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Synthesis and X-ray structural characterization of new spiroxazine

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Abstract

A novel spiroxazine containing a mesogenic group has been prepared. The colourless spiroxazine exhibit photochromism through ring opening of the oxazine ring. The crystal structure was determined by X-ray crystallography and the crystal was found to exist in the triclinic space group P_1 (No. 1).

Keywords: Spiroxazine; Photochromism; X-ray crystallography; Triclinic space group

1. Introduction

A photochromic compound is characterized by its ability to undergo a reversible colour change. Interest in the photochromism of organic materials began to increase substantially around 1940. The principal studies of photochromic compounds involved acquiring an insight into mechanisms of the photoprocesses, determining the structures of the uncoloured form and the coloured form, and developing synthetic methods.

Photochromic spiro compounds are promising objects of research [1,2], since reversible isomerization into a merocyanine dye holds the prospect of usage in optical devices including storage and switches.

Although photochromic compounds have attracted significant attention because of their potential use as sunlight-activated, self-coloured glasses and optical memory media, they still await major commercial exploitation. One of the prime reasons for the lack of industrial applications for photochromic materials, particularly organic photochromic compounds, is their poor durability. Although the photochromism of spiropyran has been extensively studied [3,4], only little work has been carried out on spiroxazine dyes. These two classes of compounds are similar in many aspects, but the replacement of the benzopyran ring by a naphthoxazine ring, which results in spironaphthoxazine, greatly improved resistance to

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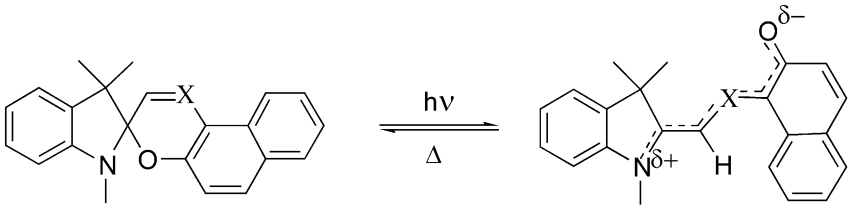


prolonged UV irradiation, which confers greater commercial importance [5].

We have previously reported on the synthesis, spectral properties, and solvatochromic properties of spiroxazines [6–8]. We have also reported the preparation and surface properties of spiroxazine monolayer on gold [9–11].

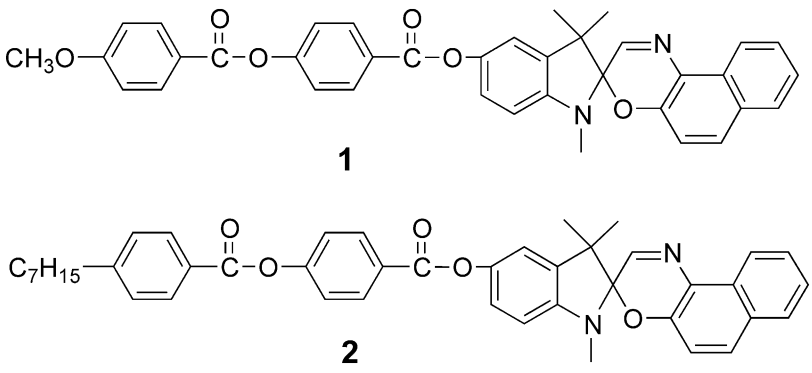
The combination of photochromic and liquid crystalline properties in one molecule may lead to very versatile materials, sensitive to light, and electric and magnetic fields.

Spiroxazine molecules **1** and **2** represent quasi-liquid-crystals that show the photochromic effect [12]. The supercooled films of these compounds form blue merocyanine molecules on UV irradiation, which are spontaneously converted back to a noncoloured spiroxazine form in the dark.

In the present paper, we describe the synthesis and crystal structure of photochromic liquid crystalline spiroxazine substituted with a mesogenic group in naphthalene ring.

