Synthesis and Absorption Spectral Properties of New Merocyanine Dyes Derived from 1,1-Diaryl-2-propyn-1-ols[1)]

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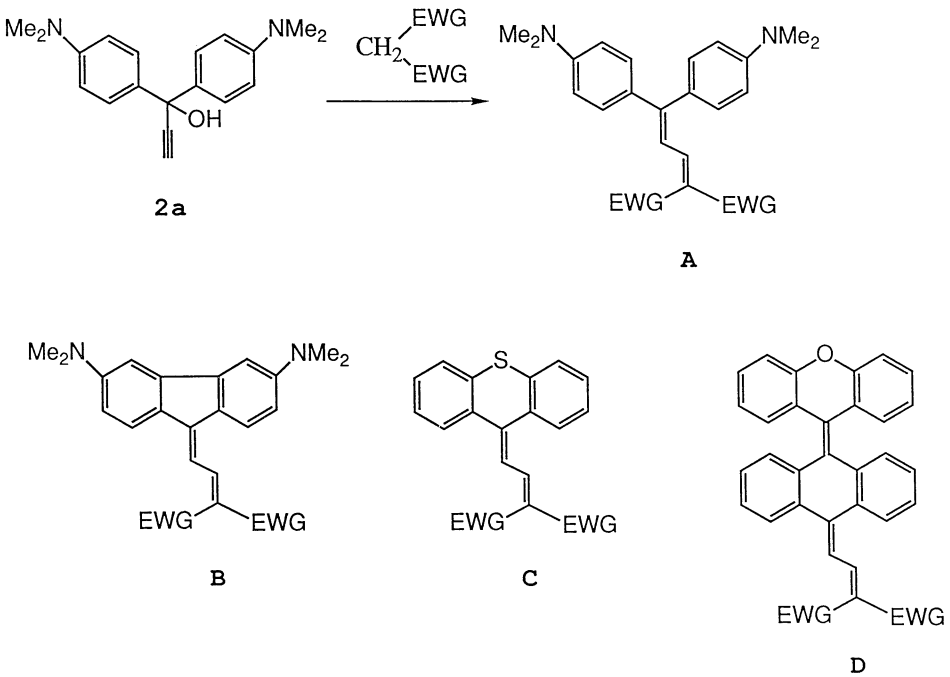
A series of push-pull butadiene dyes (new merocyanine dyes) containing 3,6-bis(dimethylamino)fluorenylidene, thioxanthenylidene, or 10-(9-xanthenylidene)-9(10*H*)-anthrylidene chromophore was easily synthesized from the corresponding 1,1-diaryl-2-propyn-1-ol systems. Their absorption spectral properties were examined and the relationship between their light absorption properties and chemical structures is discussed in comparison with the results from PPP-SCF-CI-MO calculations. The influence of the solvent polarity on the $1/\lambda_{max}$(=wave number)-values of the dyes was investigated, and the solvatochromic nature compared with the known solvent polarity parameters such as E_T30, Z, χ_R, π^*_{azo} on 2-[2-[3,6-bis(dimethylamino)fluorenylidene]ethylidene]-1,3-indandione.

Merocyanine dyes are a well-known class of dyes, which have such practical applications as photoconductive or imaging materials (photographic films or electrographic systems);[2)] they have also been proposed as dyes for organic solar cells.[3)] Moreover, these dyes are used as important materials for photophysical[4)] or biochemical investigations.[5)] More recently, special interest has been focused on these dyes as possible candidates for nonlinear optics, owing to the development of optical and laser storage technologies.[6)]

During the course of our studies on the acetylenic analogs of triphenylmethane dyes (triphenylmethane dye ethynologs),[7)] we have developed a simple and convenient method for the preparation of aryl-substituted push–pull butadienes, a family of merocyanine dyes.[8)]

In this paper we report on the syntheses of novel push–pull-type merocyanine dyes containing bis[4-(dimethylamino)]phenylmethylene (**A**), 3,6-bis(dimethylamino)-fluorenylidene (**B**), thioxanthenylidene (**C**), and 10-(9-xanthylenylidene)-9(10*H*)-anthrylidene (**D**) chromophores from the corresponding 1,1-diaryl-2-propyn-1-ols. Successively, a mutual relation between their light-



EWG=Electron-Withdrawing Group

Chart 1.

