O4—S2—N2—C8	175.6 (4)	C12—C9—C10—C6	−102.3 (6)
O3—S2—N2—C8	45.0 (5)	C4—C5—C11—C1	−1.5 (9)
C19—S2—N2—C8	−70.1 (4)	N1—C5—C11—C1	178.6 (5)
O4—S2—N2—C7	−41.5 (5)	N1—C5—C11—C10	−1.0 (6)
O3—S2—N2—C7	−172.1 (4)	O4—S2—C19—C24	20.2 (6)
C19—S2—N2—C7	72.8 (4)	O3—S2—C19—C24	151.5 (5)
C3—C4—C5—N1	−179.5 (6)	N2—S2—C19—C24	−93.5 (5)
C6—N1—C5—C11	2.1 (6)	O4—S2—C19—C20	−159.7 (5)
S1—N1—C5—C11	153.4 (4)	O3—S2—C19—C20	−28.4 (5)
C6—N1—C5—C4	−177.8 (5)	N2—S2—C19—C20	86.7 (5)
S1—N1—C5—C4	−26.5 (8)	S2—C19—C20—C21	179.7 (5)
C5—N1—C6—C10	−2.5 (6)	S2—C19—C24—C23	−178.5 (5)
S1—N1—C6—C10	−152.6 (4)	O2—S1—C25—C30	29.9 (6)
C5—N1—C6—C7	−177.3 (5)	O1—S1—C25—C30	162.7 (5)
S1—N1—C6—C7	32.5 (7)	N1—S1—C25—C30	−83.4 (5)
C8—N2—C7—C6	−44.2 (6)	O2—S1—C25—C26	−153.5 (4)
S2—N2—C7—C6	172.6 (4)	O1—S1—C25—C26	−20.8 (5)
C10—C6—C7—N2	12.0 (8)	N1—S1—C25—C26	93.2 (5)
N1—C6—C7—N2	−173.8 (5)	S1—C25—C26—C27	−177.3 (5)
C7—N2—C8—C9	66.1 (6)	S1—C25—C30—C29	177.4 (5)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O1	0.93 (1)	2.42 (1)	3.01 (1)	121.0 (6)
C18—H18···O4^{i}	0.93 (1)	2.53 (1)	3.33 (1)	144.8 (6)
C29—H29···O3^{i}	0.93 (1)	2.58 (1)	3.24 (1)	128.5 (7)
C23—H23···O1^{ii}	0.93 (1)	2.56 (1)	3.45 (1)	161.1 (9)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, 1-y, 1-z$.

The large discrepancy between the R and wR values is due to the high thermal vibration present in phenyl ring II (atoms C21, C22 and C23) on the β-carboline moiety. H atoms were geometrically positioned and refined using a riding model.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL93* and *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: PT1051). Services for accessing these data are described at the back of the journal.

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1,3,3-Trimethylindoline-2-spiro-2′-3′-methyl-2′*H*-phenanthro[9,10-*b*][1,4]oxazine

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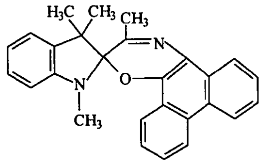
Abstract

In the title compound, $C_{27}H_{24}N_2O$, both benzo and phenanthro rings are essentially planar, the dihedral angle between them being 73.61 (4)°. The non-aromatic five- and six-membered rings adopt deformed envelope and half-chair conformations, respectively. Molecules are linked by weak intermolecular C—H···N interactions which exhibit C···N non-bonded contacts of 3.481 (2) and 3.540 (2) Å, respectively.

Comment

Spirooxazine is the most important member of one of the best known organic photochromic systems (Durr & Laurent, 1990). Many applications have been envisaged in several key areas such as high-density optical storage, optical switching, photochromic lenses, image processing and displays. In order to study the relationship between molecular structure and photochromic behaviour, the structures of several spirooxazines have been determined (Maeda *et al.*, 1994; Osano *et al.*, 1991; Clegg *et al.*, 1991), most of them concerning indolinespironaphthooxazines and indolinespiroquinolinooxazines. In this paper, we report the structure of a novel photochromic compound, (I).



(I)

The molecular dimensions (Table 1) are comparable with those in related molecules (*e.g.* Allen *et al.*, 1987; Parvez & Rusiewicz, 1996). The calculation of least-squares planes through the aromatic rings shows that they exhibit the expected planar geometries and that the benzo ring is more planar than the phenanthro ring [maximum deviations of 0.004 (1) and 0.048 (2) Å, respectively]. The dihedral angle between these two planes is 73.61 (4)°. Atoms C7 and N2 lie close to the benzo ring plane, with deviations of 0.074 (3) and 0.012 (2) Å, respectively. Similarly, atoms C11, N1 and O1 are approximately coplanar with the phenanthro ring plane, their deviations from this plane being 0.023 (2), 0.195 (2) and 0.060 (2) Å, respectively. Atom C10 is markedly displaced out of both the benzo and the phenanthro ring planes, by 0.411 (3) and 0.516 (2) Å, respectively. In contrast, the non-aromatic five- and six-membered rings are twisted and their conformations may be characterized according to the method given by Cremer & Pople (1975). The five-membered ring has a deformed envelope conformation with pseudo-rotational phase angle, φ_2, of 175.6 (2)° and a puckering amplitude, q_2, of 0.303 (2) Å. Atoms N2, C1, C6 and C7 are almost coplanar, with an N2—C1—C6—C7 torsion of 2.0 (2)° and a maximum deviation of 0.011 (1) Å. The deviation of atom C10 from the least-squares plane of this group is 0.477 (2) Å. The six-membered heteroatomic ring adopts an approximately half-chair conformation with puckering parameters (Cremer & Pople, 1975) Q = 0.353 (2) Å, θ = 111.6 (2) and φ = 165.2 (2)°. Atoms C10 and N1 lie on opposite sides of the best plane through atoms C11, C13, C26 and O1 [planar to within 0.001 (1) Å], with displacements of 0.487 (2) and −0.153 (2) Å, respectively.

