Refinement

Refinement on F
$R = 0.0429$
$wR = 0.0434$
$S = 1.33$
705 reflections
128 parameters
H-atom positions fixed, one overall U_{iso} refined
$w = 1/[\sigma^2(|F_o|) + 0.0003|F_o|^2]$
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.14$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{\text{eq}} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
N(1)	0.0604 (3)	0.1468 (4)	0.2234 (2)	4.5 (1)
N(2)	0.0778 (4)	0.2215 (4)	0.1277 (3)	5.8 (1)
N(3)	0.1891 (3)	0.0242 (4)	0.4192 (2)	4.8 (1)
N(4)	0.5303 (4)	0.0928 (6)	0.3936 (3)	8.4 (2)
C(3)	0.2079 (5)	0.2183 (6)	0.1628 (3)	5.9 (2)
C(4)	0.2772 (4)	0.1424 (5)	0.2782 (3)	4.6 (1)
C(5)	0.1788 (4)	0.0979 (5)	0.3144 (3)	4.1 (1)
C(6)	0.4170 (5)	0.1145 (6)	0.3422 (4)	5.7 (2)
C(7)	−0.0721 (4)	0.1321 (5)	0.2144 (3)	4.4 (1)
C(8)	−0.1022 (4)	0.1905 (5)	0.3065 (3)	5.0 (1)
C(9)	−0.2331 (5)	0.1820 (6)	0.2914 (4)	5.9 (2)
C(10)	−0.3323 (4)	0.1189 (6)	0.1855 (5)	6.9 (2)
C(11)	−0.3008 (5)	0.0600 (6)	0.0943 (4)	6.7 (2)
C(12)	−0.1704 (4)	0.0656 (5)	0.1075 (3)	5.6 (1)

Table 2. *Selected geometric parameters* (Å, °)

N(1)—N(2)	1.388 (5)	N(1)—C(5)	1.348 (5)
N(1)—C(7)	1.419 (6)	N(2)—C(3)	1.305 (7)
N(3)—C(5)	1.358 (4)	N(4)—C(6)	1.139 (7)
C(3)—C(4)	1.405 (5)	C(4)—C(5)	1.379 (6)
C(4)—C(6)	1.408 (7)	C(7)—C(8)	1.377 (6)
C(7)—C(12)	1.382 (5)	C(8)—C(9)	1.373 (8)
C(9)—C(10)	1.369 (7)	C(10)—C(11)	1.378 (7)
C(11)—C(12)	1.374 (7)		
N(2)—N(1)—C(5)	111.8 (3)	N(3)—C(5)—C(4)	130.5 (3)
N(2)—N(1)—C(7)	118.7 (3)	N(4)—C(6)—C(4)	179.6 (5)
C(5)—N(1)—C(7)	129.4 (3)	N(1)—C(7)—C(8)	120.9 (4)
N(1)—N(2)—C(3)	104.4 (3)	N(1)—C(7)—C(12)	117.4 (3)
N(2)—C(3)—C(4)	112.2 (4)	C(8)—C(7)—C(12)	121.6 (4)
C(3)—C(4)—C(5)	105.3 (4)	C(7)—C(8)—C(9)	119.0 (4)
C(3)—C(4)—C(6)	127.4 (4)	C(8)—C(9)—C(10)	120.3 (4)
C(5)—C(4)—C(6)	127.3 (4)	C(9)—C(10)—C(11)	120.1 (5)
N(1)—C(5)—N(3)	123.2 (3)	C(10)—C(11)—C(12)	120.7 (4)
N(1)—C(5)—C(4)	106.2 (3)	C(7)—C(12)—C(11)	118.2 (4)

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. H atoms were included as fixed contributors at the positions found by difference Fourier synthesis. One overall isotropic temperature factor for the H atoms was refined [$U_{\text{iso}} = 0.091$ (5) Å^2]. The refinement was carried out by full-matrix least-squares methods. Programs used: *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). Most of the calculations were performed at the Weizmann Institute of Science, Israel.