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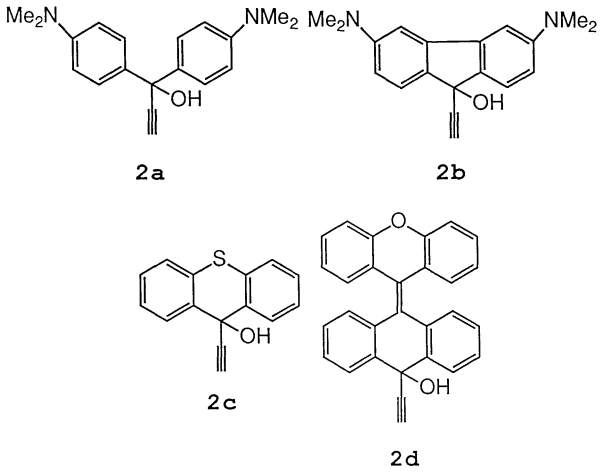
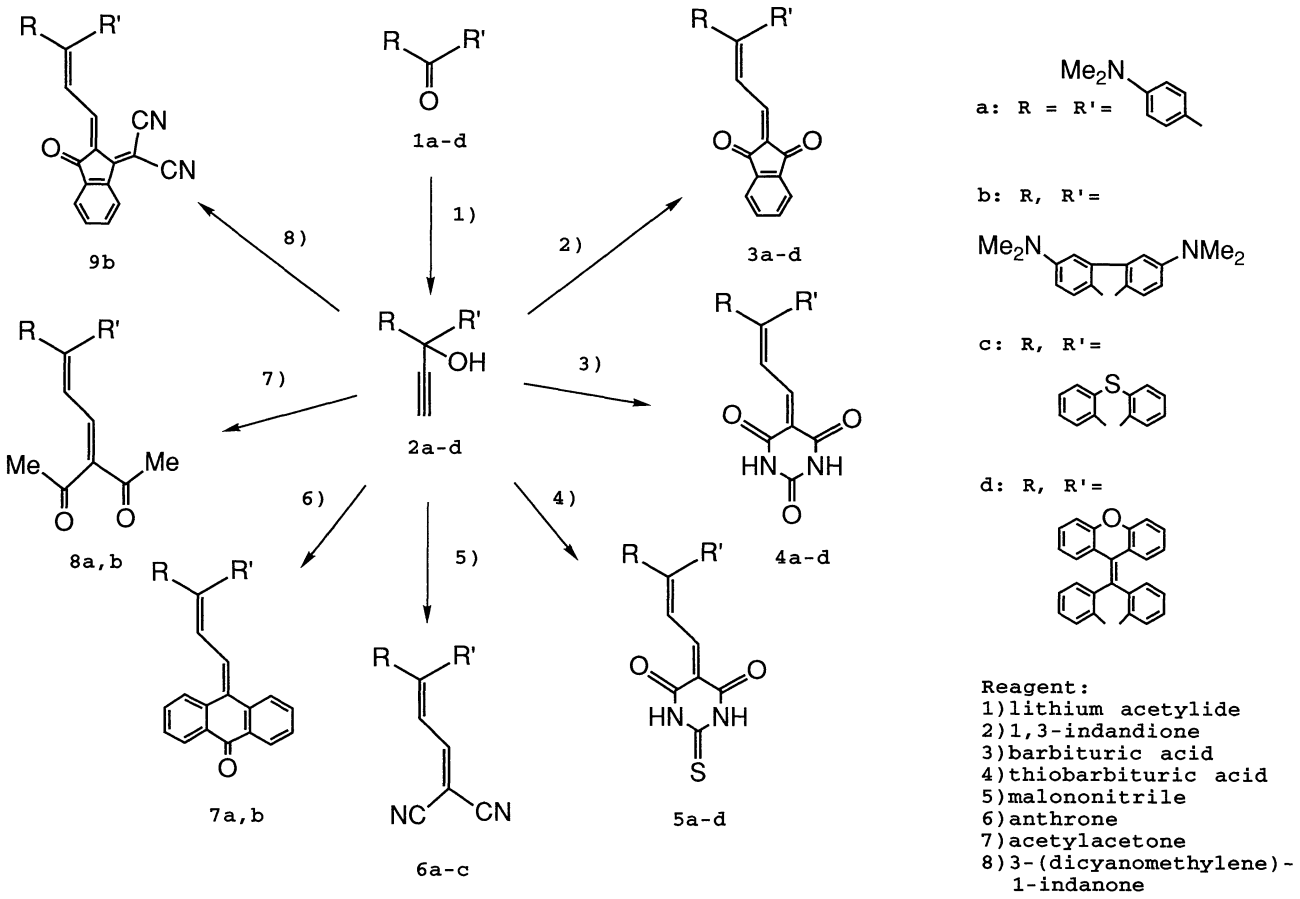
absorption properties and chemical structures was investigated and compared with Pariser–Paar–Pople MO (PPP-MO) calculations. Moreover, the solvatochromic properties were examined on 2-[2-[3,6-(dimethylamino)fluorenylidene]ethylidene]-1,3-indandione (**3b**) as a representative of the prepared dyes.

