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3-{3,3-Dimethylspiro[2,3-dihydro-1*H*-indole-2,3′-(3′*H*-naphtho[2,1-*b*][1,4]-oxazin)]-1-yl}propionic acid

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The title compound, $C_{24}H_{22}N_2O_3$, is dimerized *via* two intermolecular O—H···O hydrogen bonds contributed by two —COOH groups, resulting in the formation of a planar eight-membered ring. The spiro C atom links two planes that are almost perpendicular to each other.

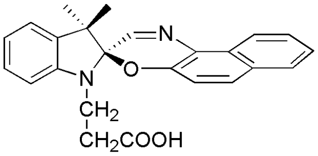
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.046
wR factor = 0.123
Data-to-parameter ratio = 12.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Spiro-oxazines are novel organic photochromic compounds that are attractive as functional materials for a wide variety of applications, including high-density optical storage devices, optical switches and non-linear optics (Swansburg *et al.*, 2000). Recently, the title compound, (I), was found to exhibit interesting photochemical properties when applied to DNA modifications (Zhang *et al.*, 2001). Thus, the elucidation of the crystal structure of (I) is of importance. To our knowledge, this is the first reported crystal structure determination of a photochromic compound dimerized *via* intermolecular O—H···O hydrogen bonds.



(I)

The spiro-center, C12, in (I) (Fig. 1 and Table 1) is tetrahedral, as expected, with the dihedral angle between the planes O1—C12—C11 and N2—C12—C13 being 89.71 (13)°. The five-membered indoline ring (C12—C13—C14—C19—N2) is non-planar, adopting a flattened envelope conformation. Atom C12 lies 0.476 (3) Å out of the plane of the other four indoline ring atoms; the torsion angle C13—C14—C19—N2 is −1.5 (3)° and the bending angle along the N2···C13 line is 30.59 (12)°. N2, C13 and the phenyl ring atoms are close to being coplanar [the interplanar angle between the phenyl ring and the plane through C13—C14—C19—N2 is only 1.82 (13)°]. Atom N2 has a pyramidal configuration and lies out of the plane of the adjacent atoms by 0.2451 (21) Å; the sum of the bond angles at N2 is 351.3 (5)°. As found for the indoline ring, the oxazine moiety also has an envelope conformation, with C12 0.334 (3) Å from the plane of the other oxazine atoms. The naphthyl ring, along with N1, C11 and O1, constitutes a roughly planar moiety, with a maximum deviation of 0.084 (18) Å at C11; the dihedral angle between this plane and C11—C12—O1 is 23.83 (14)°, indicating that spiro-atom C12 lies out of the naphthyl ring system.

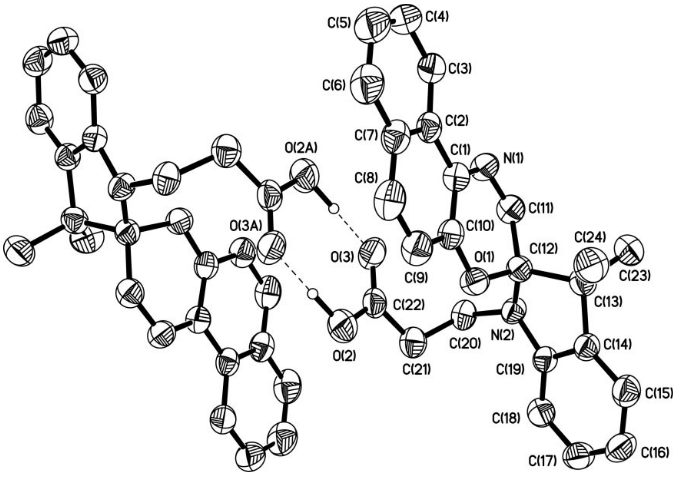


Figure 1
A view of dimerized (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The main feature of the crystal structure is the dimerization in the crystalline state (Fig. 1), which occurs when two molecules approach in a head-to-head fashion with the formation of a centrosymmetric eight-membered ring *via* hydrogen bonding of the carboxyl groups (Table 2). Osano *et al.* (1991) reported a similar structure with a methoxy group insead of a carboxyl groups, in which no dimerization was observed.

