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Synthesis and substituent effects of some novel dyes derived from indeno[2,1-*b*]thiophene compounds

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Abstract

The synthesis and characteristic absorption spectra of 2,3,8-trisubstituted-indeno[2,1-*b*]thiophene compounds **5**, **6** and **7** were reported. Cyclization of 3-dicyanovinyl-indan-1-one **3** with sulfur gave 2-amino-8-oxo-8*H*-indeno[2,1-*b*]thiophene-3-carbo-nitrile compound **5**. The reaction of compound **5** with malononitrile and with ethyl cyanoacetate gave the indeno[2,1-*b*]thiophene derivatives **6** and **7**, respectively. The absorption maxima of these compounds changed very significantly by the introduction of various substituents on the 8-position of indeno[2,1-*b*]thiophene ring system. The preparations of the corresponding azomethine dyes and azo disperse dyes were also reported. The azomethine dyes **10**, **11** and **12** were prepared by condensation reaction of compounds **5**, **6** and **7** with *N*,*N*-dimethylaminobenzaldehyde **8**. Additionally, compounds **5**, **6** and **7**, as diazo components, were diazotized using sodium nitrite in concentrated sulfuric acid, and coupled to *N*,*N*-disubstituted anilines **9a–d** to afford a series of novel azo disperse dyes **13a–d**, **14a–d** and **15a–d**, respectively. The prepared products were confirmed by elemental analysis, IR, ^{1}H NMR and MS spectral data. The substituent effects of these compounds and dyes on the electronic absorption properties in solvent are also evaluated.

Keywords: Indeno[2,1-*b*]thiophene; Azomethine dyes; Azo dyes; Substituent effect

1. Introduction

In recent years, the use of heterocyclic intermediates in the synthesis of azo disperse dyes is well established, and the resultant dyes exhibit good tinctorial strength and brighter dyeing than those aniline-based components [1–6]. Dye derivative from heterocyclic amine produces a pronounced bathochromic shift when compared to the corresponding benzoid compounds [7–9]. It is well known that some simple 2-aminothiophene and its benzo analogues are very useful compounds as intermediates in the dyestuff industry and find wide application in pharmaceutical [10–20] and electronic industries [21,22]. Thiophene-based azo dyes show generally red to blue colour with high extinction coefficient in comparison with aniline-based azo dyes. To our knowledge, there are few papers dealing with the carbocyclic fused thiophene compounds as dye intermediates. And the preparation of the corresponding azo or azomethine dyes derived from these compounds is not presented so far. In the present investigation, we report the synthesis of some new trisubstituted indeno[2,1-*b*]thiophene compounds **5**, **6** and **7** derived from 3-dicyanovinylindan-1-one **3**, as starting material. A part of our investigation focused on the synthetic utility of newly prepared heterocyclic compounds as intermediates for dyes. The synthesis of dyes with different chromophore types, such as azomethine dyes **10**, **11** and **12** and azo disperse dyes **13**, **14** and **15**, respectively, are reported in this paper. Also, the substituent effects of these dyes on their absorption properties were evaluated.

2. Results and discussion

2.1. Synthesis of intermediate compounds 5, 6 and 7

The reaction routes for the synthesis of 2,3,8-trisubstituted indeno[2,1-*b*]thiophene derivatives **5**, **6** and **7** were described,

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as shown in Scheme 1. Condensation of 1,3-indandione **1** with malononitrile **2** gave the 3-dicyanvinylindan-1-one **3** in good yield. Compound **5** was prepared by ring closure of compound **3** with sulfur in the presence of diethylamine as catalyst in absolute ethanol. This process was achieved in high yield (92%). The obtained product was characterized using IR, MS and ^{1}H NMR spectral data. The IR spectrum of product **5** showed a characteristic band at 2219 cm^{-1}, attributed to the cyano group, and a strong band at 1664 cm^{-1} was assigned to the carbonyl group. The characteristic band for the amino group appeared in the range of 3175–3299 cm^{-1}. The mass spectrum of this product revealed a molecular ion peak (*m*/*z*) at 226. The ^{1}H NMR spectrum of compound **5** was recorded in DMSO-d_6. Compound **5** showed a 2H singlet at $\delta = 8.76$ ppm assigned to the protons of amino group, and a 4H multiplet at $\delta = 7.25$–7.41 ppm is attributed to aromatic protons in the ring of indeno[2,1-*b*]thiophene. The product was actually identified as 2-amino-8-oxo-8*H*-indeno[2,1-*b*]thiophene-3-carbonitrile.

