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Synthesis and Characterization of Indodicarbocyanines

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ABSTRACT

Eight pentamethine indocarbocyanines have been synthesized and characterized by elemental analysis, visible/near-infra-red absorption, ^{1}H NMR and IR spectroscopy. The relationship between the constitution and properties of these dyes have been studied. © *1997 Elsevier Science Ltd*

Keywords: indodicarbocyanines, cyanines, synthesis, characterization, optical recording material, optical disk.

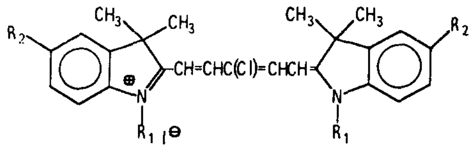
INTRODUCTION

Near-IR absorbing functional dyes have attracted the attention of researchers for many years as the use of laser diodes has grown. The Ga-As laser diode (780–830 nm) is manufactured in high quantities at low price and for this reason organic colorants in the recording layer of optical disc need to have an absorption band in the near-infra-red region (780–830 nm). Some of the first compounds of this type to be investigated were heptamethine cyanines [1–3]. These colorants have an intense absorption maxima at approximately 800 nm and they are suitable for use with the Ga-As diode laser (780–830 nm) as light source. However, since the diameter of the laser spot is proportional to the oscillation wavelength of the laser diode [4], a hoped-for trend in lasers is a reduction of the wavelength.

Development of commercially available laser diodes with oscillation wavelengths below 700 nm is technologically very difficult, but a breakthrough in the reduction of the wavelength of the laser diode has now been reported [5]. A 30-mW, 680 nm red diode laser for data recording and digital high-definition picture storage has been demonstrated using a rewritable magnetooptic (MO) disc [6]. Developments of new optical disk drivers will be a great incentive with regard to storage media. In the near future, the use of the short oscillation wavelength diode laser will continue to initiate the synthesis of new dyes and the production of novel recording layers.

In addition to having high extinction coefficients, carbocyanines exhibit excellent reflection properties (up to 40% at 800 nm) and thus yield materials with good SNR values and high signal contrast. However, as the number of vinylene groups increases, the absorption maxima of cyanine dyes undergoes a bathochromic shift and their stability becomes weak. Pentamethine cyanines show better stability than heptamethine cyanines; their absorption maxima are below 700 nm, so they are potential optical recording media for high density recording. In recent years, some patents have reported pentamethine cyanines showing good sensitivity and reflection to ≈680 nm wavelength laser [7–9]. Indocarbocyanines are particularly preferred on account of their favorable solubility properties [1, 2, 7–10]. Cyanine dye films are almost exclusively produced by wet spin-coating from solution. An increase in the stability may be achieved by the introduction of electron-withdrawing substituents, for example halogens, cyano or nitro groups, into the heterocyclic moiety, or by introduction of a halogen atom on their meso carbon atom.

This paper reports the syntheses of eight near-infra-red-absorbing indodicarbocyanine dyes, of general formula I, and also evaluates the structure-performance relationships of the dyes on the basis of their visible/near-infra-red absorption, ^{1}H NMR and IR spectra.



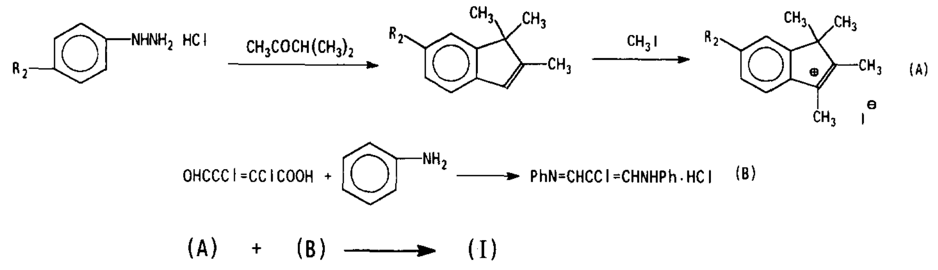
a	$R_1=CH_3$	$R_2=OCH_3$	e	$R_1=CH_3$	$R_2=NO_2$
b	$R_1=CH_3$	$R_2=CH_3$	f	$R_1=C_2H_5$	$R_2=H$
c	$R_1=CH_3$	$R_2=H$	g	$R_1=C_2H_5$	$R_2=Cl$
d	$R_1=CH_3$	$R_2=Cl$	h	$R_1=C_2H_5$	$R_2=OCH_3$

I

RESULTS AND DISCUSSION

Preparation of indodicarbocyanine dyes

Virtually all indodicarbocyanines in this work were synthesized from (un)substituted 2,3,3-trimethylindoline salts and α-chloro-β-anilinoacraldeanil, according to modified literature procedure [11]. The general procedures to prepare the indodicarbocyanine dyes are shown in Scheme 1.



