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Key indicators

Single-crystal X-ray study
 $T = 273\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.045
 wR factor = 0.139
Data-to-parameter ratio = 13.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.1,3,3-Trimethyl-6'-(4-phenylpiperazin-1-yl)-
2,3-dihydrospiro[1*H*-indole-2,3'-3*H*-naphth-
[2,1-*b*][1,4]oxazine]

The title compound, $\text{C}_{32}\text{H}_{32}\text{N}_4\text{O}$, a spirooxazine modified with a fused phenyl-piperazinyl-naphthalene moiety, has been characterized by X-ray crystallographic techniques. The piperazine ring is in a chair conformation, while the oxazine and pyrrolidine rings adopt envelope conformations.

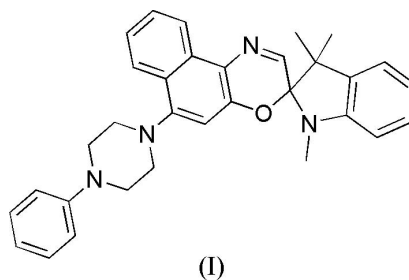
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Comment

Spiropyrans and spirooxazines are important classes of photochromic materials (Winkler *et al.*, 1998). Photochromic compounds continue to attract significant attention, in view of their general applicability as optical information storage materials or switching devices (Duerr, 1989; Dueer & Bouas-Laurent, 1990; Ichi, 2000), and also as organic photochromic materials within a plastic matrix, for example photochromic ophthalmic lenses and vehicle roof lights (Rickwood & Hepworth, 1990). Many modified spiropyrans and spirooxazines have been prepared in order to develop novel photochromic materials. The title compound, (I), is one of them. It becomes purple in sunlight, showing the suitability of the material for use in sun-lenses (Rickwood & Hepworth, 1990). Recently, our group has studied the synthesis and photochromic properties of certain spiropyrans and spirooxazines containing various functional groups (Li *et al.*, 1999; Li, Li *et al.*, 2000; Li, Wang *et al.*, 2000; Chang *et al.*, 2002; Zou *et al.*, 2003). In the course of our studies, we obtained single crystals of (I) and we report its crystal structure here.



A perspective view of (I) with the atom-labelling scheme is shown in Fig. 1. The piperazine ring is in a chair conformation, while the oxazine and pyrrolidine rings adopt envelope conformations. Some of the bond angles at the spiro atom C11 deviate significantly from the normal value of 109.5° ; the angles lie in the range 103.73 (14)– 115.08 (15) $^\circ$ (Table 1).

In the crystal packing of (I), inversion-related molecules are linked via $\text{C16}-\text{H16}\cdots\pi(\text{C27}-\text{C32})^i$ interactions [symmetry code: (i) $1 - x, 1 - y, 1 - z$]. No other hydrogen bonds are observed in the crystal structure. However, the introduction of an ethoxycarbonyl group in the 6'-position of the indoline

moiety affects the whole arrangement of the molecular self-assembly. The carbonyl O atom is involved in hydrogen bonds, leading to the formation of a helical structure (Song *et al.*, 2003).

Experimental

Compound (I) was synthesized using a method based on the reaction of an α -nitro- β -naphthol derivative with a 2-methyleneindole compound, as described by Ono *et al.* (1971). The crude product was purified by silica-gel column chromatography, using petroleum ether–ether (3:1 *v/v*) as eluant. Single crystals suitable for X-ray diffraction measurements were obtained from acetone by slow evaporation at room temperature.

Crystal data

$C_{32}H_{32}N_4O$	$D_x = 1.248 \text{ Mg m}^{-3}$
$M_r = 488.62$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1853 reflections
$a = 15.359 (3) \text{ \AA}$	$\theta = 2.7\text{--}22.1^\circ$
$b = 13.215 (3) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 12.969 (3) \text{ \AA}$	$T = 273 (2) \text{ K}$
$\beta = 99.051 (3)^\circ$	Block, colourless
$V = 2599.5 (9) \text{ \AA}^3$	$0.34 \times 0.24 \times 0.16 \text{ mm}$
$Z = 4$	

Data collection

Bruker APEX CCD area-detector diffractometer	4581 independent reflections
φ and ω scans	3018 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.037$
$T_{\text{min}} = 0.974$, $T_{\text{max}} = 0.988$	$\theta_{\text{max}} = 25.0^\circ$
13 748 measured reflections	$h = -18 \rightarrow 18$
	$k = -15 \rightarrow 12$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 0.1682P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.139$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
4581 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
337 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C22	1.367 (2)	N3—C20	1.417 (2)
O1—C11	1.465 (2)	N3—C26	1.450 (2)
N1—C2	1.404 (2)	N3—C23	1.456 (2)
N1—C11	1.436 (2)	N4—C27	1.410 (2)
N1—C1	1.455 (2)	N4—C25	1.456 (3)
N2—C12	1.272 (2)	N4—C24	1.457 (3)
N2—C13	1.411 (2)		
C2—N1—C11	107.83 (14)	O1—C11—C12	109.15 (15)
C2—N1—C1	119.73 (15)	N1—C11—C8	103.73 (14)
C11—N1—C1	118.73 (15)	O1—C11—C8	109.46 (14)
N1—C11—O1	106.18 (13)	C12—C11—C8	115.08 (15)
N1—C11—C12	112.78 (15)		

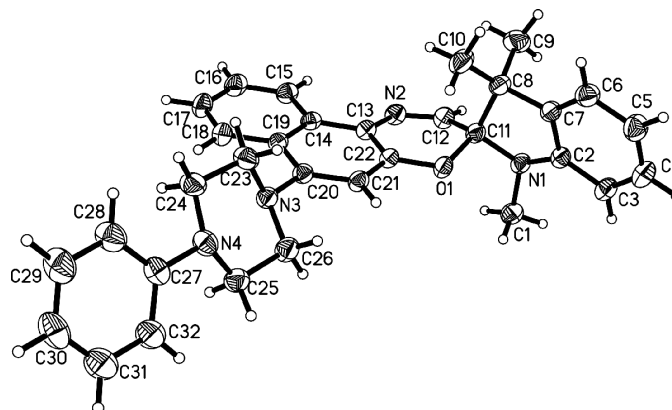


Figure 1

The structure of (I), showing 30% probability displacement ellipsoids and the atom-labelling scheme.

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 \AA , and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for other H atoms. Methyl groups were allowed to rotate freely about the C—C bond.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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