2. Experimental

Melting points were determined using an Electrothermal IA 900 apparatus and were uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 MHz FT-NMR



spectrometer with TMS as internal standard. UV–visible spectra were recorded on a Shimadzu 2100 spectrometer.

2.1. Materials

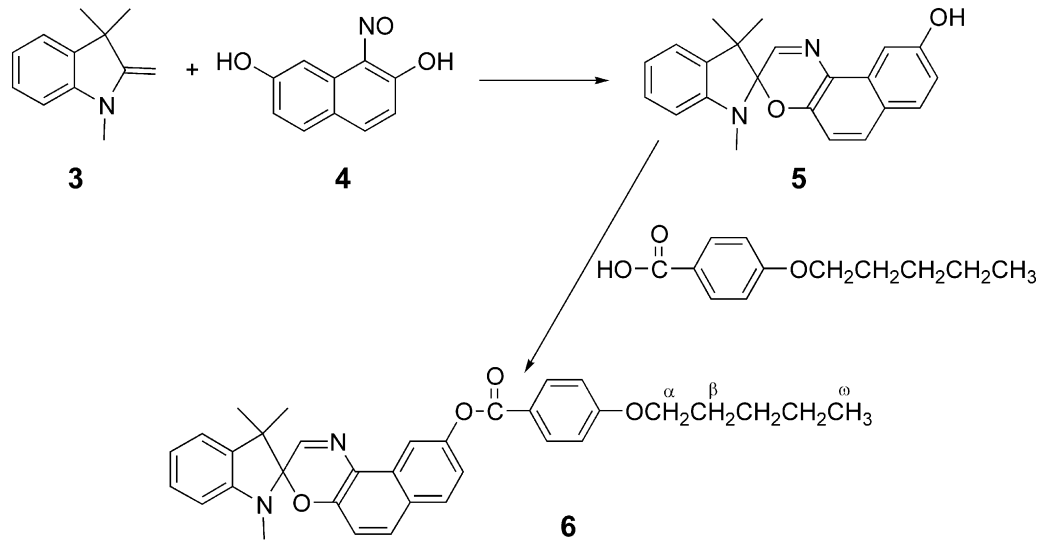
1,3,3-Trimethyl-2-methylene-indoline (Fischer's base) and 2,7-dihydroxy-naphthalene were purchased from Fluka Chemical Company. 4-(pentyloxy)benzoic acid, 1,3-dicyclohexyl-carbodiimide and 4-dimethylaminopyridine were purchased from Aldrich Chemical Company. All chemicals were of the highest grade available and were used without further purification.

2.2. Synthesis of 1,3,3-trimethyl-6′-hydroxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-b][1,4] oxazine 5

1,3,3-Trimethyl-6′-hydroxyspiro[2H]-indol-2,3′-[3H]-naphth[2,1-b][1,4] oxazine **5** was prepared from 1,3,3-trimethyl-2-methylene-indoline **3** and 1-nitroso-2,7-dihydroxy-naphthalene **4** according to the method described in Refs [13,14]. Yield 17.0 g (50%), mp. 211.5–214 °C. Elemental analysis: C; 76.89, H; 4.97, N; 8.59%. $C_{22}H_{20}N_2O_2$ requires: C; 76.72, H; 5.85, N; 8.13%.

