Dyes and Pigments 91 (2011) 370-377

Contents lists available at ScienceDirect

Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

The synthesis, spectroscopic properties and crystal structures of some rhodanine merocyanine dyes for optical recording with a blue diode laser

Qi Liu^a, Xue Wang^a, Lan-Ying Wang^{a,*}, Yi-Le Fu^a, Xiang-Han Zhang^{a,b}

^a Key Laboratory of Synthetic and Natural Functional Molecule Chemistry, Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, PR China

^b School of Life Sciences and Technology, Xidian University, Xi'an 710071, PR China

A R T I C L E I N F O

Article history: Received 29 November 2010 Received in revised form 25 March 2011 Accepted 28 March 2011 Available online 13 April 2011

Keywords: Rhodanine Merocyanine dyes for optical information storage in the blue region Microwave synthesis Spectroscopic properties Crystal structure H-bond

1. Introduction

Dyes suitable for optical recording with a blue diode laser have attracted wide attention due to their core role in super-high density recording technology. They have been extensively studied for optical disc storage [1]. The literature reported so far on these dyes includes porphyrin dyes [2], azo dyes [3,4], cyanine dyes [5,6], coumarin derivative dyes [7]. Generally, the maximum absorption wavelengths of dyes for optical recording with a blue diode laser are in the range from 350 to 500 nm and they have typical characteristic features, such as strong absorption, high films refractive index, high sensitivity and high opto-thermostability [8].

Microwave irradiation, which offers several advantages including shorter reaction times, cleaner reaction profiles and simple experimental/product isolation procedures compared to conventional chemical protocols [9], presents a powerful tool for organic reactions [10]. As the optical properties of dyes for optical recording with a blue diode laser depend not only on the spectroscopic properties of the molecules but also their crystallographic

ABSTRACT

Six rhodanine merocyanine dyes were synthesized via both a conventional solvent method and a microwave method using rhodanine, 2-methylthio quaternary salts and 1*H*-indole-3-carbaldehyde as starting materials. The products were identified using UV–Vis, IR, MS, ¹H NMR and elemental analysis. The UV–Vis absorption spectra of the dyes in chloroform, DMSO, water, acetone, ethanol and methanol were investigated. The structures of two dyes (**5a** and **5b**) were characterized and analyzed by X-ray diffraction as well. Crystallographic data revealed that dye **5a** belonged to tetragonal, *I*4 (1)/a space group, while dye **5b** belonged to monoclinic, *P*-1 space group. In the case of both dyes, intermolecular associations occurred by π - π stacking and intermolecular hydrogen bonds, which contributed to stabilize the crystal structure.

© 2011 Elsevier Ltd. All rights reserved.

arrangements [11–14], it is necessary to study the single crystal X-ray structure of the dyes, which reveal molecular conformation, intra- and intermolecular interactions in the solid state. The structural information gained from the analysis assists in understanding the technical performance of dyes.

In this paper a microwave-assisted preparation of a series of rhodanine merocyanine dyes for optical recording with a blue diode laser is described in high yield (Scheme 1). The approach provided a novel and environmentally friendly pathway to synthesise several useful rhodanine merocyanine dyes. For comparison, we also used a conventional solvent method to synthesise the target products and showed the difference on yields. Then, we explored the UV–Vis absorption of the dyes in different solvents. The detailed analysis of crystal and molecular structure for dyes **5a** and **5b**, which obtained by X-ray diffraction analysis, are also described.

2. Experimental

2.1. General

Melting points were taken on a XT-4 micromelting apparatus and uncorrected. Elemental analyses were performed with a Vario



^{*} Corresponding author. Tel.: +86 29 88302604; fax: +86 29 88303798. *E-mail address:* wanglany@nwu.edu.cn (L-Y. Wang).

^{0143-7208/\$ –} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2011.03.030



Scheme 1. Synthetic route of 1a-3a and 5a-c.

EL III instrument. IR spectra in cm⁻¹ were recorded on a Brucker Equiox-55 spectrometer. ¹H NMR spectra were recorded at 400 MHz on a Varian Inova-400 spectrometer and chemical shifts were reported relative to internal Me₄Si. MS was recorded on a HP5973 MS spectrometer. The UV–Vis absorption spectra were recorded on a General TU-1201 UV–Vis spectrometer. The used Microwave oven is Galanz Model No.WD700S-1. Single crystal Xray diffraction data were collected on a Bruker SMART APEX II CCD X-ray crystallography.

Commercial grade 2-sulfanylbenzothiazole, 1-methyl-2-quinolinethione, 2-sulfanylpyridine were purchased from Shanghai Shanpu Chemical Co. Ltd, Shanghai Jinshantingxin Chemical Reagent and Lianyungang Sanyou Fine Chemicals Factory, respectively. 1*H*-indole-3-carboxaldehyde and 5-methoxy-1*H*-indole-3carboxaldehyde were purchased from Shanghai Nuotai Chem CO. Ltd. 5-Benzyloxy-1*H*-indole-3-carboxaldehyde was purchased from Liyang Huibang Chemical Co. Ltd. The solvents were of analytical grade. All other reagents were commercially available and used as received without further purification. 2-methylthio quaternary salts **1** [15,16], **2** [17], **3** [18] and rhodanine [19] were synthesized according to the methods reported in literatures with some modification.