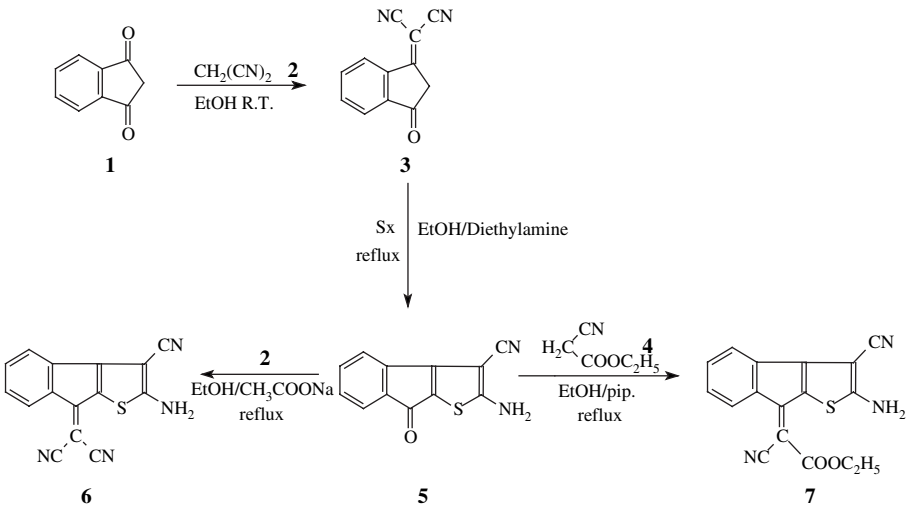
Compound **5** reacted with an excess of malononitrile **2** in absolute ethanol in the presence of anhydrous sodium acetate under reflux to afford the compound **6** in excellent yield (95%). The spectrum of compound **6** showed the absorption bands at 3196–3327 and 2219 cm^{-1} for the amino group and the cyano group, respectively. And the absorption band for carbonyl group was not observed in the IR spectrum. Compound **6** showed a 2H singlet at $\delta = 9.22$ ppm, which can be attributed to the protons of amino group, and a multiplet at $\delta = 7.16$–7.65 ppm is due to a 4H aromatic proton in the ring of indeno[2,1-*b*]thiophene. The mass spectrum of this product revealed a molecular ion peak (*m*/*z*) at 274. The structure of the compound **6** was actually identified by IR, ^{1}H NMR and MS spectra as 2-(2-amino-3-cyano-indeno-[2,1-*b*]thiophene-8-ylidene)-malononitrile. Base-catalysed reaction of compound **5** with ethyl cyanoacetate **4** in absolute ethanol afforded also a good yield (82%) of compound **7**. The IR spectrum of compound **7** showed a carbonyl absorption band of carbethoxy group at 1703 cm^{-1}, 2215 cm^{-1} for the cyano group and in the range of 3169–3325 cm^{-1} for the amino group. The ^{1}H NMR spectrum of compound **7** showed a triplet at $\delta = 1.37$ ppm ($-COOCH_2CH_3$) and a quartet at $\delta = 4.40$ ppm ($-COOCH_2CH_3$) assigned to the $COOCH_2CH_3$ group. The chemical shifts of aromatic protons showed a 4H multiplet in the region of $\delta = 7.11$–7.55 ppm. The protons of amino group showed a 2H singlet at $\delta = 8.92$ ppm. The mass spectrum of this product revealed a molecular ion peak (*m*/*z*) at 321. The structure of the compound **7** was actually identified by IR, ^{1}H NMR and MS spectra as [2-amino-3-cyano-indeno[2,1-*b*]-thiophene-(8*Z*)-ylidene]-cyano acetic acid ethyl ester. The colour of compounds **5**, **6** and **7** was orange to blue solid.

The physical data and spectral characterization of the 2,3,8-trisubstituted indeno[2,1-*b*]thiophene compounds **5**, **6** and **7** are listed in Tables 1 and 2.

Analytical and spectral data support fully the structure of all compounds.

2.2. Synthesis of dyes

In the present work, we reported the utility of the obtained compounds 2,3,8-trisubstituted indeno[2,1-*b*]thiophene derivatives **5**, **6** and **7** for the synthesis of several series of dyes with different chromophoric systems, as shown in Scheme 2. Compound **5** was condensed with *N*,*N*-dimethylaminobenzaldehyde **8** in acetic acid to yield deep red azomethine dye **10**. Compounds **6** and **7** reacted with compound **8** in acetic acid to give blue and violet azomethine dyes **11** and **12** in good yields, respectively. The structures of azomethine dyes **10**, **11** and **12** were established by elemental analysis and spectral data, as shown in Tables 1 and 2. The ^{1}H NMR spectra of azomethine dyes **10**, **11** and **12** were recorded in DMSO-d_6. Dyes **10**, **11** and **12** showed a 1H singlet at $\delta = 8.63$, 8.28 and 8.71 ppm, which can be attributed to methine proton. The signal of amino group was not observed in the ^{1}H NMR spectrum of dyes. The azomethine dye **12** showed the additional 3H triplet at $\delta = 1.34$ ppm and 2H quartet at $\delta = 4.38$ ppm, attributed to the protons of carbethoxy group at the 8-position of



Scheme 1.

