An organic photochromic compound: (2S)-2'-ethoxy-1,3,3-trimethyl-6'-(piperidin-1-yl)spiro[indoline-2,3'-3'H-naphtho[2,1-b][1,4]oxazine]

Jian Lin,[a] Wenxiang Chai,[a]* Li Song,[b] Laishun Qin[a] and Kangying Shu[a]

[a]College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, People's Republic of China, and [b]Department of Chemistry, Key Laboratory of Advanced Textile Materials and Manufacturing Technology of the Education Ministry, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China

Correspondence e-mail: wxchai_cm@yahoo.com.cn

In the course of our synthesis of hybrid photochromic compounds, the unexpected new organic photochromic title compound, $C_{29}H_{33}N_3O_2$, (I), was obtained. It is a derivative of the parent spirooxazine 1,3,3-trimethyl-6'-(piperidin-1-yl)-spiro[indoline-2,3'-3'H-naphtho[2,1-b][1,4]oxazine], (II). The 2'-ethoxy group gives (I) different photochromic properties from its parent spirooxazine (II).

Comment

Organic photochromic compounds play an important role in various organic–inorganic hybrid photochromic systems. They are employed to implement the photochromic function. In such organic compounds interesting reversible chemical and physical conversions have also been observed, based on photoinduced ring opening and closing, cycloaddition, or electron- and energy-transfer processes (Raymo & Tomasulo, 2005; Shimizu et al., 2006; Aldoshin, 2008).
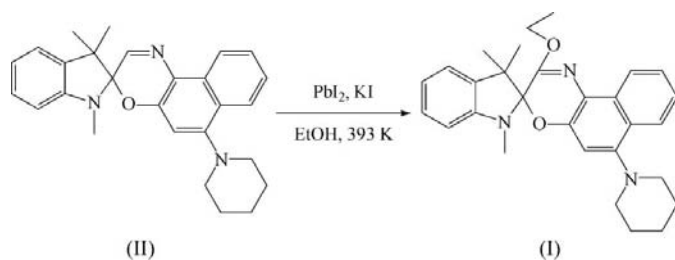
Spirooxazines are one of the well known families of organic photochromic molecules with fast photocolouring rates and high light-fatigue resistance. Over the past several decades, numerous types of spirooxazine derivatives have been characterized. It is certain that C—O bond cleavage in spiro-

oxazines induced by UV irradiation or heating is the main reason for their photochromism, and the C=N bond in the oxazine ring improves its durability (Clegg et al., 1991; Osano et al., 1991; Reboul et al., 1995; Pèpe et al., 1995; Malatesta et al., 1995; Sun et al., 1997; Liang et al., 1998; Chamontin et al., 1998; Guo et al., 2005), but there are still some details of the structure–property relationships needing further explanation. For example, it was assumed that the more planar the oxazine ring, the less photochromatic the molecule (Reboul et al., 1995). However, investigation of the molecular geometry of spirooxazines by Chamontin et al. (1998) showed that there is no obvious correlation. Additional research on the influence of substituent groups in 2'-substituted spirooxazines is also baffling (Clegg et al., 1991; Liang et al., 1998; Uznanski et al., 2001).

In the title compound, (I), there are two independent spirooxazine molecules in the asymmetric unit (Fig. 1). The dihedral angles between the benzene rings (atoms C1–C6 in molecule 1; atoms C30–C35 in molecule 2) and the naphthalene rings (atoms C10–C19 in molecule 1; atoms C39–C48 in molecule 2) are 108.4 (2) and 107.3 (2)°, respectively. Atoms N2, N3 and O2 are approximately coplanar with the naphthalene ring plane, with deviations of 0.072 (3), 0.110 (2) and 0.126 (2) Å, respectively; the corresponding values for N5, N6 and O4 in the second molecule are 0.090 (2), 0.109 (2) and 0.050 (2) Å, respectively. The five-membered rings C1/N1/C6–C8 and C30/N4/C35–C37 adopt envelope conformations, with the flaps at C8 and C37, respectively (Cremer & Pople, 1975). Furthermore, there are two substitutent groups in the molecule; the piperidine ring at the 6'-C site is in a chair conformation and the ethoxy group at the 2'-C site is approximately coplanar with the C=N group.