2.3. Synthesis of spiroxazine 6

2.0 mmol (0.69 g) of compound **5**, 4-(pentyloxy)-benzoic acid (0.42 g), 1,3-dicyclohexyl-carbodiimide and 4-dimethylaminopyridine were added into a solution of 80 ml dichloromethane. The solution was refluxed for several hours under nitrogen. After reflux, 120 ml dichloromethane was added into the reaction solution. The mixture was cooled at room temperature and filtered to remove the precipitate. The solvent was removed from filtrate and a solid product obtained was separated by column chromatography with the mixture of hexane and ethyl acetate in 3:1 (v/v) as eluent and recrystallized with hexane/ethyl acetate and ethyl acetate/acetone two times. Purified compound was white powder. Yield 0.65 g (60%), mp. 160–162 °C, M^+ 534. Elemental analysis: found C; 76.13, H; 6.51, N; 5.15. $C_{34}H_{34}N_2O_4$ requires: C; 76.38, H; 6.41, N; 5.24%. ^{1}H NMR ($CDCl_3$): 0.96 (3H, t, H(ω)), 1.347 (3H, s), 1.352 (3H, s), 1.41–1.48 (4H, m), 1.84 (2H, q, $J=7.3$ Hz, H(β)), 2.76 (3H, s), 4.06 (2H, t, H(α)), 6.58 (1H, d), 6.90 (1H, t), 6.99 (2H, d), 7.00 (1H), 7.08 (1H, d), 7.21 (1H), 7.28 (1H), 7.67 (1H, d, $J=8.9$ Hz), 7.71 (1H, s), 7.79 (1H, d, $J=8.8$ Hz), 8.20 (2H, d, $J=8.9$ Hz), 8.36 (1H, d).



2.4. X-ray crystallographic analysis

Preliminary experiments and data collection for the X-ray crystal structure determination were performed on an Enraf-Nonius CAD4 Turbo diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å). A small single crystal ($0.70 \times 0.10 \times 0.08$ mm^3) of **6** was glued to a glass fiber using epoxy resin. Twenty-five reflections taken in diverse reciprocal space were centered using an automatic search program and were used to obtain cell parameters. After the preliminary cell has been confirmed, high-angle data ($2\theta > 20^\circ$) were collected and 25 of these reflections were centered and used to obtain more accurate cell parameters. Unit cell parameters and systematic absences indicated a triclinic space group P_1 (No. 1) with $Z = 1$. Data were collected on this improved unit cell at ambient temperature up to $2\theta = 48.26^\circ$. Data reduction, including the correlation for Lorentz-polarization, decay, and absorption, were performed. Crystal structure was resolved and refined using full-matrix least-square procedure using the SHELXL97, which resulted in final R_1 and wR_2 indices of 0.0728 and 0.1909, respectively. Single crystal was obtained by slow evaporation of a mixture of ethanol and acetone.

The crystallographic data are summarized in Table 1 and the final structural parameters are presented in Table 2. The selected bond lengths and bond angles are tabulated in Table 3 and 4, respectively. The structure model was drawn using ORTEP(III), an Oak Ridge Thermal Ellipsoid Plot program and is shown in Fig. 1. Unit cell packing diagram is shown in Fig. 2.

3. Results and discussion

An interesting point in photochromic liquid crystals is how the changes of mesophase can be caused by the reversible transformations of the molecular structure of photochromic compounds. These phenomena have been attracting practical interests because photochromism induces reversible changes in various optical properties of

Table 1
Crystallographic data and structure refinement

Empirical formula	$C_{68}H_{68}N_4O_8$
Formula weight	1069.26
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P_1
Unit cell dimensions	$a = 8.459(7)$ Å, $b = 10.881(8)$ Å, $c = 16.243(1)$ Å $\alpha = 83.67(2)^\circ$, $\beta = 85.80(2)^\circ$, $\gamma = 78.90(2)^\circ$
Volume	1456.1(16) Å^3
Z	1
Calculated density	1.219 mg/m^3
Absorption coefficient	0.080 mm^{-1}
$F(000)$	568
Crystal size (mm^3)	$0.70 \times 0.10 \times 0.08$
θ Range for data collection	1.92–24.13°
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5045/3/721
Final R indices [$I > 2\sigma(I)$]	[a] $R_1 = 0.0728$, [b] $wR_2 = 0.1909$
R indices (all data)	[a] $R_1 = 0.1120$, [b] $wR_2 = 0.2403$
Goodness-of-fit on F^2	1.100[c]

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$.