Scheme 1

The indolenine salts represented by formula A were prepared in a multistage reaction, via p-(un)substituted aniline derivatives, as reported previously [12–14]. α-Chloro-β-anilinoacrylaldehyde anil was prepared by the modified method described in the literature [15]. The crude dyes were separated and purified by column chromatography, precipitated with ether and recrystallized from methanol. Their purities were established by thin layer chromatography and elemental analysis. Data on yields, melting points and elemental analyses are given in Table 1.

The electronic absorption spectra and IR spectra

Relevant UV/vis absorption spectra, IR data for dyes 1a–1h are shown in Table 2. When changing the 5-substituents R on the benzocycle, the absorption spectra showed bathochromic shifts, no matter whether the substituent was electron-withdrawing or electron-donating. The order of bathochromic shift was as follows:

$$NO_2 > OCH_3 > CH_3 > Cl > H$$

TABLE 1
Yields, Melting Points and Elemental Analyses for Dyes (1a–1h)

Dye	*M.P. (°C)*	*Yield (%)*	*Molecular Formula*	*E. A. (%)*		
				C(calc.)	*H(calc.)*	*N(calc.)*
1a	216	58	$C_{29}H_{34}ClN_2O_2I$	57.12 (57.58)	5.24 (5.66)	4.12 (4.63)
1b	246	52	$C_{29}H_{34}ClN_2I$	59.86 (60.79)	5.90 (5.98)	4.87 (4.89)
1c	241	60	$C_{27}H_{30}ClN_2I$	59.30 (59.51)	5.25 (5.55)	5.06 (5.14)
1d	272	54	$C_{27}H_{28}Cl_3N_2I$	52.33 (52.83)	4.60 (4.60)	4.33 (4.56)
1e	275	38	$C_{27}H_{28}ClN_4O_4I$	50.48 (51.08)	4.40 (4.44)	8.72 (8.82)
1f	242	35	$C_{29}H_{34}ClN_2I$	60.70 (60.79)	5.95 (5.98)	4.38 (4.89)
1g	216	58	$C_{29}H_{32}Cl_3N_2I$	53.90 (54.27)	5.02 (5.02)	4.36 (4.36)
1h	220	55	$C_{31}H_{38}ClN_2O_2I$	58.45 (58.82)	5.98 (6.05)	4.23 (4.43)

TABLE 2
UV-vis and IR Spectra Data of Dyes

Dye	*λ max(nm)**	*ε (×10^{-5} l cm^{-1}mol^{-1})*	*IR data(cm^{-1})*					
1a	670	1.68	1600	1462	1360	1304	1271	1174
			1096	1067	1012	757		
1b	665	1.82	2918	1610	1507	1477	1351	1306
			1278	1202	1106	964	841	763
1c	644	1.65	1688	1457	1358	1306	1199	1110
			1071	1034	751			
1d	655	1.99	2920	1495	1468	1349	1301	1257
			1193	1107	1037	965	747	
1e	675	2.04	1625	1495	1451	1367	1329	1302
			1282	1182	1083	796	740	
1f	644	1.65	1635	1486	1453	1366	1270	1192
			1111	1076	811	773		
1g	655	2.46	1625	1461	1359	1272	1163	1163
			1108	1073	926	741		
1h	670	2.35	1637	1458	1270	1189	1113	1072
			1020	966	752			

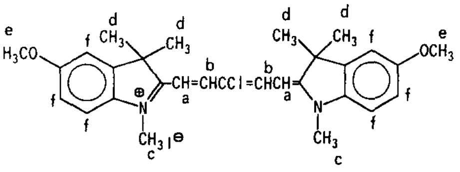
*Concentration: 1. 0–5. 0×10^{-6}; Solvent: CH_3OH.

The nature of the substituent on the heterocyclic nitrogen had only a very limited effect on the absorption maxima.

The IR spectra of dyes 1a–1h show typical aromatic absorption ($C=C$, 1600–1610, 1500, 1400(s)cm^{-1}, δ H, 700–900 cm^{-1}) and resonance conjugated unsaturated stretching modes in the chromophore ($C=C$, $C=N$, 1380–1480 cm^{-1}(S)).