2.2. Preparation of dyes 1a-5c

The synthetic strategy for the preparation of six dyes is shown in Scheme 1. The condensation of three 2-methylthio quaternary salts or three 1*H*-indole-3-carbaldehyde with rhodanine was carried out in a Galanz microwave oven. 1.3 mmol 2-methylthio quaternary salts or 1.3 mmol 1*H*-indole-3-carbaldehyde, 1.3 mmol rhodanine and a few drops of triethylamine or piperidine were mixed together at ambient temperature in a beaker. The mixture was subjected to microwave irradiation at optimized power and time under solvent-free conditions. After cooling, dye **1a** and **2a** were purified by soxhlet extraction using ethanol as solvent, while dye **3a** was purified by recrystallization from acetone. Dyes **5a**–**c** were purified by recrystallization from EtOH. The conventional solvent method gave similar results by refluxing a mixture of 2.6 mmol 2-methyl-thio quaternary salts or 2.6 mmol 1*H*-indole-3-carbaldehyde, 2.6 mmol rhodanine and a few drops of triethylamine or piperidine

in EtOH for 2–3 h. The details of reaction conditions and yields are provided in Table 1.

2.3. Structural confirmation

2.3.1. 5-(3-Methyl-2-benzothiazolinylidene)rhodanine (1a)

Yellow powder, m.p.: 254-255 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ (ppm): 13.25 (s, 1H, NH), 7.88 (d, *J* = 8.4 Hz, 1H, ArH), 7.60 (d, *J* = 8.4 Hz, 1H, ArH), 7.46–7.50(m, 1H, ArH), 7.29–7.33(m, 1H, ArH), 3.90 (s, 3H, NCH₃); IR (KBr) υ : 3446 (m. b, υ_{N-H}), 3086 (s, $\upsilon_{=C-H}$), 2928, 2834 (m, υ_{C-H}), 1622 (s, $\upsilon_{C=C}$, $\upsilon_{C=0}$), 1492, 1304 (m, δ_{N-H} , υ_{C-N}), 1442 (m, δ_{C-H}), 1254 (s, $\upsilon_{C=S}$), 741 (w, $\delta_{=C-H}$)cm⁻¹. MS (70 eV) *m*/*z* (%): 280 (51), 221 (12), 192 (100), 178 (12), 102 (26), 69 (8), 45 (8), 32 (3). Anal. Calcd. for C₁₁H₈N₂OS₃ = 279.98: C, 47.12; H, 2.88; N, 9.99; Found: C, 47.06; H, 2.48; N, 9.85. UV–Vis (MeOH) λ_{max} : 426 nm. ε : 1.69 × 10⁴ L mol⁻¹ cm⁻¹.

2.3.2. 5-(1-Methyl-2-quinolylidene)rhodanine (2a)

Brownish yellow power, m.p.: 248–249 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ (ppm): 12.85 (s, 1H, NH), 7.88 (d, J = 8.4 Hz, 1H, –CH=), 7.76 (d, J = 8.4 Hz, 1H, –CH=), 7.71–7.73 (m, 2H, ArH), 7.41–7.44 (m, 2H, ArH), 3.97 (s, 3H, NCH₃); IR (KBr) υ : 3445 (m. b, υ_{N-H}), 3100 (m, $\upsilon_{=C-H}$), 2968, 2849 (m, υ_{C-H}), 1639 (m, $\upsilon_{C=C}$), 1598 (s, $\upsilon_{C=O}$), 1558, 1313 (m, δ_{N-H} , υ_{C-N}), 1439 (m, δ_{C-H}), 1221 (s, $\upsilon_{C=S}$), 743 (w, $\delta_{=C-H}$) cm⁻¹. MS (70 eV) m/z (%): 274 (34), 215 (10), 186 (100), 172 (2), 116 (9), 93 (16), 77 (5), 69 (4), 59 (4), 45 (13). Anal. Calcd. for C₁₃H₁₀N₂OS₂ = 274.02: C, 56.91; H, 3.67; N, 10.91. Found: C, 56.37; H, 3.19; N, 10.97. UV–Vis (MeOH) λ_{max} : 478 nm. ε : 1.21 × 10⁴ L mol⁻¹ cm⁻¹.