[b] $wR_2 = \left((\Sigma \ w | F_o - F_c |)^2 / \Sigma \ w F_o^2 \right)^{1/2}$.

[c] Goodness-of-fit $= \left\{ \Sigma \left[w \left(F_o^2 - F_c^2 \right)^2 \right] / (n - p) \right\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$)

Atom	x	y	z	U(eq)[a]
O(1)	−7844(11)	14 231(7)	6924(5)	84(2)
O(2)	−11 330(12)	12 599(8)	3356(5)	94(3)
O(3)	−13 305(13)	11 960(9)	4130(6)	114(3)
O(4)	−11 717(12)	7743(8)	1652(6)	96(3)
O(5)	277(9)	8097(6)	7593(5)	72(2)
O(6)	3673(11)	9736(8)	11 201(5)	88(3)
O(7)	5701(13)	10 382(9)	10 367(6)	110(3)
O(8)	4149(12)	14 584(8)	12 889(6)	96(3)
N(1)	−6302(15)	12 610(10)	7742(7)	101(4)
N(2)	−7949(13)	12 452(8)	5808(6)	83(3)
N(3)	−2607(14)	8772(10)	7861(6)	97(3)
N(4)	343(12)	9885(8)	8703(7)	82(3)
C(1)	−5045(15)	13 126(9)	8066(8)	74(3)
C(2)	−4490(2)	12 979(12)	8851(7)	95(4)
C(3)	−3200(3)	13 522(18)	8978(14)	141(7)
C(4)	−2470(2)	14 118(15)	8371(14)	125(7)
C(5)	−2970(17)	14 254(13)	7536(13)	110(5)
C(6)	−4299(14)	13 746(9)	7430(7)	67(3)
C(7)	−5006(13)	13 628(9)	6618(7)	72(3)
C(8)	−5030(3)	14 770(2)	5986(12)	195(10)
C(9)	−3673(18)	12 773(11)	6136(7)	123(4)
C(10)	−7490(2)	12 250(2)	8226(9)	198(11)
C(11)	−6545(15)	13 157(9)	6906(7)	72(3)
C(12)	−6907(17)	12 203(11)	6365(8)	87(4)
C(13)	−8866(14)	13 660(9)	5715(7)	64(3)
C(14)	−8863(14)	14 554(11)	6277(7)	70(3)
C(15)	−9802(13)	15 733(8)	6187(7)	68(3)
C(16)	−10 798(14)	16 066(10)	5568(7)	72(3)
C(17)	−10 904(16)	15 206(10)	4968(7)	74(3)
C(18)	−9957(13)	13 994(9)	5074(7)	63(3)
C(19)	−10 108(14)	13 080(10)	4508(6)	69(3)
C(20)	−11 166(15)	13 452(11)	3921(7)	78(3)
C(21)	−12 112(18)	14 657(14)	3780(8)	97(4)
C(22)	−11 996(17)	15 546(11)	4320(9)	92(4)
C(23)	−12 384(16)	11 806(11)	3561(8)	77(3)
C(24)	−12 154(16)	10 775(10)	3013(7)	76(3)
C(25)	−11 066(18)	10 671(11)	2379(8)	84(4)
C(26)	−10 902(17)	9695(12)	1860(9)	96(4)
C(27)	−11 833(16)	8749(11)	2086(7)	79(3)
C(28)	−12 940(17)	8906(13)	2743(8)	94(4)
C(29)	−13 101(14)	9904(11)	3181(7)	75(3)
C(30)	−10 620(2)	7637(13)	950(9)	118(5)
C(31)	−10 670(2)	6331(13)	641(9)	105(5)
C(32)	−10 100(3)	5204(13)	1247(11)	153(8)
C(33)	−10 190(4)	3990(2)	900(2)	264(17)
C(34)	−9270(3)	3484(18)	393(16)	204(12)