Table 1
Physical and UV–vis absorption spectra data of compounds **5**–**7**and **10**–**15**

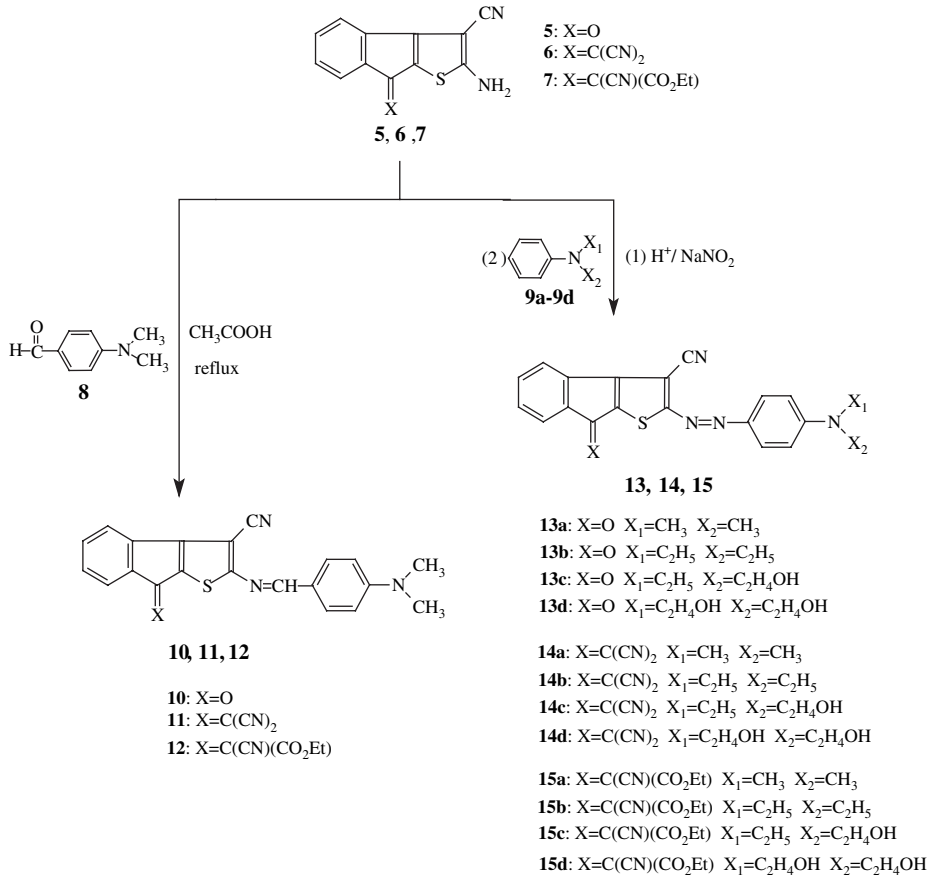
Compounds	Mol. formula	M.p. (°C)	UV λ_{max} (log ε) in acetone	Yield (%)	Elemental analysis (%): calculated/found			
					C	H	N	S
5	$C_{12}H_6N_2OS$	306–308	461(3.34)	92	63.72/63.67	2.65/2.69	12.39/12.34	14.16/14.08
6	$C_{15}H_6N_4S$	318–320	611(3.57)	95	65.69/65.61	2.19/2.28	20.44/20.39	11.68/11.72
7	$C_{17}H_{11}N_3O_2S$	>350	560(3.92)	82	63.55/63.58	3.43/3.34	13.08/13.19	9.97/9.82
10	$C_{21}H_{15}N_3OS$	316–318	531(4.38)	54	70.59/70.71	4.20/4.24	11.76/11.74	8.96/8.92
11	$C_{24}H_{15}N_5S$	304–306	629(4.07)	60	71.11/71.18	3.70/3.93	17.28/17.35	7.90/7.86
12	$C_{26}H_{20}N_4O_2S$	298–300	599(4.07)	78	69.03/69.14	4.42/4.47	12.39/12.32	7.08/7.02
13a	$C_{20}H_{14}N_4OS$	218–220	561(4.12)	65	67.04/67.10	3.91/3.94	15.64/15.61	8.94/8.90
13b	$C_{22}H_{18}N_4OS$	186–188	607(4.04)	61	68.39/68.28	4.66/4.69	14.51/14.47	8.29/8.21
13c	$C_{22}H_{18}N_4O_2S$	168–170	603(4.24)	51	65.67/65.74	4.48/4.55	13.93/13.98	7.96/7.82
13d	$C_{22}H_{18}N_4O_3S$	162–164	600(3.92)	41	63.16/63.18	4.31/4.33	13.40/13.46	7.66/7.60
14a	$C_{23}H_{14}N_6S$	186–188	691(4.03)	43	67.98/68.03	3.45/3.48	20.69/20.60	7.88/7.79
14b	$C_{25}H_{18}N_6S$	180–182	699(3.89)	48	69.12/69.18	4.15/4.19	19.35/19.32	7.37/7.35
14c	$C_{25}H_{18}N_6OS$	182–184	697(4.02)	44	66.67/66.62	4.00/4.05	18.67/18.78	7.11/7.10
14d	$C_{25}H_{18}N_6O_2S$	180–182	695(4.12)	36	64.38/64.30	3.86/3.82	18.03/18.10	6.87/6.75
15a	$C_{25}H_{19}N_5O_2S$	156–158	658(4.23)	65	66.23/66.28	4.19/4.17	15.45/15.52	7.06/6.98
15b	$C_{27}H_{23}N_5O_2S$	156–158	667(4.06)	57	67.36/67.34	4.78/4.85	14.55/14.51	6.65/6.62
15c	$C_{27}H_{23}N_5O_3S$	154–156	665(4.24)	70	65.19/65.28	4.63/4.73	14.08/13.99	6.44/6.31
15d	$C_{27}H_{23}N_5O_4S$	150–152	663(4.36)	71	63.16/63.23	4.48/4.46	13.65/13.57	6.24/6.17

