

Data collection

Siemens SMART diffractometer 4541 independent reflections
 3191 reflections with $I > 2\sigma(I)$
 Area-detector ω scans
 Absorption correction: $R_{\text{int}} = 0.053$
 multi-scan (Blessing, 1995) $\theta_{\text{max}} = 25^\circ$
 $T_{\text{min}} = 0.982$, $T_{\text{max}} = 0.995$ $h = -7 \rightarrow 7$
 14889 measured reflections $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 44$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 0.6084P]$
 $R[F^2 > 2\sigma(F^2)] = 0.057$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.135$ $(\Delta/\sigma)_{\text{max}} = 0.013$
 $S = 1.076$ $\Delta\rho_{\text{max}} = 0.184 \text{ e } \text{\AA}^{-3}$
 4541 reflections $\Delta\rho_{\text{min}} = -0.210 \text{ e } \text{\AA}^{-3}$
 317 parameters
 H atoms treated by a mixture of independent and constrained refinement
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. Selected geometric parameters (\AA , $^\circ$) for (II)

| | | | |
|------------|-----------|-------------|-----------|
| C4—C5 | 1.562 (5) | C9—C10 | 1.570 (4) |
| C5—C10 | 1.559 (4) | C13—C18 | 1.548 (4) |
| C8—C9 | 1.553 (4) | C13—C14 | 1.575 (4) |
| C8—C14 | 1.568 (4) | | |
| C6—C5—C10 | 111.1 (3) | C8—C9—C10 | 117.3 (2) |
| C6—C5—C4 | 115.2 (3) | C15—C14—C8 | 113.4 (2) |
| C10—C5—C4 | 116.9 (3) | C15—C14—C13 | 111.7 (3) |
| C11—C9—C8 | 110.0 (2) | C8—C14—C13 | 116.7 (2) |
| C11—C9—C10 | 114.3 (3) | | |

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$) for (II)

| D—H...A | D—H | H...A | D...A | D—H...A |
|-------------|----------|----------|-----------|---------|
| O4—H4A...O5 | 0.83 | 1.97 | 2.666 (4) | 140.6 |
| O5—H5...O3' | 1.20 (5) | 1.59 (5) | 2.763 (4) | 167 (3) |

Symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

The data collection nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 4.94 cm. In each case a total of 1271 frames was collected. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. Crystals of (I) were of poor quality, yielding a weak diffraction pattern and leading to a higher final residual.

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for methyl groups), and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. The scalarin structure (II) also contains a methanol of solvation in which the hydroxyl-H atom was located from a difference map.

The absolute configuration could not be determined in either case and the figures depict the same absolute configuration as scalarane (Kazlauskas *et al.*, 1980).

For both compounds, data collection: SMART (Siemens, 1994); cell refinement: SAINT (Siemens, 1994); data reduction: SAINT; program(s) used to solve structures: SHELXS97 (Sheldrick, 1990); program(s) used to refine structures: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Siemens, 1994); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1072). Services for accessing these data are described at the back of the journal.

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9-Acetyl-3-ethylidene-1,2,3,4-tetrahydro-spiro[carbazole-1,2'-[1,3]dithiolan]-4-one

TUNCER HÖKELEK,^{a*} SÜLEYMAN PATIR^b AND NESİMİ ULUDAĞ^b

^aHacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and ^bHacettepe University, Department of Science, Faculty of Education, 06532 Beytepe, Ankara, Turkey. E-mail: merzifon@eti.cc.hun.edu.tr

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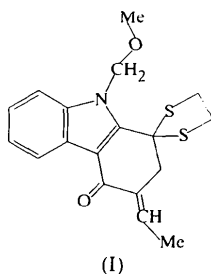
Abstract

The title compound, C₁₈H₁₉NO₂S₂, consists of a carbazole skeleton with a pentacyclic dithiolane ring spirobonded at position 1 and acetyl and ethylidene chains

at positions 9 and 3, respectively. The heteroatoms and the acetyl and ethylidene chains in the molecule are responsible for the changes in the bond lengths and angles of the carbazole core.