Results and Discussion

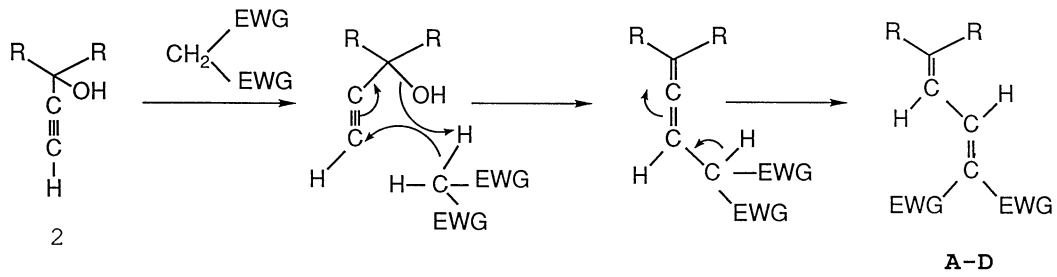
Synthesis of Dyes. Each of the precursors, i.e., the 1,1-diaryl-2-propyn-1-ol systems (**2a—d**), were prepared by ethynylation of the corresponding ketones.[9] Several nucleophiles, i.e., active methylene compounds, were allowed to react with **2a—d**, yielding a variety of new merocyanine dyes [(**3a—d**—**5a—d**), (**6a—c**), (**7a, b**), (**8a, b**), and (**9b**)], as shown in Scheme 1. In some cases the reactions proceeded easily at ambient temperature by mixing the substrates and each reagent without either heating or adding a catalyst, e.g., reactions with barbituric acid or thiobarbituric acid. Although isolated yields were good for the above-mentioned cases; in some cases appropriate heating was necessary to complete the reaction; there were also cases in which no reaction proceeded (see Experimental). It seems apparent that these reactivities depend on both the acidity of the nucleophiles employed and the electrophilicity of the substrates. A sort of acid-catalyzed propargylic rearrangement would participate in the reaction;[10] a plausible reaction process is shown in Scheme 2.



Absorption Spectral Properties. Absorption spectral data for the longest wavelength region of the prepared dyes are listed in Table 1. The bathochromic shift of the absorption band of the push–pull butadiene dyes (**A—D**) (Chart 1) depended on the electron-donating residue according to the sequence: **D>B>A>C**. The influence of the electron acceptor residue similarly followed the



Scheme 1.



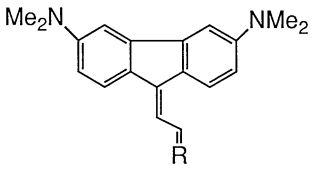
Scheme 2.