[a] U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

liquid crystalline phase and is applicable to optical recording as well as display devices. Generally, there are three ways to modify the chemical structure for liquid crystalline spiroxazine containing mesogenic group. In order to synthesize the liquid crystalline spiroxazine derivatives in this work, the authors choose the route 1 in Scheme 1. As it is fairly difficult to determine experimentally the structure of open form, we have established the X-ray structure of a closed form of spiroxazine 6, final R factors being $R_1 = 0.0728$ and $wR_2 = 0.1909$. The molecules of spiroxazine arrange themselves in a triclinic crystallographic system (P_1), unit cell of dimensions: $a = 8.459(7)$, $b = 10.881(8)$, $c = 16.243$ Å with $\alpha = 83.67(2)^\circ$, $\beta = 85.80(2)^\circ$, $\gamma = 78.90(2)^\circ$.

This closed form transforms to a coloured open form by UV irradiation. From the ORTEP diagram, we can concluded that the spiro center is tetrahedral (Fig. 1). As shown in Fig. 1, the dye molecules are disposed in the reversible direction. The bond length of C(1)–N(1) fall in the range of those of pyramidal in structure of the N(1) atom [15,16]. The indoline ring adopts the pyramidal configuration of the N(1) atom, which reduces the conjugation of the lone electron pair of the N(1) atom and the π system of the aromatic ring. The indoline heterocycle was found to be non-planar, with a dihedral angle of 21.74° between the plane N(1)–C(1)–C(6)–C(7) and N(1)–C(7)–C(11). The lack of planarity is probably due to the pyramidal structure of N atom. The conformation of six-membered oxazine ring is non-planar and is folded along the O(1)...C(12) line. The ring formed by C(1)–C(11)–C(12) is tilted from the plane of O(1)–C(12)–C(14) by 21.37°.

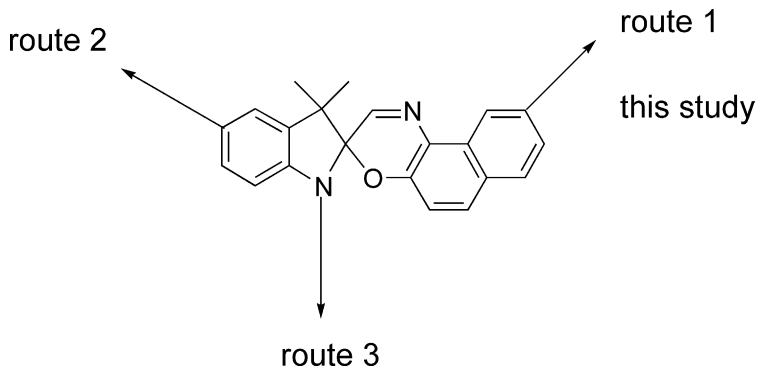
Introduction of a long alkyl chain at the naphthyl moiety in spiroxazine induces a slight elongation of the C(1)–N(1) bond to 1.449 Å, compared to unsubstituted spiroxazine, 1,3,3,-trimethylspiro[indoline-2,3′-[3H]-naphth[2,1-b][1,4]oxazine, while O(1)–C(14) [1.380 Å] and C_{spiro}(11)–N(1)

Table 3
Selected bond lengths (Å)

