Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

ELSEVIER

Dyes and Pigments 56 (2003) 189–194

DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Studies on the synthesis and spectra characteristics of stilbenylcoumarin organic materials

Yan-Ying Zhang[a], Xian-Mei Meng[b], Xin-Liang Wang[b], Long-He Xu[a,b,*]

[a]*Department of Applied Chemistry, Dalian University of Technology, Dalian 116023, PR China*
[b]*Shenyang Research Institute of Chemical Industry (SYRICI), No.8, Shenliao Dong Road, Shenyang 110021, PR China*

Received 12 August 2002; received in revised form 22 September 2002; accepted 1 October 2002

Abstract

A series of substituted stilbenylcoumarins were synthesized. The absorption-emission spectra were studied and the fluorescence quantum yields were determined. The covalent rigidification of stilbenylcoumarins produces a considerable enhancement of the fluorescence quantum yield compared to the open-chain analogs. To 3-(4-substitutedstilben-4-yl)-7-diethylaminocoumarin, the fluorescence quantum yield increases with the enhancement of the electron-withdrawing ability of the group at the 4′-position. In addition, 4′-Cl makes the stilbenylcoumarin produce strong fluorescence.

Keywords: Stilbenylcoumarins; Fluorescence quantum yield; Organic material; Donor; Acceptor

---

1. Introduction

With the development of material science, light-emitting, semi-conducting and conducting organic materials are showing increasing potential as active components for a wide range of electronic and optoelectronic devices. The preparation of well defined oligomers or smaller organic compounds with a conjugated π-system has become an important field in organic chemistry in recent years [1]. Stilbenes and compounds containing stilbene units have been noted as important photoelectric materials [2]. As a type of stilbenyl compound bridged by an ester group, 3-arylcoumarins have many advantages over simple stilbenes [3]. It has been found that the drastic increase in the fluorescence yield of coumarins is closely related to the contribution of charge transfer configuration arising from electron transfer from the styryl to the carbonyloxy group, which is also one of the important factors controlling the fluorescence properties of 7-substituted coumarins [4]. They also show high photostability and good lasing performance [5]. Many coumarin derivatives used as fluorescent brighteners and fluorescent dyes have been patented. 3-Arylcoumarins have occupied a special place in the realm of natural and synthetic coumarins because of their diverse activities. The electrical and optical activities of these materials

---

* Corresponding author. Tel.: +86-24-85869011; fax: +86-24-85869016.
E-mail address: xthzawt@mail.sy.ln.cn (L.-H. Xu).

0143-7208/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
PII: S0143-7208(02)00144-4

rely on their ability to transport electrical charges—electron or positive holes—through their structure. Here push–pull chromophores based on coumarin for nonlinear optics involve electron-donor and electron-acceptor interacting through a π-conjugating spacer [6]. In this paper, we report the relationship between molecular structure and the properties of novel stilbenylcoumarins.

2. Experimental

2.1. Materials and equipment

The spectra of ^{1}H NMR and ^{13}C NMR were recorded on a Mercury Vx 300 (Varian) with TMS as the internal standard. A Nicolet Impact 400 was used to determine the IR spectra. The mass spectra were obtained on APEXII-FTMS. UV/vis absorption spectra were taken on a HP8452A spectrometer. Fluorescence spectra were recorded using a Perkin Elmer LS-50B fluorescence spectrophotometer. Silica gel (100–140 mesh) was used for column chromatography. DMF was dried over 4A sieves, and triethylamine was desiccated with natrium slip and distilled. Elemental analyses were recorded on a Elementar Varioel apparatus.

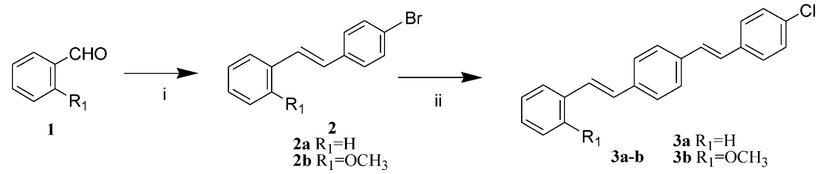
2.2. Synthesis of the compounds

Compounds **2a** and **2b** were prepared by the Wittig–Horner reaction. Then the products **3a** and **3b** were afforded by the Heck reaction with *p*-chlorostyrene (Scheme 1) [7].