This work has received partial support from FAPESP, CNPq and FINEP.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). C**50**, 2096–2098

Chemical Degradation of Spiroindolinonaphthoxazines: 8,13,13-Trimethyl-7a,8-dihydronaphtho[2,1-*b*]quinolino-[3,2-*e*][1,4]oxazine, $C_{22}H_{20}N_2O$

ROBERTO MILLINI* AND GASTONE DEL PIERO

Eniricerche SpA, Via F. Maritano 26,
I-20097 San Donato Milanese, Italy

PIETRO ALLEGRINI AND NEREO NODARI

Enichem Synthesis SpA, Via F. Maritano 26,
I-20097 San Donato Milanese, Italy

(*Received* 25 *March* 1994; *accepted* 9 *May* 1994)

Abstract

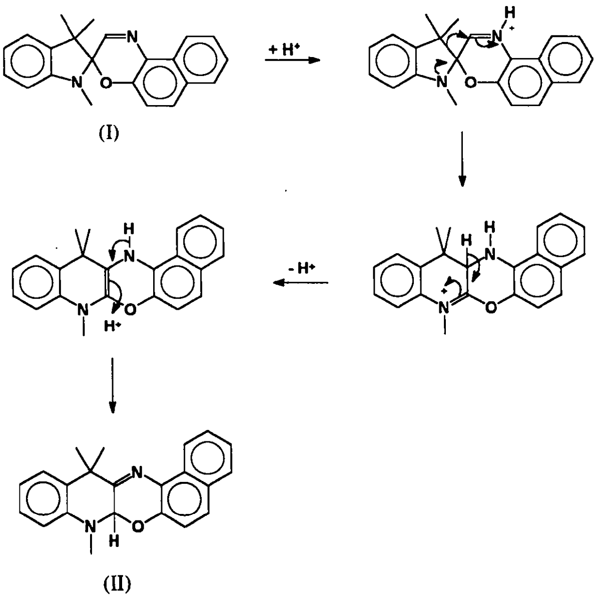
The molecular structure of the title compound consists of a naphthoxazine moiety fused to a tetrahydroquinoline fragment. The heterocyclic ring of the latter displays a 'boat' conformation. No geometrical differences from other similar compounds have been detected for the naphthoxazine system.

Comment

Spiroindolinonaphthoxazines have been extensively studied because their good photochromic properties (*i.e.* colorability and photochemical fatigue resistance) with respect to other organic photochromic compounds (Dürr, 1989). Even so, photochemical oxidative degradation and chemical incompatibility with compounds used for the preparation of manufactures may severely limit their application. Several studies have been performed to identify the products and elucidate the mechanism of photodegradation (Baillet, Giusti & Guglielminetti, 1993; Malatesta *et al.*, 1993), but no information is available on the chemical stability of spiroxazines. During our research activity on this class of compound, we focused attention on the chemical stability of spiroindolinonaphthoxazines in acidic media.

Experiments were performed by refluxing a toluene solution of 1,3,3-trimethylspiro[indoline-2,3′-[3*H*]-naphtho[2,1-*b*][1,4]oxazine] (I) (Chu, 1983) in the presence of diluted phosphoric acid for 28 h. The reaction mixture was then poured into cold aqueous sodium hydroxide (10% *w*/*w*) and the organic layer separated. The solvent was removed *in vacuo* and the components of the residual oil were separated by flash chromatography (toluene/hexane 1:1). In addition to the unreacted starting material (main component) and to other unidentified by-products, a small amount of title compound (II) was isolated.

Although further investigations are necessary for confirmation, the formation of the title compound probably involves an acid-catalysed pyrrole ring expansion (see scheme below). Crystals of (II), with a melting point of 406.4 K (from DSC analysis), were obtained by recrystallization from *n*-hexane.



The molecular conformation and atomic labelling scheme of (II) are shown in Fig. 1. Atomic coordinates for non-H atoms and main geometrical features are reported in Tables 1 and 2, respectively. The molecule consists of a naphthoxazine moiety linked to a tetrahydroquinoline fragment through the atoms C(13) and C(22). From the geometrical point of view, the most interesting feature is represented by the 'boat' conformation displayed by the saturated heterocyclic ring of the tetrahydroquinoline fragment. The atoms C(14) and N(21) are in fact located at 0.595 and 0.367 Å, respectively, above the mean plane formed by C(13), C(15), C(20) and C(22). Furthermore, N(21) displays a very low degree of pyramidalization, the sum of the valence angles around it being 356.4°. This feature can be explained by the tendency towards sp^2 hybridization of the N(21) atom.

No appreciable differences with respect to the parent compound (I) (Millini, Del Piero, Allegrini, Crisci & Malatesta, 1991) have been observed in the geometry of the naphthoxazine fragment.

The aromatic rings are planar, with r.m.s.d.'s of 0.010 and 0.012 Å for the naphthyl and phenyl moieties, respectively.