2.3.3. 5-(1-Methyl-2- pyridinylidene)rhodanine (3a)

Brown massive solid, m.p.: >300 °C. ¹H NMR(DMSO-d₆, 400 MHz) δ(ppm): 12.55 (s, 1H, NH), 8.56 (d, *J* = 8.8 Hz, 1H, ArH), 7.99 (d, *J* = 8.8 Hz, 1H, ArH), 7.60–7.64 (m, 1H, ArH), 6.81–6.84 (m, 1H, ArH), 3.97 (s, 3H, NCH₃); IR(KBr) υ: 3445 (m. b, v_{N-H}), 3057(m, $v_{=C-H}$), 2979, 2851 (m, v_{C-H}), 1679 (m, $v_{C=C}$), 1639 (s, $v_{C=0}$), 1565, 1330 (m, δ_{N-H} , v_{C-N}), 1430 (w, δ_{C-H}), 1238 (s, $v_{C=S}$) cm⁻¹. MS (70 eV) *m/z* (%): 224 (20), 165 (100), 137 (2), 122 (4), 95 (7), 77 (17), 69 (55), 55 (41). Anal. Calcd. for C₉H₈N₂OS₂ = 224.01: C, 48.19; H, 3.59; N, 12.49; Found: C, 47.73; H, 3.81; N, 12.68. UV–Vis (MeOH) λ_{max} : 435 nm. ε : 1.53 × 10⁴ L mol⁻¹ cm⁻¹.

2.3.4. 5-[(1H-Indol-3-yl)methylene]-2-(1-piperidinyl) rhodanine (**5a**)

Yellow granular crystal, m.p.: 245–246 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ (ppm): 12.01 (s, 1H, NH), 7.87 (s, 1H, pyrrole-H), 7.84 (d, *J* = 8.0 Hz, 1H, ArH), 7.75 (s, 1H, –CH=), 7.48 (d, *J* = 8.0 Hz, 1H, ArH), 7.16–7.25 (m, 2H, ArH), 3.89 (b, 2H, NCH₂), 3.62 (b, 2H, NCH₂), 1.69 (b, 4H, 2–CH₂–), 1.63 (b, 2H, –CH₂–); IR(KBr) υ : 3424 (m. b, υ_{N-H}), 3089 (m, $\upsilon_{=CH}$), 2928, 2854 (m, υ_{C-H}), 1659 (m, $\upsilon_{C=C}$), 1602(s, $\upsilon_{C=O}$), 1543 (s, $\upsilon_{C=N}$), 1443, 1383 (m, δ_{C-H}), 744 (s, $\delta_{=C-H}$, δ_{N-H}) cm⁻¹. MS (70 eV) *m/z* (%): 311 (52), 201 (3), 173 (100), 146 (5), 129 (13), 41 (3). Anal. Calcd. for C₁₇H₁₇N₃OS = 311.11:C, 65.57; H, 5.50; N,

The reaction conditions and yields for the dyes.

Dye	Solvent method		Microwave r	nethod			
	Time/h	Yield/%	Power/W	Time/min	Yield/%		
1a	2-3	57	567	3	66		
2a	2-3	53	406	2	69		
3a	2-3	64	406	3	68		
5a	2-3	83	252	3	86		
5b	2-3	80	252	3	83		
5c	2-3	76	252	3	81		

13.49; Found: C, 65.00; H, 5.50; N, 12.79. UV–Vis (MeOH) λ_{max} : 378 nm. ε : 2.76 × 10⁴ L mol⁻¹ cm⁻¹.

2.3.5. 5-[(5-Methoxy-1H-Indol-3-yl)methylene]-2-(1-piperidinyl) rhodanine(**5b**)

Yellow rod-like crystal, m.p.: 289–290 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ (ppm): 11.87 (s, 1H, NH), 7.88 (s, 1H, pyrrole-H), 7.68 (d, *J* = 2.8 Hz, ArH), 7.33–7.37 (m, 1H, ArH), 7.35 (s, 1H, –CH=), 6.81–6.85 (m, 1H, ArH), 3.88 (b, 2H, NCH₂), 3.82 (s, 3H,–OCH₃), 3.61 (b, 2H, NCH₂), 1.68 (b, 4H, 2–CH₂–), 1.62 (b, 2H, –CH₂–); IR(KBr) υ : 3445 (m. b, υ_{N-H}), 3093 (s, $\upsilon_{=CH}$), 2939, 2855 (m, υ_{C-H}), 1663 (m, $\upsilon_{C=C}$), 1602(s, $\upsilon_{C=0}$), 1548 (s, $\upsilon_{C=N}$), 1442, 1383 (m, δ_{C-H}), 1263 (s, $\upsilon_{C=O-C}$), 1062 (w, υ_{C-O-C}), 915, 877 (w, $\delta_{=CH}$), 709 (m, δ_{N-H})cm⁻¹. MS (70 eV) *m*/*z* (%): 341 (38), 231 (2), 203 (100), 188 (11), 169 (7), 147 (5), 97 (6), 44 (13). Anal. Calcd. for C₁₈H₁₉N₃O₂S = 341.12: C, 63.32; H, 5.61; N, 12.31; Found: C, 63.08; H, 5.32; N, 12.26. UV–Vis (MeOH) λ_{max} : 380 nm. ε : 2.96 × 10⁴ L mol⁻¹ cm⁻¹.