Compound **6** was synthesized by the Perkin reaction [8]. The product **7** was obtained by the Heck reaction with *p*-chlorostyrene (Scheme 2).

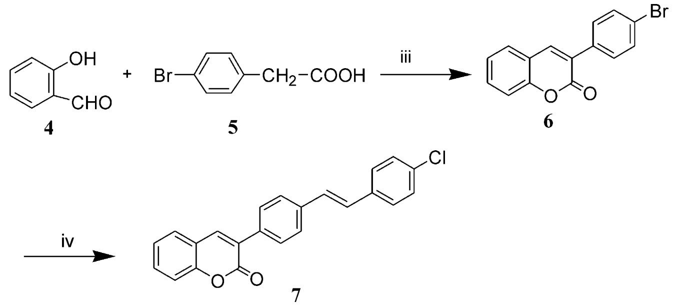
Compounds **10a** and **10b** were prepared by the conventional Knoevenagel reaction [9]. The products **11a**–**11e** were also prepared by the Heck reaction of **10b** and substituted styrene (Scheme 3).

General procedure for the Heck reaction: a mixture of 0.66 mmol stilbene or coumarin, 0.031 mmol palladium acetate, and 0.13 mmol tri-tolyphosphine were placed in a 25-mL Pyrex tube, and the tube was capped with a self-sealing, rubber-lined cap. The tube was vacuumed and flushed with nitrogen gas. DMF (5 ml), 0.3 ml NEt$_3$, and corresponding substituted styrene were added by syringe. The tube was heated to 100 °C for 20 h. Then the mixture was cooled to room temperature. Much precipitation occurred after cooling to room temperature. The solid was collected by filtration and washed twice with water, twice with



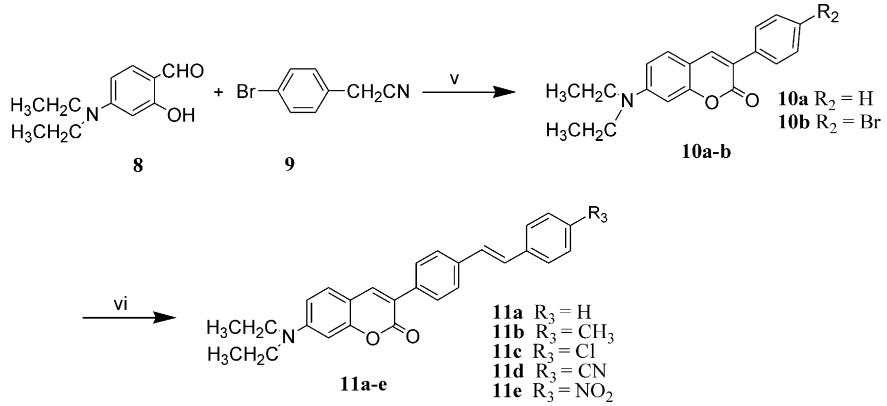
1 **2** **2a** R$_1$=H **2b** R$_1$=OCH$_3$ **3a-b** **3a** R$_1$=H **3b** R$_1$=OCH$_3$

Scheme 1. Reagents and reaction conditions: (i) P(OEt)$_3$, *p*-BrC$_6$H$_4$CH$_2$Br, KI, CH$_3$ONa, DMF; (ii) *p*-chlorostyrene, Pd(OAc)$_2$, P(*o*-tol)$_3$, DMF, NEt$_3$, 100 °C, 20 h.



4 **5** **6** **7**

Scheme 2. Reagents and reaction conditions: (iii) Ac$_2$O, pyridine, reflux 8 h; (iv) *p*-chlorostyrene, Pd(OAc)$_2$, P(*o*-tol)$_3$, DMF, NEt$_3$, 100 °C, 20 h.