Experimental

The title compound was synthesized as described by Li *et al.* (1999). The single crystal was grown by slow evaporation of a chloroform–ethanol solution at room temperature.

Crystal data

$C_{24}H_{22}N_2O_3$
$M_r = 386.44$
Monoclinic, $P2_1/n$
$a = 13.373$ (5) Å
$b = 11.527$ (4) Å
$c = 13.485$ (5) Å
$\beta = 111.538$ (6)°
$V = 1933.5$ (11) Å^3
$Z = 4$

$D_x = 1.328$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 912 reflections
$\theta = 3.2$–23.4°
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Plate, pale yellow
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.984$, $T_{\max} = 0.991$
7838 measured reflections

3399 independent reflections
2000 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\max} = 25.0°$
$h = -15 \rightarrow 14$
$k = -13 \rightarrow 8$
$l = -14 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.123$
$S = 1.02$
3399 reflections
263 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0055 (11)

Table 1
Selected geometric parameters (Å, °).

O1—C12	1.456 (2)	C11—N1	1.276 (3)
N2—C19	1.402 (3)	C11—C12	1.507 (3)
N2—C12	1.437 (3)	O2—H2	0.8501
N2—C20	1.456 (3)	C12—C13	1.567 (3)
C10—O1—C12	118.28 (16)	O1—C12—C11	109.50 (17)
C19—N2—C12	108.43 (17)	N2—C12—C13	102.79 (17)
C19—N2—C20	120.52 (18)	O1—C12—C13	108.95 (17)
C12—N2—C20	122.35 (17)	C11—C12—C13	115.17 (18)
N1—C11—C12	126.9 (2)	C14—C13—C12	100.35 (17)
C22—O2—H2	110.9	C19—C14—C13	108.98 (19)
C10—C1—N1	121.05 (19)	C14—C19—N2	109.64 (19)
C1—C10—O1	121.6 (2)	O3—C22—O2	123.7 (2)
C11—N1—C1	116.49 (19)	O3—C22—C21	122.2 (2)
N2—C12—O1	107.60 (16)	O2—C22—C21	114.2 (2)
N2—C12—C11	112.42 (18)		
N1—C1—C10—O1	1.7 (3)	N1—C11—C12—N2	141.5 (2)
C2—C1—C10—O1	178.4 (2)	N1—C11—C12—O1	22.0 (3)
N1—C1—C10—C9	−175.6 (2)	N1—C11—C12—C13	−101.2 (3)
C12—O1—C10—C1	18.9 (3)	N2—C12—C13—C14	−29.1 (2)
C12—O1—C10—C9	−163.61 (19)	O1—C12—C13—C14	84.81 (19)
C12—C11—N1—C1	−3.7 (3)	C11—C12—C13—C14	−151.73 (18)
C10—C1—N1—C11	−9.5 (3)	C12—C13—C14—C19	19.1 (2)
C19—N2—C12—O1	−84.6 (2)	C13—C14—C19—C18	177.22 (19)
C19—N2—C12—C11	154.78 (18)	C15—C14—C19—N2	−179.3 (2)
C19—N2—C12—C13	30.3 (2)	C13—C14—C19—N2	−1.5 (3)
C10—O1—C12—N2	−150.52 (18)	C12—N2—C19—C18	162.2 (2)
C10—O1—C12—C11	−28.1 (2)	C12—N2—C19—C14	−19.1 (2)
C10—O1—C12—C13	98.7 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3$^{\rm i}$	0.85	1.78	2.632 (3)	178

Symmetry code: (i) $2 - x, -y, -z$.

H atoms were located geometrically and included in the structure-factor calculations.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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