indeno[2,1-*b*]thiophene moiety. The IR spectrum of azomethine dyes **10**, **11** and **12** showed that the absorption bands at 2224, 2217 and 2218 cm^{-1} assigned to cyano group, respectively. The dye **11** revealed the absence of the carbonyl absorption band in the IR spectrum.

A series of azo disperse dyes **13**, **14** and **15** were prepared by diazotizing 2-amino-indeno[2,1-*b*]thiophene intermediates using nitrosyl sulfuric acid and the subsequent coupling with various *N*,*N*-disubstituted anilines **19a**–**d**. 2-Amino-indeno[2,1-*b*]thiophene compound **5** containing a strong electron-withdrawing substituent at the 8-position was then used as diazo component. Thus, compound **5** was diazotized with nitrosylsulfuric acid at 0–5 °C to give the diazonium salt solution, followed by coupling with various *N*,*N*-disubstituted anilines **9a**–**d** as coupling components to produce azo disperse dyes **13a**–**d** in moderate yield. The colour of these azo disperse dyes **13a**–**d** was violet to blue-green solids. The preparations of azo disperse dyes **14** and **15** are similar to those of the dyes **13**, except that the diazo components are replaced by other aminoindeno[2,1-*b*]thiophene derivatives **6** and **7**. The colour of the dyes **14** and **15** is deep