Scheme 3. Reagents and reaction conditions: (v) pyridine, EtOH, reflux 8 h; (vi) substituted styrene, $Pd(OAc)_2$, P(o-tol)$_3$, DMF, NEt_3, 100 °C, 20 h.

ethyl acetate and dried. The products were purified by recrystallization from DMF. The yields of the products are isolated yield.

2.2.1. 1-(4-Chlorostyryl)-4-styrylbenzene **3a**

Light green flake (0.182 g, 86.5% yield), m.p. 264–266 °C; ^{1}H NMR (300 MHz, DMF) δ 7.17–7.18 (m, 4H), 7.22–7.25 (m, 1H), 7.31–7.36 (m, 4H), 7.53–7.59 (m, 8H); IR (KBr) 3020, 1490, 1090, 965, 825, 750, 690, 540 cm^{-1}; HRMS calcd. For $C_{22}H_{17}Cl$ 316.1013, found 316.1018 (E= 1.3 ppm).

2.2.2. 1-(4-Chlorostyryl)-4-(2-methoxystyryl)benzene **3b**

Light green flake (0.189 g, 82.1% yield), m.p. 189–191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 3H, CH_3), 6.91 (d, J=8.1 Hz, 1H), 6.98 (t, J=7.6 Hz, 1H), 7.07 (s, 2H, olefin H), 7.11 (d, J=16.4 Hz, 1H), 7.26 (td, J=8.1, 1.6 Hz, 1H), 7.32 (d, J=8.6 Hz, 2H), 7.45 (d, J=8.6 Hz, 2H), 7.48 (d, J=8.6 Hz, 2H), 7.54 (d, J=8.6 Hz, 2H), 7.52 (d, J=16.4 Hz, 1H), 7.61 (dd, J=7.6, 1.6 Hz, 1H); IR (KBr) 3010, 2920, 2840, 1660, 1630, 1590, 1510, 1480, 1460, 1340, 1240, 960, 820, 750 cm^{-1}; HRMS calcd for $C_{23}H_{19}ClO$ 346.1119, found 346.1118 (E=0.2 ppm).

2.2.3. 3-(4′-Chlorostilben-4-yl)coumarin **7**

Light green flake (0.187 g, 78.6% yield), m.p. 225–227 °C; ^{1}H NMR (300 MHz, DMCO-d_6) δ 7.36 (s, 2H, olefin H), 7.36–7.44 (m, 2H), 7.42 (d, J=8.4 Hz, 2H), 7.67 (dd, J=7.8, 2.1 Hz, 1H), 7.71 (d, J=8.6 Hz, 2H), 7.77 (d, J=8.4 Hz, 2H), 7.79 (dd, J=8.4, 1.8 Hz, 1H), 7.84 (d, J=8.6 Hz, 2H, aromat. H), 8.22 (s); IR (KBr) 3040, 2920, 1720, 1660, 1630, 1610, 1480, 1450, 1110, 1090, 950, 820, 760 cm^{-1}; Anal. calcd for: C, 76.99%; H, 4.21%. Found: C, 77.19%; H, 4.35%.

2.2.4. 3-(Stilben-4-yl)-7-diethylaminocoumarin **11a**

Yellow needle (0.127 g, 48.4% yield), m.p. 176–178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, 6H, CH_3), 3.42 (m, 4H, CH_2), 6.53 (d, J=2.4 Hz, 1H), 6.60 (dd, J=8.7, 2.4 Hz, 1H), 7.14 (s, 2H, olefin H), 7.26 (t, J=7.2 Hz, 1H), 7.32 (d, J=8.7 Hz, 1H), 7.37 (t, J=7.2 Hz, 2H), 7.54 (d, J=7.2 Hz, 2H), 7.56 (d, J=8.4 Hz, 2H), 7.73 (d, J =8.4 Hz, 2H), 7.73 (s); IR (KBr) 3020, 2980, 2930, 2900, 1710, 1620, 1590, 1525, 1445, 1410, 1350, 1305, 1270, 1230, 1190, 1130, 1080, 1020, 960, 930, 870, 820, 745, 690, 555, 480, 420 cm^{-1}; Anal. calcd for: C, 81.99%; H, 6.37%; N, 3.54%. Found: C, 81.58%; H, 6.28%; N, 3.34%.