Comment

The title compound can be considered as a synthetic precursor of a tetracyclic indole alkaloid, dehydro-de-(*N*-methyl)uleine, which has been isolated from *Aspidosperma* (Joule *et al.*, 1965). The integration of the amino-functionalized group on the C4 atom (according to the carbazole numbering) following the ring cyclization could constitute a new synthetic entry in to the total synthesis of dehydro-de-*N*-methyluleine, similar to the synthesis of the tetracyclic indole alkaloids in the dasycarpidone series (Patir, 1995; Patir *et al.*, 1996). The structure determination of the title compound, (I), was undertaken in order to understand the effects of the acetyl and ethylidene groups at positions 9 and 3, respectively, on the geometry of the carbazole system and to compare the obtained results with those of spiro[carbazole-1(2*H*),2'-[1,3]dithiolan]-4-one (Hökelek *et al.*, 1998).



The title compound consists of a carbazole skeleton, a pentacyclic dithiolane ring spiro-bonded at position 1 and acetyl and ethylidene chains at positions 9 and 3, respectively. The interatomic distances $N9 \cdots H8$ 2.77 (2), $S1 \cdots H122$ 2.69 (2), $S1 \cdots H21$ 2.69 (2), $S2 \cdots H22$ 2.83 (2), $O1 \cdots H5$ 2.66 (2), $O1 \cdots H141$ 2.482 (4) and $O2 \cdots H102$ 2.56 (2) Å indicate the close contacts causing changes in the values of bond lengths and angles of the carbazole skeleton.

The C—N bonds [$N9—C8a$ 1.396 (2) and $N9—C9a$ 1.377 (2) Å] are nearly the same as the corresponding values [$N9—C8a$ 1.382 (2) and $N9—C9a$ 1.356 (3) Å] in spiro[carbazole-1(2*H*),2'-[1,3]dithiolan]-4-one (Hökelek *et al.*, 1998), but shorter than the corresponding values [$N9—C8a$ 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), even though there is a $—CH_2—O—CH_3$ protecting group at the N9 position. The $—CH_2—O—CH_3$ protecting group and $—CH_2—CH_3$ chain at the N9 and C3 positions cause notable conformation changes on the geometry of the carbazole

core leading to angle size increases [$C1—C2—C3$ 114.3 (2), $C4—C4a—C9a$ 124.5 (2), $C9a—C1—S1$ 115.9 (1), $O1—C4—C3$ 122.9 (2)°] and decreases [$C3—C4—C4a$ 114.6 (2), $C4—C4a—C5a$ 127.5 (2), $C4a—C9a—C1$ 122.8 (2), $C9a—N9—C8a$ 108.1 (1), $C9a—C1—S2$ 106.7 (1), $C2—C1—S1$ 106.3 (1)°] according to the corresponding values [112.3 (2), 122.0 (2), 112.8 (1), 121.5 (2), 115.9 (2), 130.9 (2), 124.3 (2), 109.6 (1), 108.0 (1) and 109.5 (1)°, respectively] in spiro[carbazole-1(2*H*),2'-[1,3]dithiolan]-4-one (Hökelek *et al.*, 1998). An examination of the deviations from the least-squares planes through the individual rings shows that rings A (C5a, C5, C6, C7, C8, C8a) and B (C4a, C5a, C8a, N9, C9a) are planar. The C (C1, C2, C3, C4, C4a, C9a) and D (C1, S1, C10, C11, S2) rings are not planar with maximum deviations at C2 [0.315 (2)] and C11 [−0.487 (2) Å]. They are also twisted with respect to each other. The dihedral angles between the best least-squares planes are $A^{\wedge}C = 4.91$ (4), $A^{\wedge}D = 83.78$ (5), $B^{\wedge}C = 4.51$ (6), $B^{\wedge}D = 82.79$ (5) and $C^{\wedge}D = 80.77$ (5)°. Ring C has a sofa conformation with a local pseudo mirror running along $C2 \cdots C4a$, 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.

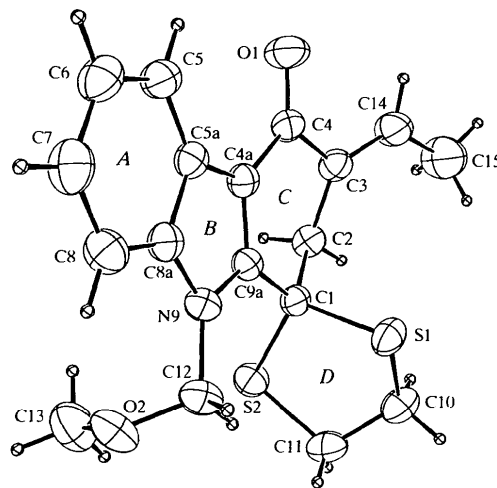


Fig. 1. An ORTEP (Johnson, 1976) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