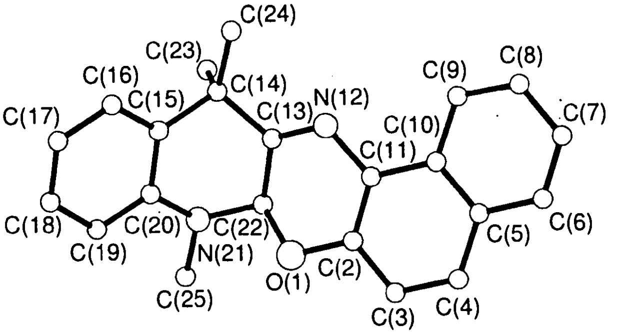


Fig. 1. View of the molecule with the numbering scheme adopted.

Experimental

Crystal data

$C_{22}H_{20}N_2O$
$M_r = 328.41$
Orthorhombic
Pccn
$a = 29.464\ (7)$ Å
$b = 13.861\ (4)$ Å
$c = 8.515\ (2)$ Å
$V = 3477.5\ (15)$ Å^3
$Z = 8$
$D_x = 1.2545$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 30 reflections
$\theta = 14$–$28°$
$\mu = 0.5726$ mm^{-1}
$T = 293$ K
Prism
1.0 × 0.6 × 0.4 mm
Pale yellow

Data collection

Siemens AED diffractometer
θ–2θ scans
Absorption correction: none
3776 measured reflections
3312 independent reflections
2038 observed reflections [$I > 2.5(I)$]

$\theta_{\max} = 70°$
$h = 0 \rightarrow 35$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 10$
1 standard reflection monitored every 100 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.0564$
$wR = 0.0453$