2.2.5. 3-(4′-Methylstilben-4-yl)-7-diethylamino coumarin **11b**

Yellow needle (0.077 g, 28.4% yield), m.p. 208–209 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (t, 6H, CH_3), 2.37 (s, 3H, CH_3), 3.44 (m, 4H, CH_2), 6.60 (single broad band), 6.68 (double broad band, J=8.6 Hz, 1H), 7.07 (d, J=16.5 Hz, 1H), 7.14 (d, J=16.5 Hz, 1H), 7.18 (d, J=8.2 Hz, 2H), 7.34 (d, J=8.6 Hz, 1H), 7.44 (d, J=8.2 Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.73 (s); IR (KBr) 3020, 2980, 2910, 2890, 1705, 1610, 1590, 1515, 1470, 1405, 1345, 1305, 1270, 1210, 1190, 1130, 1070, 1010, 980, 930, 820, 700, 540, 470 cm^{-1}; HRMS calcd. for $C_{28}H_{27}NO_2$ 409.2036, found 409.2033 ($E = 0.6$ ppm).

2.2.6. 3-(4′-Chlorostilben-4-yl)-7-diethylamino coumarin **11c**

Golden needle (0.035 g, 32.4% yield), m.p. 214–215 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (t, 6H, CH_3), 3.43 (q, 4H, CH_2), 6.60 (single broad band), 6.69 (double broad band), 7.08 (s, 2H, olefin H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.7$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.7$ Hz, 2H), 7.73 (s); IR (KBr) 3100, 3080, 3020, 2980, 1690, 1610, 1590, 1510, 1405, 1350, 1305, 1280, 1220, 1190, 1125, 1085, 1010, 980, 930, 830, 550 cm^{-1}. Anal. calcd for: C, 75.43%; H, 5.62%; N, 3.26%. Found: C, 75.30%; H, 5.57%; N, 3.10%.

2.2.7. 3-(4′-Cyanostilben-4-yl)-7-diethylamino coumarin **11d**

Yellow flake (0.018 g, 6.4% yield), m.p. 232–234 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (t, 6H, CH_3), 3.44 (m, 4H, CH_2), 6.56 (d, $J = 2.1$ Hz, 1H), 6.63 (dd, $J = 8.8$, 2.1 Hz, 1H), 7.12 (d, $J = 16.5$ Hz, 1H), 7.24 (d, $J = 16.5$ Hz, 1H), 7.34 (d, $J = 8.8$ Hz, 1H), 7.58 (d, $J = 8.1$ Hz, 2H), 7.60 (d, $J = 9.0$ Hz, 2H), 7.65 (d, $J = 9.0$ Hz, 2H), 7.76 (s), 7.76 (d, $J = 8.1$ Hz, 2H); IR (KBr) 3090, 3060, 3020, 2980, 2940, 1710, 1620, 1590, 1520, 1410, 1350, 1305, 1270, 1220, 1190, 1130, 1080, 1015, 930, 820, 550 cm^{-1}; Anal. calcd for: C, 79.98%; H, 5.75%; N, 6.66%. Found: C, 79.77%; H, 5.58%; N, 6.36%.

2.2.8. 3-(4′-Nitrostilben-4-yl)-7-diethylamino coumarin **11e**

Red flake (0.226 g, 77.4% yield), m.p. 242 °C; ^1H NMR (300 MHz, $CDCl_3 + DMSO\text{-}d_6$) δ 1.26 (t, 6H, CH_3), 3.52 (m, 4H, CH_2), 7.05 (single broad band), 7.16 (double broad band), 7.22 (d, $J = 16.4$ Hz, 1H), 7.34 (d, $J = 16.4$ Hz, 1H), 7.54 (d, $J = 8.7$ Hz), 7.64 (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.78 (d, $J = 8.2$ Hz, 2H), 7.88 (s), 8.24 (d, $J = 8.8$ Hz, 2H); IR (KBr) 3090, 3060, 3020, 2980, 2940, 1710, 1620, 1590, 1515, 1410, 1335, 1270, 1220, 1190, 1130, 1105, 1080, 1010, 930, 830, 810, 745, 680, 530, 460, 430 cm^{-1}; Anal. calcd for: C, 73.62%; H, 5.49%; N, 6.36%. Found: C, 73.45%; H, 5.43%; N, 6.05%.