Table 2
Spectral data of compounds **5**–**7** and **10**–**15**

Compounds	MS (*m/e* M^+)	FT-IR(KBr) ν (cm^{-1})	^{1}H NMR (DMSO-d_6) δ (ppm)
5	226	1664 (C=O), 2219 (C≡N), 3175–3299 (N–H)	7.25–7.41 (m, 4H, Ar–H), 8.76 (s, 2H, NH_2)
6	274	2219 (C≡N), 3196–3327 (N–H)	7.16–7.65 (m, 4H, Ar–H), 9.22 (s, 2H, NH_2)
7	321	1703 (C=O), 2215 (C≡N), 3169–3325 (N–H)	1.37 (t, 3H, CH_3), 4.40 (q, 2H, CH_2), 7.11–7.55 (m, 4H, Ar–H), 8.92 (s, 2H, NH_2)
10	357	1686 (C=O), 2224 (C≡N)	3.12 (s, 6H, CH_3), 6.55–7.90 (m, 8H, Ar–H), 8.63 (s, 1H, =CH–)
11	405	2217 (C≡N)	3.16 (s, 6H, CH_3), 6.80–8.01 (m, 8H, Ar–H), 8.28 (s, 1H, =CH–)
12	452	1705 (C=O), 2218 (C≡N)	1.34 (t, 3H, CH_3), 3.16 (s, 6H, CH_3), 4.38 (q, 2H, CH_2), 6.86–8.33 (m, 8H, Ar–H), 8.71 (s, 1H, =CH–)
13a	358	1702 (C=O), 2221 (C≡N)	3.16 (s, 6H, CH_3), 6.78–7.97 (m, 8H, Ar–H)
13b	386	1699 (C=O), 2220 (C≡N)	1.05 (t, 6H, CH_3), 4.29 (q, 4H, CH_2), 6.82–7.85 (m, 8H, Ar–H)
13c	402	1700 (C=O), 2220 (C≡N)	1.19 (t, 3H, CH_3), 3.64–3.72 (m, 6H, CH_2), 6.98–8.02 (m, 8H, Ar–H)
13d	418	1698 (C=O), 2218 (C≡N)	3.66 (t, 4H, CH_2), 3.78 (t, 4H, CH_2), 7.04–7.99 (m, 8H, Ar–H)
14a	406	2221 (C≡N)	3.09 (s, 6H, CH_3), 6.65–8.02 (m, 8H, Ar–H)
14b	434	2221 (C≡N)	1.21 (t, 6H, CH_3), 3.90 (q, 4H, CH_2), 6.83–8.06 (m, 8H, Ar–H)
14c	450	2221 (C≡N)	1.21 (t, 3H, CH_3), 3.69–3.80 (m, 6H, CH_2), 6.81–8.01 (m, 8H, Ar–H)
14d	466	2220 (C≡N)	3.68 (t, 4H, CH_2),3.73 (t, 4H, CH_2), 7.06–8.25 (m, 8H, Ar–H)
15a	453	1712 (C=O), 2214 (C≡N)	1.34 (t, 3H, CH_3), 3.16 (s, 6H, CH_3), 4.37 (q, 2H, CH_2), 6.75–8.34 (m, 8H, Ar–H)
15b	481	1713 (C=O), 2215 (C≡N)	1.15 (t, 6H, CH_3), 1.29 (t, 3H, CH_3), 4.21 (q, 4H, CH_2), 4.29 (q, 2H, CH_2), 6.71–8.31 (m, 8H, Ar–H)
15c	497	1712 (C=O), 2215 (C≡N)	1.18 (t, 3H, CH_3), 1.34 (t, 3H, CH_3), 3.62–4.29 (m, 6H, CH_2), 4.34 (q, 2H, CH_2), 6.87–8.27 (m, 8H, Ar–H)
15d	513	1712 (C=O), 2213 (C≡N)	1.34 (t, 3H, CH_3), 3.66 (t, 4H, CH_2), 3.67 (t, 4H, CH_2), 4.33 (q, 2H, CH_2), 6.98–8.24 (m, 8H, Ar–H)



Scheme 2.

blue-greenish. The structures of azo disperse dyes **13**, **14** and **15** were established by elemental analysis and spectral data, as shown in Tables 1 and 2. The IR spectrum of the dyes **13**, **14** and **15** showed the absorption band in the range from 2213 to 2221 cm^{-1} due to the presence of cyano group. It was observed that the carbonyl absorption appeared in the range from 1698 to 1713 cm^{-1} in the IR spectrum of dyes **13** and **15** except that in dye **14**. The absorption band of amino group was not present in the IR spectrum of dyes **13**, **14** and **15**. The ^1H NMR spectra of azo dyes were recorded in DMSO-d_6. Azo dyes **13**, **14** and **15** showed a 8H multiplet in the range from $\delta = 6.65-7.06$ to 7.99–8.34 ppm, which can be attributed to the protons of the two aromatic groups, one (4H) on the indeno[2,1-*b*]thiophene moiety and the other (4H) on the aniline ring. The signal of amino group was not observed in the ^1H NMR spectrum of azo dyes.

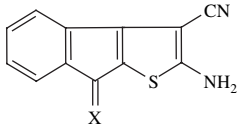
The physical and spectral data of the azomethine dyes **10**, **11** and **12** and azo disperse dyes **13a–d**, **14a–d** and **15a–d** are summarized in Tables 1 and 2.

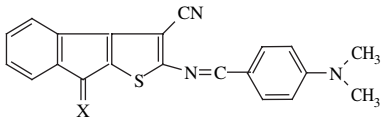
Analytical and spectral data support fully the structure of all dyes.

2.3. Substituent effects

The electronic absorption spectra of prepared compounds were recorded in acetone at a concentration of 3×10^{-5} M (Table 1). The absorption maxima of compounds **5**, **6** and **7** showed their absorption band in the visible region 461, 611 and 560 nm, respectively. As shown in Table 3, compounds **6** and **7** showed the pronounced bathochromic shift of 150 and 99 nm, respectively, when compared to the analogous compound **5**. The large shifts of compounds **6** and **7** indicated that the absorption maxima of these compounds changed very significantly and exhibited a strong substituent dependence in the order: $C{=}C(CN)_2 > C{=}C(CN)(COOEt) > C{=}O$. The deep colour of these products was attributed to the presence of extended conjugation and the introduction of strong electron-withdrawing substituents. The influences of substituents at the ring position of both azomethine and azo dyes on the visible absorption maxima have been evaluated. As shown in Table 1, in comparison to the absorption spectra of dyes **10** and **13a** and the starting compound **5**, the absorption maxima of the dyes **10** and **13a** showed also a larger bathochromic shift of 70 and 100 nm than the corresponding compound **5**. It is observed in Table 3 that the azomethine dyes **10**, **11** and **12** exhibited the absorption maxima in the visible region 531, 629 and 599 nm, respectively. The introduction of the substituents $C(CN)_2$ and C(CN)(COOEt) groups into the dye **10** at the 8-position of indeno[2,1-*b*]thiophene ring giving dyes **11** and **12** results in a large bathochromic shift, which can be attributed to the strong electron-withdrawing dicyanovinyl and cyanocarbethoxyvinyl groups that enhance the delocalisation