The oxazine rings (the key zone of the photochromism) suggest bond delocalization involving the C, N and O atoms, including the adjacent aromatic ring (Sun et al., 1997; Liang et al., 1998.). This is confirmed by the bond lengths involving the C, N and O atoms. For instance, the C1—N1 and C30—N4 bond lengths are 1.395 (3) and 1.394 (3) Å, respectively, which is between the value of 1.48 Å for a C—N single bond and 1.28 Å for a C=N double bond (Allen et al., 1987), indicating partial delocalization of the π-electron density over the indole ring. Similarly, the C19—O2 and C48—O4 bond lengths are 1.370 (2) and 1.378 (2) Å, respectively, which is between the value of 1.39 Å for a C—O single bond and 1.23 Å for a C=O double bond (Allen et al., 1987). The C10—N2 and C39—N5 bond lengths are 1.408 (3) and 1.411 (3) Å, respectively, indicating that atoms O2 and N2 in the oxazine ring are conjugated with the π-electron system of the naphthalene ring. All of these delocalizations are beneficial to the stabilization of the open-ring form of the spirooxazine.

The C_{spiro}—O and C_{spiro}—N bond lengths are two key points in the structure of (I). The former cleaves upon photoexcitation to give an open form of the spirooxazine, and the latter has an influence on the stability of the open form. Here, the C_{spiro}—O bond lengths are 1.458 (2) and 1.466 (3) Å for C8—O2 and C37—O4, respectively, and the C_{spiro}—N bond lengths are 1.423 (3) and 1.434 (3) Å for C8—N1 and
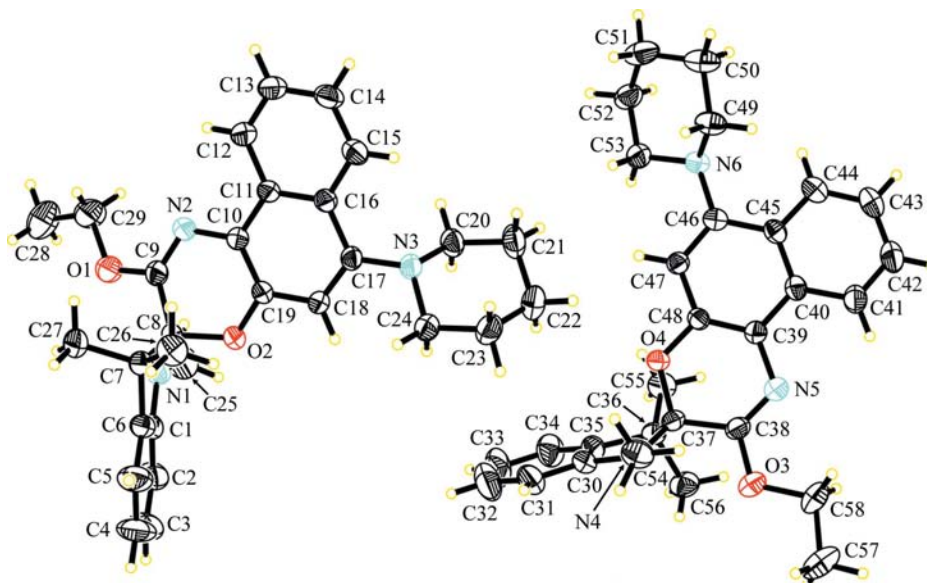
organic compounds

Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atom N4 is obscured by atom C54.

C37—N4, respectively. These bond lengths show no significant differences compared with other photochromic spirooxazines (Clegg *et al.*, 1991; Osano *et al.*, 1991; Reboul *et al.*, 1995; Pèpe *et al.*, 1995; Malatesta *et al.*, 1995; Sun *et al.*, 1997; Liang *et al.*, 1998; Chamontin *et al.*, 1998; Guo *et al.*, 2005).