2.3.6. 5-[(5-Benzyloxy-1H-Indol-3-yl)methylene]-2-(1-piperidinyl) rhodanine (**5c**)

Yellow needle-like crystal, m.p.: >300 °C. ¹H NMR (DMSO-d₆, 400 MHz) δ (ppm): 11.87 (s, 1H, NH), 7.88 (s, 1H, pyrrole-H), 7.69 (s, 1H, ArH), 7.40–7.43 (m, 6H, ArH, –CH=), 7.34 (d, *J* = 6.8 Hz, 1H, –CH=), 6.93 (d, *J* = 6.8 Hz, 1H, ArH), 5.19 (s, 2H, –OCH₂Ph), 3.89 (b, 2H, NCH₂), 3.62 (b, 2H, NCH₂), 1.69 (b, 4H, 2–CH₂–), 1.63 (b, 2H, –CH₂–); IR (KBr) v: 3454 (m. b, v_{N-H}), 3097 (m, v_{=CH}), 2921, 2853 (m, v_{C-H}), 1650 (m, v_{C=C}), 1595 (s, v_{C=O}), 1542 (s, v_{C=N}), 1443, 1375 (m, δ_{C-H}), 1262 (s, v_{C-O-C}), 1056 (w, v_{C-O-C}), 901, 836 (m, $\delta_{=C-H}$), 746 (m, δ_{N-H}) cm⁻¹; MS (70 eV) *m/z* (%): 417 (12), 334 (90), 206 (30), 169 (100), 147 (72), 119 (28), 77 (30), 69 (66), 44 (83). Anal. Calcd. for C₂₄H₂₃N₃O₂S = 417.15: C, 69.04; H, 5.55; N, 10.06; Found: C, 68.64; H, 5.39; N, 9.31.UV–Vis (MeOH) λ_{max} : 397 nm. ε : 2.17 × 10⁴ L mol⁻¹ cm⁻¹.

2.4. Crystal data

Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the dyes in ethanol. All the measurements were made on a Bruker SMART APEX II CCD X-ray crystallography equipped with a graphite monochromated Mo K α radiation ($\lambda = 0.071073$ nm) by using ω scan technique at room temperature. The structures were solved by direct methods with SHELXL-97 [20], and refined using the full-matrix least-squares procedures on F^2 with anisotropic thermal parameters for all nonhydrogen atoms using SHELXL-97 [21]. Hydrogen atoms were generated geometrically. Figs. 1 and 2 show the molecular structures with numbering systems of dye **5a** and **5b**, respectively. The crystal data, details concerning data collection and structure refinement for dye **5a** and **5b** are summarized in Table 2.

3. Results and discussion

3.1. Synthesis

In all cases investigated, we found that the rhodanine merocyanine dye formation reactions proceeded efficiently with high to excellent yields in short reaction times. A series of rhodanine merocyanine dyes were successfully synthesized with high yields 66–86% within 2–3 min by using microwave method. The products were purified by recrystallized from ethanol or acetone. In order to get effective results, we examined the difference between two different methods (Table 1). There was no doubt that microwave method was more effective and novel, for its high yields, shorter reaction times and environmental protection. From irradiation power it could be found that the sequence of the reaction activity for

Т



Fig. 1. X-ray crystal structure of dye 5a: (a) top view and (b) side view showing the planarity.

2-methylthio quaternary salts with rhodanine was 2-methylthio-1methylquinolinium iodide (**2**) \approx *N*-methyl-2-thiomethylpyridinium iodide (**3**) > 3-methyl-2-methylthiobenzothiazolium iodide (**1**). The reason was suggested that the group attached to C = N⁺ in (**2**) and (**3**) was -CH=CH- but it was -S- in (**1**), as the electron-withdrawing ability of the group was -CH=CH->-S-, leading to the order of the 2-carbon's electrophilicity in investigated 2-methylthio quaternary salts was 2-methylthio-1-methylquinolinium iodide (**2**) \approx *N*-methyl-2-thiomethylpyridinium iodide (**3**) > 3-methyl-2-methyl



Fig. 2. X-ray crystal structure of dye 5b: (a) top view and (b) side view showing the planarity.

5	ы	ρ	2	
α	vr	L	4	

Crystal data and structure refinement for dye 5a and 5b.

3	3	
Empirical formula	$C_{17}H_{18}N_{3}O_{1.5}S~(\bm{5a})$	$C_{39}H_{46}N_6O_6S_2\left(\bm{5b}\right)$
Formula weight	324.40	758.94
Temperature (K)	296(2)	273(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic
Space group	I4 (1)/a	P-1
Unit cell dimensions (Å)	a = 17.9910(12)	a = 9.3426(17)
	b = 17.9910(12)	b = 14.619(3)
	c = 20.4515(15)	c = 16.462(4)
Volume (Å ³)	6619.7(8)	2003.4(7)
Ζ	16	2
Calculated density (Mg/m ³)	1.286	1.258
Absorption coefficient (mm ⁻¹)	0.205	0.185
F(000)	2704	804
Crystal size (mm ³)	$0.86 \times 0.84 \times 0.75$	$0.31 \times 0.21 \times 0.11$
θ Range for data collection	2.26-25.03	1.60-25.10
Limiting indices h,k,l	-19 < 21, -18	-11 < 11, -17
	< 21, -23 < 24	<17, -18<19
Refinement method	Full-matrix	Full-matrix
	least-squares on F ²	least-squares on F ²
Goodness-of-fit on F ²	1.000	1.007
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0461$,	$R_1 = 0.0753,$
	$wR_2 = 0.1194$	$wR_2 = 0.1949$
R indices (all data)	$R_1 = 0.0726$,	$R_1 = 0.1361$,
	$wR_2 = 0.1232$	$wR_2 = 0.2173$

