for 3 h and then washed with water. The organic layer was dried with magnesium sulfate and the solvent was evaporated. The compound was obtained after column chromatography using silica gel and chloroform/ethyl acetate (1:1), according to the literature method of Patır *et al.* (1987). The compound was recrystallized from ethyl acetate [m.p. 443 K; 0.72 g (66%) yield].

Crystal data

$C_{27}H_{32}N_2O_4S_2$
$M_r = 512.681$
Triclinic
$P\bar{1}$
$a = 10.223\,(1)$ Å
$b = 11.480\,(1)$ Å
$c = 12.058\,(1)$ Å
$\alpha = 81.619\,(8)°$
$\beta = 70.668\,(6)°$
$\gamma = 87.605\,(6)°$
$V = 1321.1\,(2)$ Å^3
$Z = 2$
$D_x = 1.2888$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9–18°$
$\mu = 0.237$ 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)
$T_{\min} = 0.933$, $T_{\max} = 0.955$
5672 measured reflections
5356 independent reflections

4340 reflections with $F > 3\sigma(F)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 26.3°$
$h = -12 \rightarrow 0$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.063$
$wR = 0.079$
$S = 1.31$
4340 reflections
316 parameters
H atoms constrained
$w = 1/[\sigma(F)^2 + (0.02\,F)^2 + 1.0]$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.74$ e Å^{-3}
$\Delta\rho_{\min} = -0.09$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å)*

S1—C1	1.835 (3)	O2—C16	1.393 (5)
S1—C10	1.795 (4)	C1—C2	1.543 (5)
S2—C1	1.854 (3)	C4—N2	1.480 (3)
S2—C11	1.822 (4)	C4—C3	1.521 (4)
C4a—C9a	1.374 (4)	C15—C14	1.538 (3)
C4a—C4	1.513 (4)	C10—C11	1.482 (5)
C4a—C5a	1.435 (4)	N2—C18	1.361 (4)
C9a—C1	1.502 (4)	N2—C14	1.458 (4)
C9a—N9	1.391 (4)	N9—C12	1.457 (4)
C8a—N9	1.376 (4)	O1—C12	1.396 (4)
C8a—C5a	1.403 (4)	O1—C13	1.359 (6)
O3—C15	1.384 (4)	O4—C18	1.218 (4)
O3—C17	1.413 (4)	C3—C2	1.518 (4)
O2—C15	1.397 (4)	C18—C19	1.492 (5)

The H atoms were geometrically positioned at 0.95 Å from parent C atom and a riding model was used during the refinement process.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1042). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 677–678

4-(4-Methylbenzoyl)-6-(4-methylbenzylidene)-3-phenyl-2-oxa-3-azabicyclo[3.3.0]-oct-7-ene

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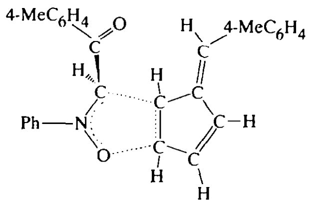
Abstract

The title compound, $C_{28}H_{25}NO_2$, is a minor product resulting from a 1,3-dipolar nitrone–fulvene [3+2] cycloaddition.

Comment

In the course of our work on periselectivity of [3+2] cycloadditions of *C*-aroyl-*N*-phenylnitrones on 6-arylfulvenes we have already shown that the major product (60% yield) results from an unexpected approach of the nitrone dipole on the side of dipolarophile fulvene close to the bulky aryl substituent (Kubicki *et al.*, 1998). By varying the substituents on both the nitrone and the fulvene reactants we were able to isolate and crystallize the minor adduct (40%), (1). Cycloaddition involves one of the two fulvenic double bonds, as expected. In contrast to the major product already described, cycloaddition leading to the minor product occurs on the less hindered side of the fulvene. Significant bond lengths are C2—C3 1.522 (4) and C4—C5 1.326 (4) Å.



(1)

The central saturated cycle is puckered and exhibits a 'boat-like' geometry over the planar C1—C2—C3—O1 unit. The dihedral angles involving this unit and the O1—N—C1 and C2–C6 planes are equal to 39.2 (2) and 58.4 (2)°, respectively. The fulvene derived fragment in (1) is roughly planar with the dihedral angle between the C2–C6 and C8–C13 planes equal to 19.9 (2)°. A perspective view of the title molecule is shown in Fig. 1.

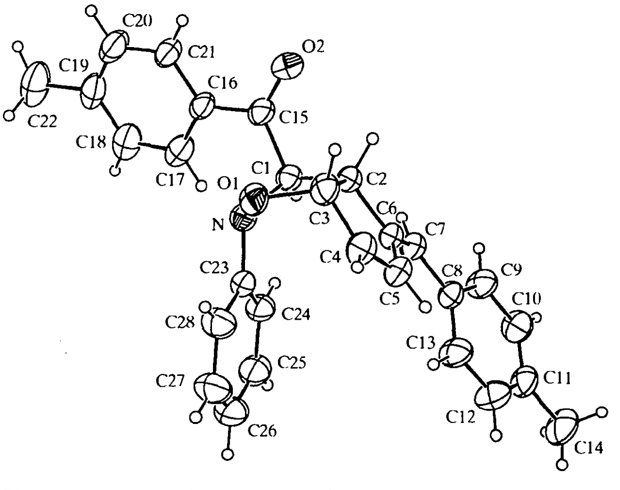


Fig. 1. The molecular structure of (1) showing 30% probability displacement ellipsoids.

Experimental

A mixture of 3 mmol of 6-*p*-tolylpentafulvene and 5 mmol of nitrone was refluxed for 15 h in toluene. After evaporation

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