Table 1. Light Absorption Properties of Merocyanine Dyes **A**, **B**, **C**, **D**

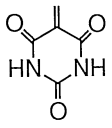
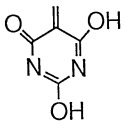
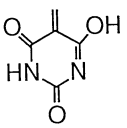
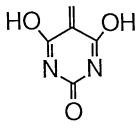
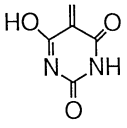
Compound	λ_{max}/nm ($\varepsilon\times10^{-4}$)			Compound	λ_{max}/nm ($\varepsilon\times10^{-4}$)			Compound	λ_{max}/nm ($\varepsilon\times10^{-4}$)	
	CH_2Cl_2	EtOH	Calcd[a]		CH_2Cl_2	EtOH	Calcd[a]		CH_2Cl_2	EtOH
3a	565 (4.98)	578 (4.33)	459	**3b**	588 (5.89)	610 (5.62)	492	**3c**	473 (2.38)	472 (2.40)
4a	566 (5.60)	558 (3.86)	489	**4b**	598 (3.41)	597 (1.22)	523	**4c**	486 (1.62)	464 (1.25)
5a	595 (8.06)[b]	592 (5.67)	548	**5b**	634 (1.85)	637 (1.07)	579	**5c**	514 (0.94)	486 (0.68)
6a	498 (3.32)[b]	497 (4.19)	493	**6b**	531 (4.91)	529 (2.83)	532	**6c**	454 (1.69)	447 (1.38)
7a	503 (2.28)	504 (2.98)	507	**7b**	526 (3.50)	525 (2.38)	525	**3d**	672 (3.43)	667 (1.48)
8a	442 (3.04)	445 (1.83)	454	**8b**	473 (1.34)	481 (1.30)	488	**4d**	652 (3.13)	650 (2.05)
				9b	707 (6.40)	707 (—)[c]		**5d**	664 (4.01)	665 (1.14)

a) Calcd by PPP-SCF-CI-MO. b) Reported in Ref. 8. c) Insoluble.

Table 2. Calculated Results for the First and Second Absorption Bands of **4b** with Various Tautomers



B

	4b$_1$	**4b**$_2$	**4b**$_3$	**4b**$_4$	**4b**$_5$
R=					
λ_{max_1}	523	530	527	510	513
λ_{max_2}	498	485	496	486	478

order: 3-(dicyanomethylene)-1-indanone>thiobarbituric acid>barbituric acid>1,3-indandione>malononitrile> anthrone>acetylacetone. The dicyanovinylindanone derivative of 3,6-bis(dimethylamino)fluorenylidene dye (**9b**) absorbs in the longest region among the dyes investigated (707 nm). The calculated results by the PPP-SCF-CI-MO method are also shown in Table 1.[11] The calculations were carried out on some of the **A** and **B** systems with the normal parameter sets proposed by Griffiths.[12] Although reasonable results were obtained in some of the compounds studied, there is some disagreement regarding **3a**, **b** and for the barbiturate series (or thiobarbiturate series), which in some cases showed deviations of 50—70 nm between the observed and calculated results with diketo forms. In barbituric or thiobarbituric acid derivatives, tautomeric effects might be considered to explain the experimental results. From the calculated results of **4b**, considering not only diketo forms but also keto/enol or dienol forms (see Table 2), however, no significant difference was observed between them, giving slightly better results in the keto/enol forms (**4b**$_2$ and **4b**$_3$). The bathochromic behavior of the thiobarbituric acid derivatives, compared with that of barbituric derivatives, agreed well with the calculated results. Also, the bathochromic tendency by ring closure of the *o*- and *o'*-positions of the diphenylmethane

component of **A** to the fluorenylidene component, **B**, was well reproduced by a MO calculation, i.e., a lowering tendency of the LUMO level of the diphenylmethane component by ring closure was elucidated by a comparison of each of the MO energy levels.[13] This shift was calculated to be 18—39 nm, showing reasonable agreement to the experimental shift (21—45 nm in EtOH).

Since one of the most remarkable shifts was observed for **3b**, we further investigated the solvatochromic effect by using 17 kinds of solvents. As shown in Table 3, the linear bathochromicity of the absorption of the longest wavelength was observed according to an increase in the solvent polarity. The correlation was investigated between the solvatochromism of the dye and the commonly used solvent polarity parameters: Dimroth and Reicharts' E_T30;[14] Kosower's Z;[15] Brooker's χ_R;[16] as well as recently proposed Buncel's π^*_{azo}.[17] As shown in Fig. 1, a good correlation was observed for the latter two, which are both based on merocyanine dyes. On the contrary, a weaker correlation was found for the former two (Correlation coefficient: r=0.92 and 0.87), both based on ionic betaine dyes. Because of the case of preparation and clear solvatochromic behavior, **3b** would be a possible candidate for a solvent polarity parameter.