Table 3
Substituent effect of compounds **5**–**7**, **10**–**12** in acetone





Compounds	λ_{max}	X	$\Delta\lambda$[a]	Compounds	λ_{max}	X	$\Delta\lambda$[a]
5	461	O	–	**10**	531	O	–
6	611	$C(CN)_2$	+150	**11**	629	$C(CN)_2$	+98
7	560	$C(CN)(CO_2E)$	+99	**12**	599	$C(CN)(CO_2Et)$	+68

[a] Relative to compounds **5**, **10** (X = O), respectively.

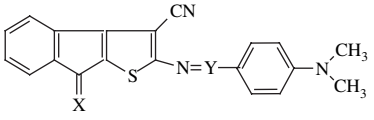
of conjugated system of dyes. The azomethine dyes **11** and **12** showed the absorption maxima at longer wavelength than that of the corresponding dye **10**. The $\Delta\lambda$ of dyes **11** and **12** is +98 and +68 nm, compared to dye **10** in acetone.

The absorption maxima of azo disperse dyes **13a**–**d**, **14a**–**d** and **15a**–**d** showed the absorption bands in the visible regions at around 561–607 nm, 691–699 nm and 658–667 nm, respectively. The shift of electronic absorption maxima of dyes depends on the nature of both components and the nature of the substituents at the terminal group. Table 4 shows the chromophore effect of azomethine and azo dyes. The azo disperse dyes **13a**, **14a** and **15a** containing azo chromophore (–N=N–) have the absorption maxima at longer wavelengths than the corresponding azomethine dyes **10**, **11** and **12** with an imino chromophore (–N=CH–). It can be seen that the azo group is regarded as an imino group in which the CH group has been replaced by an N-atom. The absorption maxima of the azo dyes resulted in a bathochromic shift of 30, 62 and 59 nm, respectively, when the azomethine dyes **10**, **11** and **12** (Y = CH) are taken as the parent molecules. The shifts observed for the azo dyes **13a**, **14a** and **15a** can be attributed to the effect of nitrogen atom with lone pair electron.

The substituent effects at the 8-position of indeno[2,1-*b*]thiophene diazo component of azo dyes, are listed in Table 5. The absorption maxima of dyes **13a**, **14a** and **15a** showed the absorption bands in the visible regions at 561, 691 and 658 nm, respectively. Replacement of carbonyl group in the indeno[2,1-*b*]thiophene moiety by a dicyanovinyl group or cyano carbethoxyvinyl group shifts the absorption maximum to longer wavelengths. Dye **14a** showed a significantly higher $\Delta\lambda$ (=130 nm) than dye **13a**. Dye **15a** containing cyano carbethoxy group absorbed also at 97 nm which is higher than that of dye **13a**. Introduction of strong electron-withdrawing substituents into the diazo component results in a large bathochromic shift. This may be due to increasing conjugation of dye molecule. The same results were also observed for the other azo dyes **13b**–**d**, **14b**–**d** and **15b**–**d**.

The substituent effects at the terminal amino group of coupling components are listed in Table 6. Dyes **13b**, **14b** and **15b** containing *N*,*N*-diethylamino group at the terminal position of coupling component have absorption maxima at longer wavelengths than those of dyes **13a**, **14a** and **15a**, respectively. Replacement of the *N*,*N*-diethylamino group by

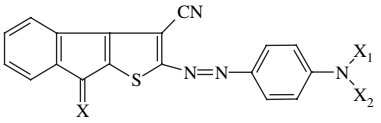
Table 4
Effect of aza substitution in dyes **10**, **11**, **12**, **13a**, **14a** and **15a** in acetone



Compounds	λ_{max}	X	Y	$\Delta\lambda$[a]
10	531	O	CH	–
13a	561	O	N	+30
Compounds	λ_{max}	X	Y	$\Delta\lambda$[b]
11	629	$C(CN)_2$	CH	–
14a	691	$C(CN)_2$	N	+62
Compounds	λ_{max}	X	Y	$\Delta\lambda$[c]
12	599	$C(CN)(CO_2Et)$	CH	–
15a	658	$C(CN)(CO_2Et)$	N	+59

[a] Relative to **10** (X = O, Y = CH).
[b] Relative to **11** (X = $C(CN)_2$, Y = CH).
[c] Relative to **12** (X = $C(CN)(CO_2Et)$, Y = CH).