O(1)–C(14)	1.380(13)	C(13)–C(14)	1.406(14)
O(1)–C(11)	1.443(13)	C(13)–C(18)	1.413(15)
O(2)–C(23)	1.356(14)	C(14)–C(15)	1.372(14)
O(2)–C(20)	1.407(14)	C(15)–C(16)	1.334(14)
O(3)–C(23)	1.169(14)	C(16)–C(17)	1.441(15)
O(4)–C(27)	1.350(14)	C(17)–C(18)	1.405(15)
O(4)–C(30)	1.416(16)	C(17)–C(22)	1.423(17)
N(1)–C(10)	1.321(18)	C(18)–C(19)	1.455(13)
N(1)–C(11)	1.433(15)	C(19)–C(20)	1.332(16)
N(1)–C(1)	1.449(16)	C(20)–C(21)	1.403(18)
N(2)–C(12)	1.281(14)	C(21)–C(22)	1.397(17)
N(2)–C(13)	1.390(13)	C(23)–C(24)	1.482(16)
C(1)–C(6)	1.356(16)	C(24)–C(25)	1.329(16)
C(1)–C(2)	1.372(16)	C(24)–C(29)	1.349(15)
C(2)–C(3)	1.37(2)	C(25)–C(26)	1.408(17)
C(3)–C(4)	1.31(3)	C(26)–C(27)	1.415(17)
C(4)–C(5)	1.43(2)	C(27)–C(28)	1.369(16)
C(5)–C(6)	1.374(17)	C(28)–C(29)	1.342(17)
C(6)–C(7)	1.515(15)	C(30)–C(31)	1.567(19)
C(7)–C(11)	1.514(17)	C(31)–C(32)	1.51(2)
C(7)–C(8)	1.52(2)	C(32)–C(33)	1.50(2)
C(7)–C(9)	1.542(15)	C(33)–C(34)	1.20(4)
C(11)–C(12)	1.519(14)		

Table 4
Selected bond angles (°)

C(14)–O(1)–C(11)	120.4(8)	C(15)–C(14)–C(13)	122.1(11)
C(23)–O(2)–C(20)	118.5(9)	O(1)–C(14)–C(13)	118.2(10)
C(27)–O(4)–C(30)	118.6(11)	C(16)–C(15)–C(14)	120.8(9)
C(10)–N(1)–C(11)	121.6(12)	C(15)–C(16)–C(17)	121.1(10)
C(10)–N(1)–C(1)	121.9(12)	C(18)–C(17)–C(22)	121.0(10)
C(11)–N(1)–C(1)	108.6(9)	C(18)–C(17)–C(16)	117.6(11)
C(12)–N(2)–C(13)	118.0(9)	C(22)–C(17)–C(16)	121.3(11)
C(6)–C(1)–C(2)	120.7(13)	C(17)–C(18)–C(13)	120.9(9)
C(6)–C(1)–N(1)	108.7(11)	C(17)–C(18)–C(19)	119.0(11)
C(2)–C(1)–N(1)	130.3(12)	C(13)–C(18)–C(19)	120.1(10)
C(1)–C(2)–C(3)	118.2(16)	C(20)–C(19)–C(18)	117.0(11)
C(4)–C(3)–C(2)	121.8(18)	C(19)–C(20)–C(21)	126.1(12)
C(3)–C(4)–C(5)	121.9(18)	C(19)–C(20)–O(2)	118.6(11)
C(6)–C(5)–C(4)	115.2(15)	C(21)–C(20)–O(2)	115.2(12)
C(1)–C(6)–C(5)	122.1(13)	C(22)–C(21)–C(20)	117.8(12)
C(1)–C(6)–C(7)	110.1(11)	C(21)–C(22)–C(17)	119.0(12)
C(5)–C(6)–C(7)	127.3(13)	O(3)–C(23)–O(2)	120.2(11)
C(6)–C(7)–C(11)	102.4(10)	O(3)–C(23)–C(24)	127.5(11)
C(6)–C(7)–C(8)	114.1(12)	O(2)–C(23)–C(24)	112.3(11)
C(11)–C(7)–C(8)	121.1(11)	C(25)–C(24)–C(29)	119.2(11)
C(6)–C(7)–C(9)	105.6(9)	C(25)–C(24)–C(23)	123.4(11)
C(11)–C(7)–C(9)	118.9(9)	C(29)–C(24)–C(23)	117.4(11)
C(8)–C(7)–C(9)	94.5(14)	C(24)–C(25)–C(26)	122.0(12)
N(1)–C(11)–O(1)	108.2(9)	C(25)–C(26)–C(27)	117.2(12)
N(1)–C(11)–C(7)	105.3(10)	O(4)–C(27)–C(28)	119.7(11)
O(1)–C(11)–C(7)	108.1(9)	O(4)–C(27)–C(26)	122.1(11)
N(1)–C(11)–C(12)	111.2(10)	C(28)–C(27)–C(26)	118.1(11)
O(1)–C(11)–C(12)	111.3(10)	C(29)–C(28)–C(27)	121.2(12)
C(7)–C(11)–C(12)	112.4(10)	C(28)–C(29)–C(24)	121.9(11)
N(2)–C(12)–C(11)	124.4(11)	O(4)–C(30)–C(31)	105.6(12)
N(2)–C(13)–C(14)	122.8(11)	C(32)–C(31)–C(30)	115.0(13)
N(2)–C(13)–C(18)	119.8(9)	C(33)–C(32)–C(31)	111.3(18)
C(14)–C(13)–C(18)	117.2(9)	C(34)–C(33)–C(32)	127(3)
C(15)–C(14)–O(1)	119.7(9)		