^{1}H NMR Spectra

The ^{1}H NMR chemical shift data was in accordance with the dye structures. For example, data for dye 1a are shown in Scheme 2; other dyes are shown in Table 3.



a,	6.18 (d, 2H)	b,	8.32 (d, 2H)
c,	3.60 (s, 6H)	d,	1.70 (s, 12H)
e,	3.85 (s, 6H)	f,	7.20–7.55 (m, 6H)

Scheme 2

TABLE 3
^{1}H NMR Spectroscopy Data of Dyes

Dye	*^1H NMR Spectroscopy Data*						
1a	6.18 (d, 2H)	8.32 (d, 2H)	3.60 (s, 6H)	1.70 (s, 12H)	3.85 (s, 6H)	7.20–7.55 (m, 6H)	
1b	6.25 (d, 2H)	8.35 (d, 2H)	3.65 (s, 6H)	1.70 (s, 12H)	2.50 (s, 6H)	7.15–7.68 (m, 6H)	
1c	6.30 (d, 2H)	8.15 (d, 2H)	4.15 (s, 6H)	1.65 (s, 12H)	7.00–7.45 (m, 8H)		
1d	6.28 (d, 2H)	8.35 (d, 2H)	3.70 (s, 6H)	1.65 (s, 12H)	7.45–7.75 (m, 6H)		
1e	6.42 (d, 2H)	8.25 (d, 2H)	3.80 (s, 6H)	1.65 (s, 12H)	7.10–7.42 (m, 6H)		
1f	6.30 (d, 2H)	8.45 (d, 2H)	1.30 (t, 6H)	4.20 (q, 4H)	1.70 (s, 12H)	7.12–7.55 (m, 8H)	
1g	6.30 (d, 2H)	8.45 (d, 2H)	1.30 (t, 6H)	4.20 (q, 4H)	1.75 (s, 12H)	7.40–8.00 (m, 6H)	
1h	6.28 (d, 2H)	8.47 (d, 2H)	1.45 (t, 6H)	4.22 (q, 4H)	1.90 (s, 12H)	3.86 (6H, s)	6.82–7.40 (m, 6H)

EXPERIMENTAL

Instruments

Melting points were measured on an X4 micro-melting point apparatus and are uncorrected. IR spectra were taken on Perkin-Elmer 683 spectrometer, visible/near-infrared spectra on a Hitachi UV-8451 A spectrophotometer and the ^{1}H NMR spectra on a Brucker Ac-200, using TMS as internal standard and $CDCl_3$ or DMSO-d_6 as solvent.

Synthesis

α-chloro-β-anilinoacryaldehyde anil hydrochloride
Mucochloric acid, CHOCCl:CClCOOH (10 g) was dissolved by heating in 40 mL alcohol; a solution of aniline (11 g) in 40 mL alcohol was then rapidly added to the mucochloric acid solution and the mixture heated until evolution of carbon dioxide ceased. During this time the solution became golden brown. Golden yellow crystals of the product formed and were collected by filtering the cooled solution. The product was crystallized from alcohol; an 82% yield (16.4 g) was obtained (Found: C, 60.08; H, 5.65; N, 8.13. Calc. for $C_{15}H_{14}N_2Cl_2+C_2H_5OH$: C, 60.19; H, 5.94; N, 8.26). m.p. 228°C (decomp.).

10-chloro-1,1′,3,3,3′,3 -hexamethylindodicarbocyanine iodide(1a)
A mixture of 1,2,3,3-tetramethylindoleninium iodide (2mmol), α-chloro-β-anilinoacrylaldehyde anil hydrochloride (1 mmol) and anhydrous potassium acetate (2 mmol) in 20 mL acetic anhydride was heated under reflex for 1 h. The dye which separated on cooling was repeatedly crystallized from acetone, forming bright green crystals with a gold reflex, m.p. 240–241°C (decomp.).

The synthesis of the other indodicarbocyanines 1b–1h was similarly effected.

REFERENCES

1. Kunikane, M. and Abe, M., US Patent 4 460 665 (1984).
2. Namba, K. and Asami, S., JP Patent 59–55 795 (1984).
3. Oba, H. and Ueda, Y., GB-Appl. 2 165 658 (1986).
4. Hikanelectronicszairyomanual, Optoelectronics, Tokyo (1986).
5. Carlin, D. B. and Tsunoda, Y., *Proceedings of the IEEE,* (1994), **82**(4), pp. 469–480.
6. Tatsuno, K. and Takahashi, M., *IEEE Denshi Tokyo,* (1992), **31**, 133–135.
7. Tatsusuke, K. and Yasuo, K., JP Patent 07–70 453 (1995).
8. Asushi, O and Takayuki, I., JP Patent 06–336 086 (1994).

9. Atsushi, Y. and Yasunshi, A., JP Patent 06–199 045 (1994).
10. Kiroko, N. and Hidetaka, N., JP Patent 07–47 769 (1995).
11. Beattie, S. and Morris, I., *Journal of. Chem. Soc.*, (1932) 260.
12. Daleep, S. D. and Shiam, J., *Journal of Org. Chem.* (1968), **33**, 4283.
13. Schofield, K. and Theobald, R. S., *Journal of Chem. Soc.*, (1949) 796.
14. Dieckmann, W. and Platz, L., *Ber.* (1904), **37**, 4638.
15. Reyolds, G. A. and Drexhage, K. H., *Journal of Org. Chem.* (1979), **42**(5), 885.