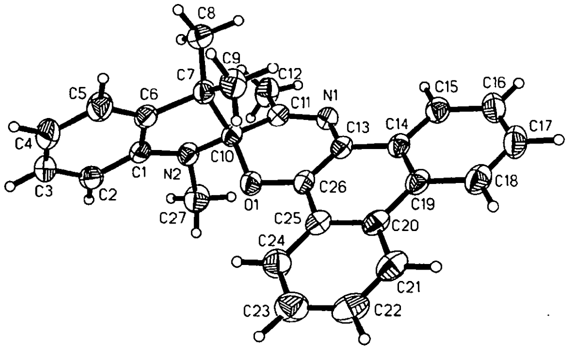


Fig. 1. A view of the molecule showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms have been assigned a small arbitrary radius for clarity.

The π-electron delocalization of the aromatic rings extends its influence to the adjacent atoms. This is confirmed by the bond lengths and torsion angles involving atoms N2, C7 and O1. For instance, the C1—N2 bond length is 1.407 (2) Å, which is between that for a C—N single bond (1.48 Å) and a C=N double bond (1.28 Å) (Allen *et al.*, 1987), indicating partial delocalization of π-electron density over the benzo ring and the N2 lone pair. Similarly, the C26—O1 bond length of 1.364 (2) Å is shorter than a C—O single bond (1.43 Å) and longer than a C=O double bond (1.23 Å) (Allen *et al.*, 1987), indicating that O1 is conjugated with the π-electron system of the phenanthro ring. The observed C3—C2—C1—N2, C4—C5—C6—C7 and C24—C25—C26—O1 torsion angles of −179.1 (1), 176.7 (2) and 1.3 (2)°, respectively, indicate a nearly planar configuration.

Examination of the intermolecular distances associated with N1, N2 and O1 suggests that each N1 atom forms two weak hydrogen bonds with H atoms on C21 and C27 of the nearest neighbouring molecules [C21—H21 0.93, H21···N1^{i} 2.71, C21···N1^{i} 3.481 (2) Å and C21—H21···N1^{i} 140°; C27—H27*A* 0.96, H27*A*···N1^{ii} 2.64, C27···N1^{ii} 3.540 (2) Å and C27—H27*A*···N1^{ii} 157°; symmetry codes: (i) $x-\frac{1}{2}$, $-y+\frac{1}{2}$, $z-\frac{1}{2}$; (ii) $-x$, $-y$, $2-z$]. These intermolecular C—H···N interactions (Taylor & Kennard, 1982) contribute to the stabilization of the crystal packing and no other intermolecular hydrogen-bonding interactions are found in the structure.

Experimental

A mixture of 1,3,3-trimethyl-2-ethylindolium iodide (1.6 g, 5.3 mmol), 9,10-phenanthrenequinone monooxime (1.1 g, 4.9 mmol) and triethylamine (3 ml) were dissolved in absolute ethanol (50 ml). The solution was refluxed for 6 h. After evaporation of the solvent, the residue was chromatographed on silica gel (yield: 56%, m.p. 470–473 K). The crystal was obtained by recrystallization from ethanol–petroleum ether (1:1).

Crystal data

$C_{27}H_{24}N_2O$
M_r = 392.48
Monoclinic
$P2_1/n$
a = 9.766 (2) Å
b = 16.184 (3) Å
c = 13.456 (2) Å
β = 100.82 (2)°
V = 2088.8 (7) Å^3
Z = 4
D_x = 1.248 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 30 reflections
θ = 5–15°
μ = 0.076 mm^{-1}
T = 293 K
Prism
0.35 × 0.30 × 0.30 mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction: none
4693 measured reflections
3666 independent reflections
2450 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.025$
$\theta_{\max} = 25°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 19$
$l = -16 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.109$
$S = 0.946$
3666 reflections
274 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.047 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C26	1.364 (2)	C6—C7	1.509 (2)
O1—C10	1.466 (2)	C7—C9	1.527 (2)
N1—C11	1.283 (2)	C7—C8	1.543 (2)
N1—C13	1.412 (2)	C7—C10	1.573 (2)
N2—C1	1.407 (2)	C10—C11	1.529 (2)
N2—C10	1.439 (2)	C11—C12	1.500 (2)
N2—C27	1.451 (2)		
C26—O1—C10	117.61 (11)	C1—N2—C27	118.66 (13)
C11—N1—C13	118.60 (14)	C10—N2—C27	119.06 (12)
C1—N2—C10	107.78 (12)		

All non-H atoms were refined anisotropically. H atoms were placed in geometrically calculated positions and allowed to refine, riding on the atoms to which they are attached, with a common isotropic displacement parameter of 0.090 (2) Å^2 for methyl and 0.067 (2) Å^2 for aromatic groups.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1991). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1186). Services for accessing these data are described at the back of the journal.

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