Scheme 1.

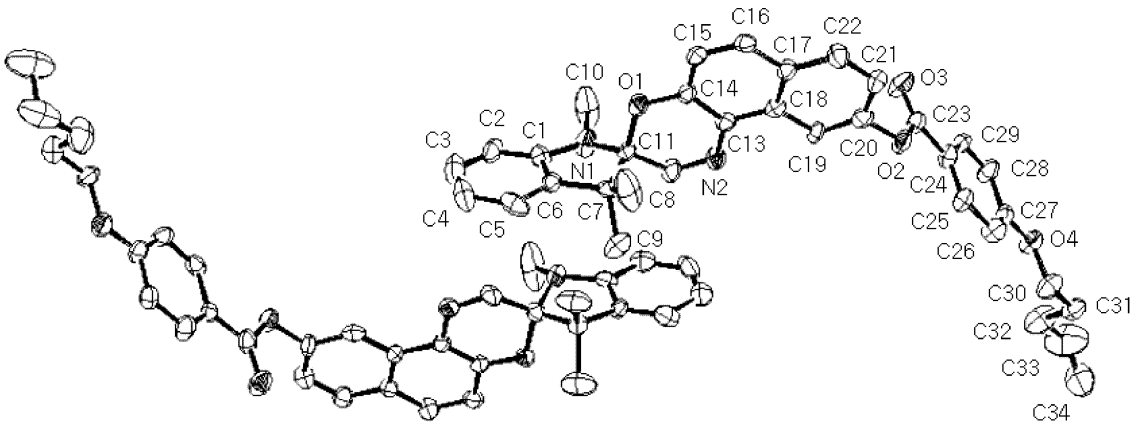


Fig. 1. Ortep view of molecular structure with thermal ellipsoids drawn at 50% probability level and atomic numbering for dye **6**.