2.3. Determination of the fluorescence quantum yield

Fluorescence quantum yields were determined using a previously published procedure [10] with quinine sulfate as the reference standard. That the use of the absorbance ($A \leqslant 0.05$) of the solution is avoided as it cannot be determined accurately. Thus the determination error of the fluorescence quantum yield can be reduced.

The absorption and fluorescent emission spectra were recorded on a HP8452A spectrophotometer and a PE LS-50B luminescence spectrometer respectively [11]. Due to the low solubility of some compounds in commonly used organic solvents, THF as a polar aproton solvent was selected.

Table 1 lists the UV–vis absorption maxima ($\lambda_{a,max}$), emission maxima ($\lambda_{e,max}$), Stokes shift ($\Delta\lambda$), extinction coefficient (ε/mol $\lambda_{e,max}$ l^{-1} cm^{-1}), and fluorescent quantum yield (Φ) of tested compounds.

3. Results and discussion

Comparing **7** with **3a** (Scheme 1), one double bond of **7** is bridged by an ester group and the other is still open. This covalent rigidification produces a considerable enhancement of fluorescence quantum yield from 0.047 to 0.687 and a 34 nm bathochromic shift of emission maxima (Table 1, entries 1 and 3) [13]. The fluorescence that compound **7** emits in THF is not blue but green-blue. Compound **3b** with $-OCH_3$ also has a higher fluorescence quantum yield than **3a** (Table 1, entries 1 and 2) [14].

The difference between **7** and **11c** is the group at the 7-position. The introduction of a strong electron-donor ($-NEt_2$) causes the absorption maximum of **11c** a greater increase (57 nm) than **7** (Table 1, entries 3 and 7).

Stilbenylcoumarins **11a–e** (Scheme 3) are π-conjugated organic small molecules and have the same electron-donor at the 7-position and differ-

Table 1
Absorption and emission maxima, Stokes shift, fluorescence quantum yield and extinction coefficient of tested compounds

Entry	Compounds	$\lambda_{a,max}$ (nm)[a]	$\lambda_{e,max}$ (nm)	$\Delta\lambda$ (nm)	ϵ/mol l^{-1} cm^{-1}	Φ[b]
1	**3a**	358	418	60	73,222	0.047
2	**3b**	364	428	64	61,211	0.761
3	**7**	354	452	98	46,317	0.687
4	**10a**	394	456	62	41,037	0.530
5	**11a**	410	480	70	39,424	0.350
6	**11b**	410	479	69	72,041	0.212
7	**11c**	411	479	68	55,600	0.540
8	**11d**	416	498	82	51,338	0.455
9	**11e**	426	625	199	37,656	0.003
10	DisperseYellow 184	430	480	50	57,730	0.544

[a] Excitation wavelength was selected at the intersection of two absorbance curves of the standard and tested sample.

[b] Φ is determined by using 10^{-5} M quinine sulfate in 1N H_2SO_4 (Φ, 0.55) as a standard [12].