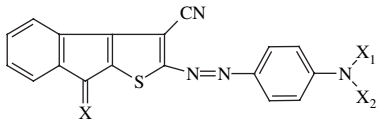
Table 5
Substituent effect of azo dyes **13a**–**13d**, **14a**–**14d** and **15a**–**15d** in acetone



Compounds	λ_{max}	X	X_1	X_2	$\Delta\lambda$[a]
13a	561	O	CH_3	CH_3	–
14a	691	$C(CN)_2$	CH_3	CH_3	+130
15a	658	$C(CN)(CO_2Et)$	CH_3	CH_3	+97
Compounds	λ_{max}	X	X_1	X_2	$\Delta\lambda$[b]
13b	607	O	C_2H_5	C_2H_5	–
14b	699	$C(CN)_2$	C_2H_5	C_2H_5	+92
15b	667	$C(CN)(CO_2Et)$	C_2H_5	C_2H_5	+60
Compounds	λ_{max}	X	X_1	X_2	$\Delta\lambda$[c]
13c	603	O	C_2H_5	C_2H_4OH	–
14c	697	$C(CN)_2$	C_2H_5	C_2H_4OH	+94
15c	665	$C(CN)(CO_2Et)$	C_2H_5	C_2H_4OH	+62
Compounds	λ_{max}	X	X_1	X_2	$\Delta\lambda$[d]
13d	600	O	C_2H_4OH	C_2H_4OH	–
14d	695	$C(CN)_2$	C_2H_4OH	C_2H_4OH	+95
15d	663	$C(CN)(CO_2Et)$	C_2H_4OH	C_2H_4OH	+63

[a] Relative to **13a** (X = O, $X_1 = CH_3$, $X_2 = CH_3$).
[b] Relative to **13b** (X = O, $X_1 = C_2H_5$, $X_2 = C_2H_5$).
[c] Relative to **13c** (X = O, $X_1 = C_2H_5$, $X_2 = C_2H_4OH$).
[d] Relative to **13d** (X = O, $X_1 = C_2H_4OH$, $X_2 = C_2H_4OH$).

Table 6
Effect of substituent on coupling components of compounds **13**–**15** in acetone



Compounds	λ_{max}	X	X_1	X_2	$\Delta\lambda$[a]
13a	561	O	CH_3	CH_3	–
13b	607	O	C_2H_5	C_2H_5	+46
13c	603	O	C_2H_5	C_2H_4OH	+42
13d	600	O	C_2H_4OH	C_2H_4OH	+39
14a	691	$C(CN)_2$	CH_3	CH_3	–
14b	699	$C(CN)_2$	C_2H_5	C_2H_5	+8
14c	697	$C(CN)_2$	C_2H_5	C_2H_4OH	+6
14d	695	$C(CN)_2$	C_2H_4OH	C_2H_4OH	+4
15a	658	C(CN) (CO_2Et)	CH_3	CH_3	–
15b	667	C(CN) (CO_2Et)	C_2H_5	C_2H_5	+9
15c	665	C(CN) (CO_2Et)	C_2H_5	C_2H_4OH	+7
15d	663	C(CN) (CO_2Et)	C_2H_4OH	C_2H_4OH	+5

[a] Relative to compounds **13a**, **14a**, **15a** ($X_1 = X_2 = CH_3$), respectively.

N,*N*-β-hydroxyethyl or *N*,*N*-di-β-hydroxyethyl group shifted the absorption maxima only to slightly longer wavelengths, as shown in Table 6. The results indicated that the absorption maxima of dyes **14a**–**d**, **15a**–**d** did not change significantly with the terminal substituents of coupling component with exception of dyes **13a**–**d**. This can be attributed to the influence of strong electron-withdrawing substituent at the side of diazo component.

3. Experimental

The chemicals were obtained from Aldrich Chemical Company and used without further purification. All melting points were determined on an electrothermal apparatus and are uncorrected. Infrared spectra were recorded as KBr pellets on a JASCO FTIR-3 spectrometer. The ^{1}H NMR spectra were obtained on a Joel-EX-400 MHz NMR spectrometer, and the chemical shifts are expressed in δ ppm using TMS as an internal standard. The mass spectra were obtained from a Finnigan TSQ-700 GC/LC/MS spectrometer. Microanalytical data for C, H, N and S were performed on a Perkin–Elmer 2400(II) elemental analyzer. UV–vis absorption spectra were recorded on a Heliosa UV1 in acetone. The solvents were of spectroscopic grade. 3-Dicyanovinylindan-1-one **3**, as starting material was prepared in good yield by knovenagel reaction of 1,3-indandione with malononitrile in ethanol based on the published literature [23].