thiobenzothiazolium iodide (1). The stronger the 2-carbon's electrophilicity was, the easier was the reaction of 2-methylthio quaternary salts with rhodanine. The irradiation power also indicated that the reaction of 1*H*-indole-3-carbaldehyde with rhodanine was easier than that of 2-methylthio quaternary salts. The reason was that the electrophilicity of C=O in the indolylaldehyde was much stronger than that of the 2-carbon atom in 2-methylthio quaternary salts.

3.2. The UV-Vis spectra of dyes in different solvent

The UV–Vis spectra of all the dyes in several common solvents were determined. All the data were collected at room temperature and measured at a concentration of approximately 10^{-4} mo1/L . The λ_{max} and ε of the dyes in different solvents are represented in Table 3. As indicated in the table, the λ_{max} ranges from 425 to 483 nm for dyes **1a**–**3a** and from 378 to 397 nm for dyes **5a**–**c** in different solvents. At the same time, the ε values were in the range of 2000 to 22,800 L mol⁻¹ cm⁻¹ and 12,500 to 31,100 L mol⁻¹ cm⁻¹for **1a**–**3a** and **5a**–**c**, respectively. The order of the λ_{max} for dyes **1a**–**3a** is **2a** > **3a** > **1a**. This is due to increasing conjugation in the dyes. To be specific, the groups attached to the donor- π -

Table 3 The λ_{max} and ε of dyes in different solvents.

Dye	Solvent	CHCl₃	DMSO	H_2O	CH ₃ COCH ₃	EtOH	MeOH
1a	λ_{max}/nm	431	430	431	425	426	426
	$\epsilon imes 10^{-4}/L \ mol^{-1} \ cm^{-1}$	1.80	1.61	0.20	1.69	1.66	1.69
2a	λ _{max} /nm	483	481	478	476	479	478
	$\varepsilon \times 10^{-4}$ /L mol ⁻¹ cm ⁻¹	1.37	1.36	0.51	2.28	1.23	1.21
3a	λ _{max} /nm	436	439	439	439	437	439
	$\varepsilon \times 10^{-4}$ /L mol ⁻¹ cm ⁻¹	1.88	1.76	1.81	1.65	1.74	1.53
5a	λ _{max} /nm	389	384	394	378	391	391
	$\varepsilon \times 10^{-4}$ /L mol ⁻¹ cm ⁻¹	2.21	2.75	1.97	2.91	3.11	2.76
5b	λ _{max} /nm	395	390	396	386	396	397
	$\varepsilon \times 10^{-4}$ /L mol ⁻¹ cm ⁻¹	2.84	2.91	2.57	2.93	2.98	2.96
5c	λ _{max} /nm	396	390	397	384	396	397
	$\varepsilon \times 10^{-4}$ /L mol ⁻¹ cm ⁻¹	2.72	2.18	1.25	2.36	2.23	2.17



Fig. 3. Absorption spectra of dye 5b in different solvents.

acceptor skeleton for dye **2a** and **3a** are -S- and -CH=CH-, while the groups attached to the donor- π -acceptor skeleton for dye **1a** are both -S-, the conjugated degree of $\pi-\pi$ in dye **2a** and **3a** is greater than that of $p-\pi$ in dye **1a**, therefore the λ_{max} values of dye **2a** and **3a** are larger than **1a**. Similarly, in the case of dyes **5a–c**, the sequence of the λ_{max} is **5c** > **5b** > **5a**. Interestingly, it is also observed that the λ_{max} of dyes **1a–3a** (425–483 nm) is greater than that of dyes **5a–c** (378–397 nm), which is because the former has more conjugated system than the latter one. Specifically speaking, the *N*-methyl groups in dyes **1a–3a** contribute more to the increase of conjugation compared with the hydrogen atom connected with nitrogen atom in indole ring. This finding clearly indicates that the absorption bands of these dyes undergo bathochromic or hypsochromic shifts according to increasing or decreasing conjugation in the dye molecules.