ent stilbene electron-acceptor at the 4′-position. The electron-donating and electron-accepting ability of these substituted groups are different at ground state and excited state and both increase in the excited state [15]. One extended substituted styrene can cause a red shift (16–32 nm) in $\lambda_{a,max}$ (Table 1, entries 5–9 and 4). The bathochromic shifts and fluorescence quantum yields increase with the enhancement of the electron-withdrawing ability of the 4′-groups in styrene. When the 4′-position is CH_3 group in **11b**, two electron-donating groups at both ends of **11b** make the electron cloud density on the double bond increase, which readily leads to trans-cis transfer. Thus its fluorescence quantum yield is lower than **11a** (entries 5 and 6). However, **11d** has a greater fluorescence quantum yield and Stokes shift than **11a** and**11b** (entries 5, 6 and 8). The electron-donor (–NEt_2) at the 7-position and the electron-acceptor (–CN) at the 4′-position cause **11d** a stronger intramolecular charge-transfer. This transfer makes electron cloud accumulate on the two ends of **11d**. The electron cloud density on the double bond of **11d** decreases accordingly, which reduces the chance of free rotation of the double bond [14]. As a result, the fluorescence quantum yield of **11d** was enhanced. Moreover, 4′-NO_2 in **11e** causes a red shift (10 nm) of $\lambda_{a,max}$ than **11d**. **11e** has almost no fluorescence (entry 9). It is apparent that NO_2 has a strong extinction effect on fluorescence intensity. Surprisingly, the fluorescence quantum yield of **11c** is also high (entry 7). Compared with commercial **Disperse Yellow 184**, **11c** have greater Stokes shift and almost the same fluorescence quantum yield (entries 7 and 10).

In conclusion, the covalent rigidification of stibenylcoumarins by an ester group, produces a considerable enhancement of fluorescence quantum yield compared to the open-chain analogs. For 7-diethylamino-4′-substituted stilbenylcoumarins, the fluorescence quantum yields increase with the enhancement of the electron-withdrawing ability of groups at the 4′-position. In addition, the 4′-Cl makes 7-diethylamino-stilbenylcoumarin produce strong fluorescence.

Acknowledgements

This work was supported by the Shenyang Research Institute of Chemical Industry (SYRICI). The authors would like to thank Professor Wu Shi-Kang for his valuable guidance and also thank Mr. Zhi Shuang for providing Disperse Yellow 184.

References

[1] Freemantle M. Organic materials get more active. C & EN, 23 April 2001. p.49.

[2] Meier H. The photochemistry of stilbenoid compounds and their role in materials technology. Angew Chem, Int Ed Engl 1992;31:1399–420.

[3] Kazuyoshi O, Hinohara T, Matsui K. Kogyo Kagaku Zasshi 1968;71(7):1010–5.

[4] Hinohara T, Honda M, Amano K, Cho S, Matsui K. Excited states and fluorescence properties of 7-substituted coumarins. Nippon Kagaku Zassh 1981;4:477–80.
[5] Vijayan KK. One step synthesis of 3-phenylcoumarins and benzylidene coumaran-2-ones Indian J Heterocyclic Chem 1998;8:1–6.
[6] Raimundo JM, Blanchard P, Frère P, Mercier N, Ledoux-Rak I, Hierle R, et al. Push-pull chromophores based on 2,2′-bi(3,4-eth-ylene dioxythiophene) (BEDOT) π-conjugating spacer. Tetrahedron Lett 2001;42:1507–10.
[7] Heck R.F. Org. React. vol. 27. New York: John Wiley & Sons; 1982. p.345.
[8] Crawford M, Shaw JAM. The course of the Perkin coumarin synthesis part, I. J Chem Soc 1953:3435.
[9] Horst N, Hans JR, Eberhard G, Horst H. East German patent DD 224,592, 1984.
[10] Ci YX, Jia X, Chin J. Anal Chem 1986;14:616–7.
[11] Li B, Miao WR, Chen LB. Synthesis and fluorescence properties of 9,10-bis (phenylethynyl)anthracences. Dyes and Pigments 1999;43:161–5.
[12] Ke YK, Dong HR. Fen Xi Hua Xue Shou Ce, 2nd ed. Chemical Industry Press; 1998.
[13] Jousselme B, Blanchard P, Frere P, Roncali J. Enhancement of the π-electron delocalization and fluorescence efficiency of 1,6-diphenyl-1,3,5-hexatriene by covalent rigidification. Tetrahedron Lett 2000;41:5057–61.
[14] Fan MG. Photochemistry fundamental principles and photon material science. Science Press; 2001.
[15] You XZ. Molecular-based materials—opto-electronic functional compounds. Shanghai Scientific Technology Press; 2001.