$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

$S = 1.54$
2038 reflections
226 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(1)	0.0710 (1)	0.0464 (2)	0.3216 (4)	0.049 (1)
C(2)	0.0928 (1)	0.0824 (3)	0.1900 (5)	0.044 (1)
C(3)	0.0687 (2)	0.1456 (3)	0.0905 (6)	0.050 (1)
C(4)	0.0901 (2)	0.1838 (3)	−0.0385 (6)	0.049 (1)
C(5)	0.1361 (2)	0.1589 (3)	−0.0713 (5)	0.045 (1)
C(6)	0.1585 (2)	0.1967 (3)	−0.2060 (6)	0.054 (2)
C(7)	0.2022 (2)	0.1720 (4)	−0.2358 (6)	0.062 (2)
C(8)	0.2258 (2)	0.1083 (4)	−0.1379 (6)	0.060 (2)
C(9)	0.2053 (2)	0.0689 (4)	−0.0099 (6)	0.051 (2)
C(10)	0.1596 (1)	0.0938 (3)	0.0241 (5)	0.042 (1)
C(11)	0.1369 (1)	0.0556 (3)	0.1602 (5)	0.041 (1)
N(12)	0.1581 (1)	−0.0184 (3)	0.2483 (5)	0.046 (1)
C(13)	0.1409 (1)	−0.0382 (2)	0.3829 (5)	0.044 (2)
C(14)	0.1570 (2)	−0.1214 (3)	0.4811 (6)	0.048 (2)
C(15)	0.1139 (2)	−0.1762 (3)	0.5264 (6)	0.048 (2)
C(16)	0.1113 (2)	−0.2770 (4)	0.5289 (7)	0.060 (2)
C(17)	0.0724 (2)	−0.3229 (4)	0.5812 (7)	0.071 (2)
C(18)	0.0364 (2)	−0.2699 (5)	0.6299 (8)	0.079 (2)
C(19)	0.0374 (2)	−0.1699 (4)	0.6250 (7)	0.064 (2)
C(20)	0.0759 (2)	−0.1237 (3)	0.5731 (6)	0.051 (2)
N(21)	0.0789 (1)	−0.0216 (3)	0.5717 (5)	0.054 (1)
C(22)	0.1027 (2)	0.0237 (3)	0.4485 (5)	0.045 (1)
C(23)	0.1796 (2)	−0.0801 (4)	0.6291 (6)	0.062 (2)
C(24)	0.1917 (2)	−0.1819 (4)	0.3930 (7)	0.066 (2)
C(25)	0.0461 (2)	0.0378 (4)	0.6558 (6)	0.064 (2)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(2)	1.385 (5)	O(1)—C(22)	1.463 (6)
C(2)—C(3)	1.411 (6)	C(2)—C(11)	1.375 (4)
C(3)—C(4)	1.373 (7)	C(4)—C(5)	1.426 (8)
C(5)—C(6)	1.423 (7)	C(5)—C(10)	1.398 (6)
C(6)—C(7)	1.356 (8)	C(7)—C(8)	1.399 (8)
C(8)—C(9)	1.361 (8)	C(9)—C(10)	1.420 (7)
C(10)—C(11)	1.439 (6)	C(11)—N(12)	1.416 (6)
N(12)—C(13)	1.283 (6)	C(13)—C(14)	1.501 (6)
C(13)—C(22)	1.522 (6)	C(14)—C(15)	1.529 (8)
C(14)—C(23)	1.536 (7)	C(14)—C(24)	1.520 (8)
C(15)—C(16)	1.399 (7)	C(15)—C(20)	1.393 (8)
C(16)—C(17)	1.385 (8)	C(17)—C(18)	1.355 (9)
C(18)—C(19)	1.387 (9)	C(19)—C(20)	1.376 (8)
C(20)—N(21)	1.418 (6)	N(21)—C(22)	1.409 (6)
N(21)—C(25)	1.458 (7)		
C(2)—O(1)—C(22)	112.3 (3)	O(1)—C(2)—C(11)	119.4 (4)
O(1)—C(2)—C(3)	118.5 (4)	C(3)—C(2)—C(11)	122.2 (4)
C(2)—C(3)—C(4)	119.3 (5)	C(3)—C(4)—C(5)	120.0 (4)
C(4)—C(5)—C(10)	120.9 (4)	C(4)—C(5)—C(6)	120.6 (5)
C(6)—C(5)—C(10)	118.5 (4)	C(5)—C(6)—C(7)	119.9 (5)
C(6)—C(7)—C(8)	121.3 (5)	C(7)—C(8)—C(9)	120.7 (5)
C(8)—C(9)—C(10)	119.1 (5)	C(5)—C(10)—C(9)	120.6 (4)
C(9)—C(10)—C(11)	121.0 (3)	C(5)—C(10)—C(11)	118.4 (3)
C(2)—C(11)—C(10)	119.2 (3)	C(10)—C(11)—N(12)	119.2 (3)
C(2)—C(11)—N(12)	121.0 (3)	C(11)—N(12)—C(13)	117.0 (3)
N(12)—C(13)—C(22)	120.0 (4)	N(12)—C(13)—C(14)	122.5 (4)
C(14)—C(13)—C(22)	117.5 (4)	C(13)—C(14)—C(24)	111.2 (4)
C(13)—C(14)—C(23)	107.9 (4)	C(13)—C(14)—C(15)	105.1 (4)
C(23)—C(14)—C(24)	108.6 (5)	C(15)—C(14)—C(24)	114.1 (4)
C(15)—C(14)—C(23)	109.8 (4)	C(14)—C(15)—C(20)	118.7 (4)
C(14)—C(15)—C(16)	123.0 (5)	C(16)—C(15)—C(20)	118.2 (5)
C(15)—C(16)—C(17)	120.6 (5)	C(16)—C(17)—C(18)	119.8 (6)
C(17)—C(18)—C(19)	121.1 (6)	C(18)—C(19)—C(20)	119.5 (5)
C(15)—C(20)—C(19)	120.8 (4)	C(19)—C(20)—N(21)	121.3 (5)
C(15)—C(20)—N(21)	118.0 (5)	C(20)—N(21)—C(25)	121.2 (4)
C(20)—N(21)—C(22)	118.8 (4)	C(22)—N(21)—C(25)	116.4 (4)
C(13)—C(22)—N(21)	113.0 (4)	O(1)—C(22)—N(21)	109.2 (4)
O(1)—C(22)—C(13)	108.8 (3)		

The structure was solved by direct methods (*MULTAN*80; Main *et al.*, 1980) and refined by block-matrix least squares (*SHELX*76; Sheldrick, 1976). Other programs used: *PARST* (Nardelli, 1983) and *PLUTO* (Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: NA1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). C**50**, 2098–2100

Stereochemistry of Rings. XVIII.†
8-*tert*-Butyl-1,4-dithiaspiro[4.5]decane

GABRIELE BOCELLI* AND ANDREA CANTONI

Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, I-43100 Parma, Italy

PIETRO COZZINI

Dipartimento di Chimica Generale e Inorganica, Chimica Analitica e Chimica Fisica, Viale delle Scienze, I-43100 Parma, Italy

(*Received* 20 *December* 1993; *accepted* 26 *May* 1994)

Abstract

The two mean ring planes of the title compound, $C_{12}H_{22}S_2$, are almost perpendicular [dihedral angle

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† Part XVII: Bocelli (1990).

Acta Crystallographica Section C
ISSN 0108-2701 ©1994