The spectra of the dyes show that the profile is basically not changed in different solvents due to the fact that the energy level distribution of the first excited electronic state is not obviously affected by solvents. The absorption spectra of the first absorption band are produced by electronic excitation from the ground state to different energy levels of the first electronic excited states and the

Table 4

Some selected bond lengths ((A), bond angles	(°) and torsion angl	es for dye 5a .
------------------------------	------------------	----------------------	------------------------

Bond lengths			
N(1)-C(1)	1.360(4)	C(10)-C(11)	1.488(4)
C(1)-C(6)	1.401(4)	C(11)-O(1)	1.238(3)
C(6)-C(7)	1.450(4)	C(11)-N(2)	1.361(4)
C(7)–C(8)	1.371(4)	C(12)-N(2)	1.303(4)
N(1)-C(8)	1.356(3)	S(1)-C(12)	1.775(3)
C(7)–C(9)	1.440(4)	C(12)-N(3)	1.321(4)
C(9)-C(10)	1.329(4)	C(17)–N(3)	1.459(4)
S(1)-C(10)	1.748(3)	C(13)–N(3)	1.465(4)
Bond angles			
C(1)-N(1)-C(8)	109.51(2)	S(1)-C(12)-N(2)	117.72(2)
N(1)-C(8)-C(7)	110.32(3)	C(12)-N(2)-C(11)	110.8(3)
C(8) - C(7) - C(6)	105.55(2)	N(2)-C(11)-O(1)	123.33(3)
C(7)-C(6)-C(1)	106.6(3)	C(10)-C(11)-O(1)	121.77(3)
C(8)-C(7)-C(9)	128.81(3)	S(1)-C(12)-N(3)	119.41(2)
C(7)-C(9)-C(10)	130.11(3)	N(2)-C(12)-N(3)	122.86(3)
C(9)-C(10)-S(1)	128.54(2)	C(12)-N(3)-C(17)	124.40(3)
C(9)-C(10)-C(11)	123.11(3)	C(12)-N(3)-C(13)	119.99(3)
C(10)-S(1)-C(12)	88.25(15)		
Torsion angles			
C(8)-C(7)-C(9)-C(10)	-7.4(5)	S(1)-C(12)-N(3)-C(17)	-8.0(4)
C(7)-C(9)-C(10)-S(1)	-1.9(5)		.,

Table 5

Bond lengths			
N(3)-C(12)	1.381(5)	C(7)-N(2)	1.362(5)
C(12)-C(17)	1.395(6)	C(6)-N(2)	1.310(5)
C(17)-C(10)	1.445(5)	C(6)-S(1)	1.755(4)
C(10)-C(11)	1.374(5)	C(8)-S(1)	1.736(4)
C(11)-N(3)	1.348(5)	C(6)-N(1)	1.333(5)
C(10)-C(9)	1.441(5)	N(1)-C(1)	1.459(5)
C(9)-C(8)	1.349(5)	N(1)-C(5)	1.459(5)
C(8)-C(7)	1.476(5)	C(15)-O(2)	1.358(5)
C(7)-O(1)	1.235(4)	O(2)-C(18)	1.412(6)
Bond angles			
C(11) - N(3) - C(12)	110.4(3)	C(8) - C(7) - N(2)	114.6(4)
N(3)-C(12)-C(17)	106.9(4)	C(7) - N(2) - C(6)	109.9(3)
C(12)-C(17)-C(10)	107.1(4)	N(2)-C(6)-S(1)	118.3(3)
C(17) - C(10) - C(11)	106.3(4)	C(6)-S(1)-C(8)	88.02(19)
C(10)-C(11)-N(3)	109.4(4)	S(1)-C(6)-N(1)	119.3(3)
C(11)-C(10)-C(9)	129.2(4)	C(6) - N(1) - C(1)	123.2(4)
C(10)-C(9)-C(8)	129.8(4)	C(6) - N(1) - C(5)	121.6(3)
C(9)-C(8)-S(1)	127.0(3)	C(14) - C(15) - O(2)	115.5(5)
S(1)-C(8)-C(7)	109.1(3)	C(15)-O(2)-C(18)	117.1(4)
Torsion angles			
C(11)-C(10)-C(9)-C(8)	-0.5(7)	S(1)-C(6)-N(1)-C(1)	12.0(5)
C(10)-C(9)-C(8)-S(1)	0.6(7)	C(13)-C(14)-C(15)-O(2)	-179.3(5)

shape of the first absorption band is determined by the distribution of energy levels at the first electronic excited state [22]. Taking dye **5b** as an example (Fig. 3), the absorption spectra suggest that the dyes in different solvents exist mainly in the monomeric form and do not aggregate in spite of the change in solvents. Moreover, the data given in Table 3 show that the change of solvents has a different effect on the variation of λ_{max} . The change of solvents in dyes **1a**, **2a** and **3a** results in the change ranges of λ_{max} by 6 nm, 7 nm and 3 nm. While in dyes **5a–c**, the changes are 10 nm, 11 nm and 13 nm respectively. Thereby, it may be concluded that dyes **5a–c** are prone to be affected by the change of solvents, compared with dyes **1a–3a** and the change of solvents does have an effect on the λ_{max} of investigated dyes but it is relatively slight.

3.3. Crystal structure analysis

The molecular structures of dye **5a** and **5b** are shown in Figs. 1 and 2. Although the space groups of dye **5a** and **5b** are different



Fig. 4. The diagram of crystal packing of dye 5a along b axis.



Fig. 5. The diagram of crystal packing of dye 5a along *c* axis.

from each other, there are distinct similarities in bond length homogenization and skeleton carbon configuration. Selected bond lengths, angles and torsion angles of dye **5a** and **5b** are recorded in Tables 4 and 5, respectively.