Experimental

The title compound, (I), was prepared from the reaction of lithium bis(trimethylsilyl)amide (15 mmol) in 30 ml tetrahydrofuran and 9-methoxymethyl-2,3-dihydrospiro[1*H*-carbazole-1,2'-[1,3]dithiolane]-4-one (4.0 g, 12.52 mmol) (Masamune *et al.*, 1982). The resulting mixture was stirred at 223 K for 2 h and then acetaldehyde (1 ml, 18 mmol) was added and stirring continued overnight. The mixture was then poured into HCl solution (50 ml, 10%), extracted with chloroform, dried over $MgSO_4$ and evaporated. The title compound

(I), was obtained from column chromatography [m.p. 404 K, 3.2 g (74%) yield] and recrystallized from ethyl acetate.

Crystal data

C₁₈H₁₉NO₂S₂
M_r = 345.49
 Orthorhombic
Pbca
a = 9.202 (1) Å
b = 18.870 (3) Å
c = 19.138 (2) Å
V = 3323.2 (7) Å³
Z = 8
D_x = 1.381 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 9–11°
 μ = 0.324 mm⁻¹
T = 298 K
 Block
 0.30 × 0.25 × 0.20 mm
 Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical via ψ scans (*MolEN*; Fair, 1990)
T_{min} = 0.910, *T_{max}* = 0.940
 3816 measured reflections
 3363 independent reflections
 2922 reflections with *F* > 2σ(*F*)

R_{int} = 0.023
 θ_{\max} = 26.3°
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 23$
 $l = 0 \rightarrow 23$
 3 standard reflections every 250 reflections
 frequency: 120 min
 intensity decay: 1%

Refinement

Refinement on *F*
R = 0.038
wR = 0.048
S = 1.22
 2922 reflections
 256 parameters
 H atoms: see text
 $w = 1/[\sigma(F)^2 + (0.02F)^2 + 1.0]$

(Δ/σ)_{max} = 0.01
 $\Delta\rho_{\max} = 0.34 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

| | | | |
|-----------|------------|------------|-----------|
| S1—C1 | 1.856 (2) | C3—C4 | 1.495 (3) |
| S1—C10 | 1.815 (2) | C4—C4a | 1.449 (3) |
| S2—C1 | 1.832 (2) | C4a—C5a | 1.439 (3) |
| S2—C11 | 1.799 (2) | C4a—C9a | 1.384 (2) |
| O1—C4 | 1.224 (2) | | |
| C1—S1—C10 | 97.89 (9) | C3—C4—C4a | 114.6 (2) |
| C1—S2—C11 | 95.04 (9) | C1—C9a—C4a | 122.8 (2) |
| S1—C1—S2 | 107.37 (9) | S1—C10—C11 | 109.0 (2) |
| S2—C1—C2 | 112.1 (1) | S2—C11—C10 | 107.2 (1) |
| C2—C1—C9a | 108.6 (1) | C4—C4a—C9a | 124.5 (2) |
| C1—C2—C3 | 114.3 (2) | C8a—N9—C9a | 108.1 (1) |
| C2—C3—C4 | 115.1 (2) | | |

Most of the H-atom positions were located by difference synthesis and refined isotropically. The remaining ones were positioned geometrically 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: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (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: SK1227). Services for accessing these data are described at the back of the journal.

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4-(2,5-Di-*tert*-butylphenyl)nitrilomethylidyne)-2-methoxyphenol

YALÇIN ELERMAN,^a AYHAN ELMALI,^a ENGIN KENDİ^b AND SÜHEYLA ÖZBEY^b

^aDepartment of Physics Engineering, Faculty of Sciences, University of Ankara, 06100 Besevler, Ankara, Turkey, and ^bDepartment of Physics Engineering, Hacettepe University, 06532 Beytepe, Ankara, Turkey. E-mail: elmali@science.ankara.edu.tr

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Abstract

The title compound, C₂₂H₂₉NO₂, is a monodentate Schiff base. There are two independent molecules in the asymmetric unit. In each molecule the two planar phenyl rings bridged by a C=N imino moiety are nearly perpendicular to one another [79.80 (4) and 81.14 (4)°]. Each molecule contains intramolecular (O—H···O) and intermolecular (O—H···N) hydrogen bonds.

Comment

Schiff bases and their transition metal complexes have been extensively studied during the last decade.