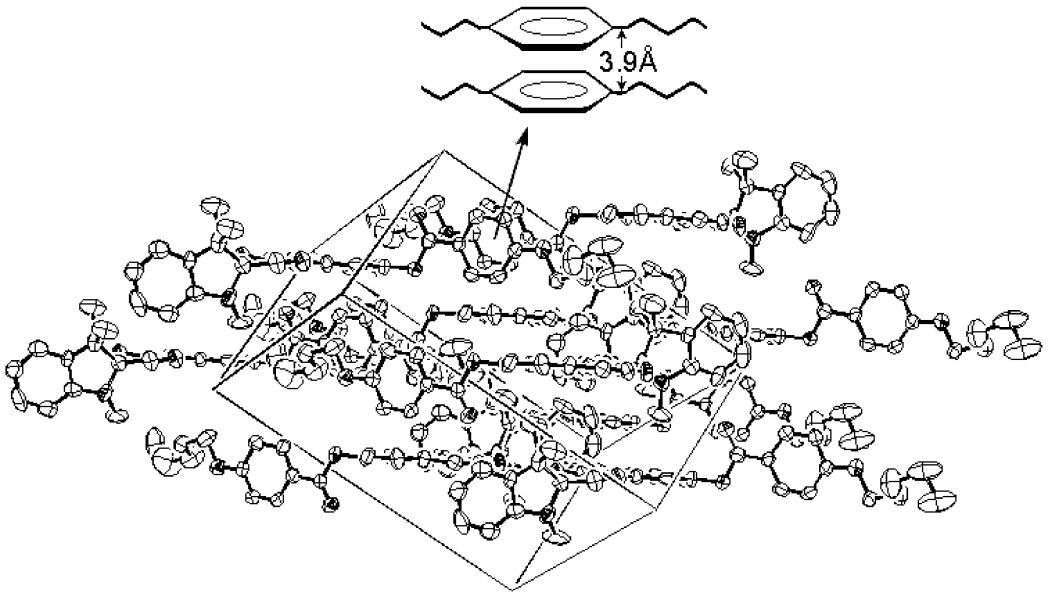


Fig. 2. Unit cell packing diagram of dye **6**.

(1.433 Å) bond lengths are unchanged [17]. The crystal packing scheme was shown in Fig. 2. Only the phenyl groups overlapped with face-to-face geometry, with an interplanar separation of 3.9 Å. The major force of molecular packing might come from these aromatic π–π stacking interaction between the molecules.

Our research on the photochromical phase transition behaviors of spiroxazine liquid crystalline systems aims the optical-image storage devices. The liquid crystalline properties of the spiroxazines synthesized in this paper will be reported separately.

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References

[1] Brown GH, editor. Photochromism. New York: John Wiley and Sons, 1991.
[2] Durr H, Bonas-Laurent H, editors, Photochromism molecules and systems. Amsterdam: Elsevier, 1990.
[3] Kawauchi S, Yoshida H, Yamashita N, Ohira M, Saeda S, Werie MI. Bulletin of Chemical Society of Japan 1990; 63:267.
[4] Reeves DA, Wilkinson F. Journal of Chemical Society, Faraday Transition 1973;69:1341.
[5] Okudahida T. Seni Kakkaishi Japan 1992;48:253.
[6] Kim SH, Lee SN. Chemistry Express 1992;7:849.
[7] Kim SH, Park LS, Kim DJ, Kil KJ, Jung SC. Chemistry Express 1993;7:713.
[8] Kim SH, Park SJ, Song KH. Chemistry Express 1993; 8:741.
[9] Kim SH, Lee SM, Park JH, Kim JH, Koh KN, Kang SW. Dyes and Pigments 2000;45:55.
[10] Kim SH, Ock KS, Im JH, Kim JH, Koh KN, Kang SW. Dyes and Pigments 2000;46:55.
[11] Kim SH, Ock KS, Kim JH, Koh KN, Kang SW. Dyes and Pigments 2000;48:1.
[12] Shrabina L, Buchholtz F, Yitzchaik S, Krongauz UA. Molecular Crystal Liquid Crystals 1990;7:643.
[13] Kakishita T, Matsumoto K, Kiyotsukuri T, Matsumura K, Hosoda M. J Heteorcyclic Chem 1992;29:1709.
[14] Dürr H, Ma Y., Corterllaro G. Synthesis, 1995; March: 294.
[15] Brown G, Marsh RE. Acta Crystallogr 1963;191–204.
[16] Fukuyo H, Hirotsu K, Higuchi K. Acta Crystallogr Sect B 1982;28:640–3.
[17] Millini R, Del Piero G, Allegrini P, Crisci L, Malatesta V. Acta Crystallogr Sect C 1991;47:2567–9.