Obviously, in dye **5a** (Table 4), it can be seen that the carboncarbon bond lengths on the rhodanine ring and indole ring are intermediate between typical C-C single (1.54 Å) and C=C double (1.34 Å) bonds, and carbon–nitrogen bond lengths are also



Fig. 6. The diagram of crystal packing of dye 5b along *a* axis.

376	
Table	6

	Intermolecular	H-bonds	geometry	(Å. °) for d	ve 5a
--	----------------	---------	----------	-------	---------	--------------

D—Н…А	D-H	Н…А	D…A	$D{-}H{\cdots}A$
$N1-H1\cdots01^{a}$	0.86	1.98	2.833	170

^a Symmetry operation 1/2 + x, y, 1/2-z.

intermediate between C–N typical single (1.47 Å) and C=N double (1.27 Å) bonds. This means that the carbon–carbon bond and the carbon-nitrogen bond in both rings have double bond character and contribute to form a conjugate system. While the bond lengths of C–C and C–N in the piperidine ring are normal, which indicates that the piperidine ring is not involved in conjugate system and that the carbon atoms in the ring have mainly sp³ hybridization. The bond lengths for C12-N3 between the piperidine ring and rhodanine ring in dye **5a**, that is 1.321 Å, is also intermediate between C–N typical single and C=N double bonds, which again reveals that the bond lengths represent $p-\pi$ conjugation between the p orbital of the lone pair electrons of nitrogen atom in piperidine ring and π orbital of C=N in rhodanine ring. All C-C-C, C–N–C and C–C–N bond angles in five-membered ring are close to 108°, while C–S–C bond angles are 88.25° for 5a. This indicates that the sulfur atom in the rhodanine ring makes a contribution to the distortion of the five-membered ring. At the same time, in the six-membered ring and the vinyl chain, all C-C-C, C-N-C and C-C-N bond angles are close to 120°. The torsion angles of C(8)-C(7)-C(9)-C(10) for **5a** shows that the indole ring is not significantly distorted from coplanarity with the rhodanine ring. Dye 5b is similar (Table 5). In both dyes the piperidine ring is in the chair conformation.

Dye **5a** crystallizes in the I4(1)/a space group with sixteen dye molecules and six water molecules per unit cell. However, in the case of dye **5b**, the compound crystallizes in the *P*-1 space group with two dye molecules, two ethanol molecules and two methanol molecules. As can be seen from the packing diagrams (Figs. 4–6), in the packing of dye **5a**, adjacent molecules are stacked through $\pi - \pi$ stacking, with face-to-face distances of 3.475 Å. Interestingly, the conjugated molecules are also arranged in a head-to-tail fashion along the *a* and *b* axis due to the intermolecular hydrogen bonds (Table 6), which stabilize the molecular packing. That is to say, the indole moiety from one molecule interacts with the rhodanine ring from another molecule via N-H···O bonds. As a result, the extension of the dye molecules forms a square aperture threedimensional framework viewing along c axis with the cavities and the molecules of water are arranged in the cavities of the framework (Fig. 5). Atom N1, in the rhodanine ring, acts as hydrogen-bond donor to O1. In this manner, each sheet is linked to its two immediate neighbors, thus generating a continuous threedimensional framework. Identically, in dye 5b, the conjugated molecules form stacked arrays with interlayer associations by means of $\pi - \pi$ stacking interaction with a face-to-face separation of 3.786 Å. (Fig. 6). Intermolecular hydrogen bonds (Table 7) are also observed. The existence of N3-H3N...O3 and N6-H6N...O1 hydrogen bonds between adjacent molecules contributes to the arrangement in a head-to-tail fashion along the bc plane. Specifically, the indole moiety from one molecule interacts with the

Table 7

Intermolecular H-bonds geometry (Å, °) for dye 5b.

D—Н…А	D-H	H…A	D…A	D−H…A
N3-H3N····O3 ^a	0.86	2.13	2.914	151
N6-H6N····O1 ^b	0.86	1.94	2.788	169

^a Symmetry operation x, y, -1 + z.

^b Symmetry operation 1 - x, 1 - y, 1 - z.

rhodanine ring from another molecule. In dyes **5a** and **5b**, the H-bonds are formed due to the attraction between the oxygen atoms in rhodanine rings and the hydrogen atoms connected with nitrogen atoms in indole rings. The solvent molecules are distributed in the vacancies of the dye crystal lattice, and the Van der Waals force is not strong enough to disorder the domain structure, therefore these are not indicated in the packing diagram.

In summary, the single crystals of dye **5a** and dye **5b** were grown in ethanol solution and their crystal structures were characterized by X-ray analysis. In view of the single molecule for both dyes, supramolecular interactions, including $\pi - \pi$ stacking and intermolecular hydrogen bonds, generate a unique supramolecular architecture in the solid state of the dyes.