A characteristic of (I) is that there is an ethoxy group at the 2′-position. A similar ethoxy-substituted compound, 2′-ethoxy-1,3,3-trimethyl-5-nitrospiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine], was synthesized by Uznanski *et al.* (2001), but it displays no photochromic properties. Interestingly, this ethoxy substituent at the 2′-position (atoms C2 and C38) leads to an obvious change in (I) compared with the parent spirooxazine, (II). The parent shows no colour change under UV light or sunlight, but the substituted compound displays various photochromic conversions in different solvents under UV exposure.

The different photochromic properties found in compound (I) require further study of its structure–property relationships. Research on the mechanism of the ethoxy reaction at the 2′-position of spirooxazine is also in progress.

Experimental

Lead(II) iodide (24 mg, 0.05 mmol), potassium iodide (17 mg, 0.1 mmol) and the parent spirooxazine, 1,3,3-trimethyl-6′-(piperidin-1-yl)spiro[indoline-2,3′-3′*H*-naphtho[2,1-*b*][1,4]oxazine] (21 mg, 0.05 mmol) were heated in a Teflon-lined stainless steel autoclave with ethanol (10 ml) at 393 K. Block-shaped pale-yellow crystals of (I) were obtained by slow evaporation from the reaction solution. Compound (I) dissolves in ethanol (EtOH), dimethylbenzene (C_8H_{10}), dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$), and appears colourless, yellow, pale-green and colourless, respectively. After irradiation with UV light, these solutions change colour to aqua green, light-blue, green and pale-blue–green, respectively. A pale-green solution is observed when (I) is dissolved in deuterochloroform ($CDCl_3$) which turns purple when exposed to sunlight. However, no colour change was observed under UV light.

Crystal data

$C_{29}H_{33}N_3O_2$	$\gamma = 83.62\ (3)°$
$M_r = 455.58$	$V = 2513.6\ (9)\ \text{Å}^3$
Triclinic, $P\bar{1}$	$Z = 4$
$a = 10.001\ (2)\ \text{Å}$	Mo $K\alpha$ radiation
$b = 12.345\ (3)\ \text{Å}$	$\mu = 0.08\ \text{mm}^{-1}$
$c = 20.513\ (4)\ \text{Å}$	$T = 296\ \text{K}$
$\alpha = 88.49\ (3)°$	$0.43 \times 0.37 \times 0.28\ \text{mm}$
$\beta = 87.32\ (3)°$	

Data collection

Rigaku R-AXIS RAPID diffractometer	24807 measured reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	11325 independent reflections
	5097 reflections with $I > 2\sigma(I)$
$T_{min} = 0.968$, $T_{max} = 0.979$	$R_{int} = 0.033$
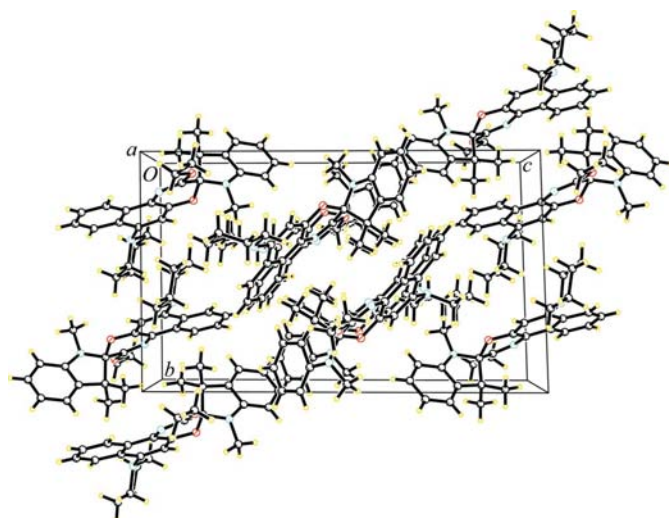
Figure 2
A packing diagram for (I), viewed along the *a* direction.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	621 parameters
$wR(F^2) = 0.189$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
11325 reflections	$\Delta\rho_{min} = -0.28$ e Å^{-3}

H atoms were added at calculated positions and refined using a riding model, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for all others.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3034). Services for accessing these data are described at the back of the journal.

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