*3.1. Synthesis of 2,3,8-trisubstituted indeno [2,1-b]thiophenes **5**, **6** and **7***

*3.1.1. 2-Amino-8-oxo-8H-indeno[2,1-b]thiophene-3-carbonitrile (**5**)*

To a solution of 3-dicyanovinylindan-1-one **3** (1.94 g, 0.01 mol) and sulfur (0.32 g, 0.01 mol) in 50 ml absolute ethanol at room temperature, 5 ml diethylamine was added. The reaction mixture was refluxed for 3 h, and then cooled. The precipitate product was filtered, washed with ethanol and was crystallized from ethanol to give compound **5** (2.08 g, yield 92%). Characteristic data of compound **5** are given in Tables 1 and 2.

*3.1.2. 2-(2-Amino-3-cyano-indeno[2,1-b]thiophene-8-ylidene)-malononitrile (**6**)*

To a solution of compound **5** (2.26 g, 0.01 mol) and anhydrous sodium acetate (1.07 g, 0.013 mol) in 50 ml absolute ethanol, malononitrile **2** (1.32 g, 0.02 mol) was added at room temperature. The reaction mixture was refluxed for 5 h, and then cooled. The precipitated product was filtered, washed with ethanol and recrystallized from ethanol to give compound **6** (2.60 g, yield 95%). Characteristic data of compound **6** are given in Tables 1 and 2.

*3.1.3. [2-Amino-3-cyano-indeno[2,1-b]thiophene-(8Z)-ylidene]-cyano-acetic acid ethyl ester (**7**)*

To a suspension of compound **5** (2.26 g, 0.01 mol) and 2 ml piperidine in 50 ml absolute ethanol, ethyl cyanoacetate **4** (2.26 g, 0.02 mol) was added gradually at room temperature. The reaction mixture was refluxed for 6 h, and then cooled. The precipitated product was filtered, washed with ethanol several times and was crystallized from ethanol to give compound **7** (2.63 g, yield 82%). Characteristic data of compound **8** are given in Tables 1 and 2.

*3.2. Synthesis of azomethine dyes **10**, **11** and **12***

Indeno[2,1-*b*]thiophene heterocyclic amines also can be used in condensation reaction with aldehyde derivatives. A general procedure is described below for the preparation of azomethine dye **10**; other dyes **11** and **12** were prepared in a similar manner. The yields of the azomethine dyes are in the range of 54–78%. Characterization data are shown in Tables 1 and 2.

*3.2.1. 2-(4-N,N-Dimethylamino-benzyldeneamino)-8-oxo-8H-indeno[2,1-b]thiophene-3-carbonitrile (**10**)*

A mixture of compound **5** (2.26 g, 0.01 mol) and *N*,*N*-dimethylaminobenzaldehyde **8** (1.49 g, 0.01 mol) in acetic acid (30 ml) was heated under reflux for 6 h, until the reaction solution changed to dark red, and then the solution was cooled to room temperature. The precipitated product was filtered, washed with water, dried and recrystallized from DMF–methanol to give the azomethine dye **10** as red solid (1.92 g, yield 54%).

*3.3. Synthesis of azo dyes **13a–d**, **14a–d** and **15a–d***

Dyes **13a**–**d**, **14a**–**d** and **15a**–**d** were prepared by diazotization of indeno[2,1-*b*]thiophene amines in nitrosyl sulfuric acid, followed by coupling with *N*,*N*-disubstituted-anilines. The syntheses of azo dyes **13a**–**d**, **14a**–**d** and **15a**–**d** followed the same procedures as described below for the preparation of dye **13a**. The yields of the azo dyes are in the range of 41–71%. Characterization data are shown in Tables 1 and 2.

*3.3.1. 2-(4-N,N-Dimethylamino-phenylazo)-8-oxo-8H-indeno[2,1-b]thiophene-3-carbonitrile (**13a**)*

Sodium nitrite (0.8 g, 0.012 mol) was slowly added to the 5 ml of sulfuric acid (98%) at 10 °C and stirred for 1 h at 60 °C, followed by cooling to below 5 °C. Then, compound **5** (2.26 g, 0.01 mol) was slowly added into the nitrosyl sulfuric acid solution freshly prepared and stirred for 1 h at 0–5 °C to give the diazonium salt solution **5**. The diazonium salt solution **5** was then added slowly into a hydrochloric acid solution (5 ml) containing compound *N*,*N*-dimethylaniline **9a** (1.8 g, 0.01 mol). The reaction solution was stirred for 2 h under 5 °C and the pH value of the reaction solution was maintained around 4–5 by addition of 10% sodium carbonate. The resulting product was filtered and the pre-cake washed with water, dried and recrystallized from DMF–methanol to give the azo dye **13a** as blue crystals (2.32 g, 65%).

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