4. Conclusions

Six different rhodanine merocyanine dyes were synthesized using both microwave and solvent methods and their UV–Vis spectra were investigated. The absorption bands of the synthesized rhodanine merocyanine dyes were from 379 to 483 nm and exhibited intensive absorption in blue light region. Therefore, they have great potential for application as dyes for optical recording with a blue diode laser. X-ray powder diffraction of dye **5a** and **5b** demonstrated that the π electrons in the dye molecules were delocalized. Intermolecular hydrogen bonding and $\pi - \pi$ stacking interactions were displayed in the molecular system. These supramolecular interactions were effective in the molecular packing.

Acknowledgement

We appreciate the financial support for this research by a grant from the Natural Science Foundation of Shaanxi Province (No.SJ08B04), NWU Doctorate Dissertation of Excellence Founds (08YYB04) and NWU Graduate Cross-discipline Funds (No. 09YJC20).

Supplement material

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication nos, CCDC 724578 for dye **5a** and 726899 for dye **5b**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

References

- Huang FX, Wu YQ, Gu DH, Gan FX. Progress of the organic materials used for the new generation high density recordable digital versatile disc. Progress in Physics 2003;23(3):312–20 [in Chinese].
- [2] Nakamura T, Goromaru H, Takeuchi M, Maeda S, Kobayashi T, Chen JW, et al. Porphyrin dye showing excellent light fastness suitable for blue laser sensitive high density optical recording medium. JP 2006256295; 2006.
- [3] Miyazawa T, Kurose Y. Optical recording medium showing improved light stability suitable for blue laser light, metal complex compound and organic dye compound. WO 2006104196; 2006.
- [4] Pays C. Pyridine N-oxide based azo dyes and their metal complexes for use in optical layers for optical data recording. WO 2006061398; 2006.
 [5] Li FM, Wang LY, Wang SK, Zhang ZX. Solvent-Free synthesis of styryl dyes
- [5] Li FM, Wang LY, Wang SK, Zhang ZX. Solvent-Free synthesis of styryl dyes with quinoline nucleus using microwave irradiation. Chinese Journal of Organic Chemistry 2004;24(1):50–2 [in Chinese].
- [6] Wang LY, Zhang XG, Shi YP, Zhang ZX. Microwave-assisted solvent-free synthesis of some hemicyanine dyes. Dyes and Pigments 2004;62(1):21–5.
- [7] Hung TT, Lu YJ. Super-resolution near-field blue laser type optical disk with modified coumarin dye recording layer and poly (methyl methacrylate) contrast enhanced layer. Japanese Journal of Applied Physics 2008;47(7): 6042-4.
- [8] Bing YJ, Huang L, Zhang FS. Researches on organic recording materials for blue laser recordable disc. China Mediatech 2008;2:25–8 [in Chinese].

- [9] Zhang XH, Wang LY, Nan ZX, Tan SH, Zhang ZX. Microwave-assisted solvent-free synthesis and spectral properties of some dimethine cyanine dyes as fluorescent dyes for DNA detection. Dyes and Pigments 2008;79(2):205–9.
 [10] Loupy A. Microwave in organic synthesis. Weinheim: Wiley-VCH: 2002.
- [11] Biswas N, Umapathy S. Structures, vibrational frequencies, and normal modes of substituted azo dyes: infrared, Raman, and density functional calculations. Journal of Physical Chemistry 2000;104(12):2734–45.
- [12] Willner I, Rubin S. Control of the structure and functions of biomaterials by light. Angewandte Chemie 1996;35(4):367–85.
- [13] Beata J, Artur R. The synthesis and spectroscopic investigation of dichromophoric hemicyanine dyes. Dyes and Pigments 2009;80(3):297–306.
- [14] Lee JE, Kim HJ, Han MR, Lee SY, Jo WJ, Lee SS, et al. Crystal structures of C.I. Disperse Red 65 and C.I. Disperse Red 73. Dyes and Pigments 2009;80(1):181–6.
- [15] Heilbron Ivan. Dictionary of organic compounds I. Beijing: Science press; 1964 [in chinese].

- [16] Kendall JD, Suggate HG. Reactivity of the alkylmercapto group in nitrogen ring compounds. Journal of the Chemical Society; 1949:1503–9.
- [17] Heilbron Ivan. Dictionary of organic compounds IV. Beijing: Science Press; 1966 [in chinese].
- [18] Fry DJ, Kendall JD. Formation and fission of quaternary salts of heterocyclic bases containing reactive alkylmercapto groups. Journal of the Chemical Society 1951;2:1716–22.
- [19] The Merck index. 11th ed. Rahway, NJ: Merck & Co., Inc.; 1989.
- [20] Sheldrick GM. SHELXS-97, Program for Solution Crystal Structure. Germany: University of Göttingen; 1997.
- [21] Sheldrick GM. SHELXS-97, Program for Solution Crystal Structure and Refinement. Germany: University of Göttingen; 1997.
- [22] West W, Geddes AL. Effects of solvents and of solid substrates on the visible molecular absorption spectrum of cyanine dyes. Journal of Physical Chemistry 1964;68(4):837–47.