In conclusion, four series of push–pull butadiene-type merocyanine dyes **A**—**D** were prepared by reactions of the corresponding diarylpropynols with various nucleophiles. The absorption spectral properties of **A**—**D** were investigated along with the calculated results by PPP-MO method, showing the characteristic spectral behavior derived from the electron-donating nature of the donor part and electron-withdrawing nature of the acceptor part. The solvatochromic nature of **3b** was estimated by using 17 solvent sets to make comparisons with the commonly used E_T30, Z, χ_R, or π^*_{azo} giving good correlations with the latter two.

Tale 3. Longest Absorption Maxima of **3b** in Various Solvents

Solvent	λ_{max}/nm	Solvent	λ_{max}/nm
Hexane	528	Ethylmethylketone	587
Cyclohexane	532	CH_2Cl_2	588
CCl_4	546	$CHCl_3$	596
Dioxane	552	DMF	600
Toluene	554	*i*-PrOH	608
Benzene	560	EtOH	610
THF	568	BuOH	612
Acetone	576	MeOH	612
Acetonitrile	578		

Experimental

All of the melting points are uncorrected. UV-visible spectra were recorded on Shimadzu UV-265F and Hitachi 210 spectrometers. IR spectra were obtained on a JASCO IRA 810 spectrophotometer. ^{1}H NMR spectra were measured on a JNM-GX 400 spectrometer; the chemical shifts are given in δ-values with respect to TMS used as an internal standard. MS spectra were taken using a JEOL JMS-DX 303 mass spectrometer.

Preparation of Alcohols (2b—d):[9] **General Method.** The reaction of an excess amount (ca. 5—15 equiv) of lithium acetylide (prepared by Midland's method[18]) with the ketones[19] in THF at −60 °C for several h gave the corresponding alcohols

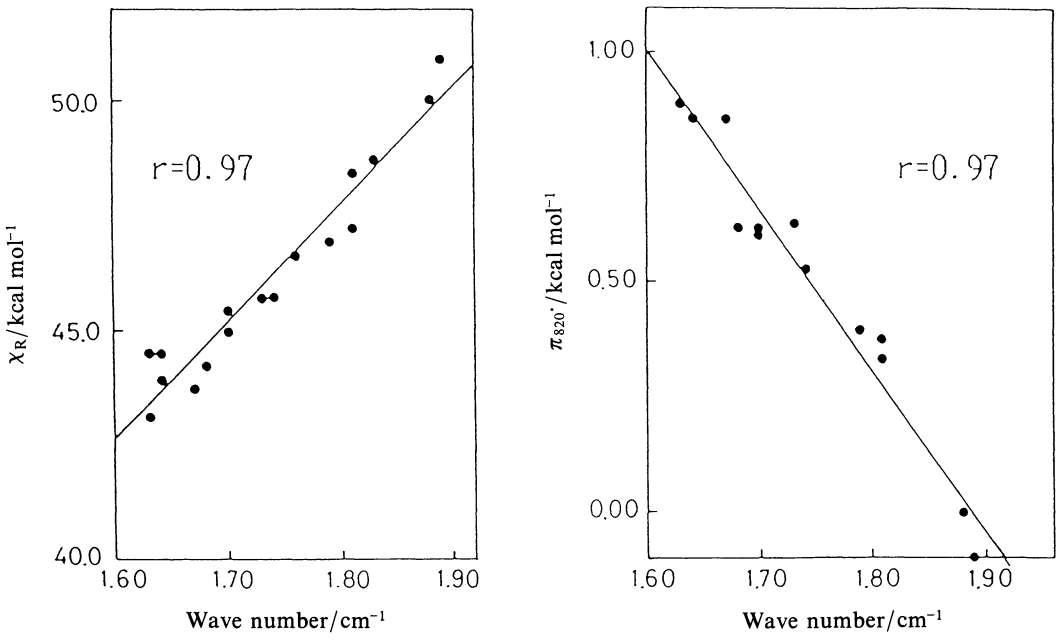


Fig. 1. Correlation diagram of the wave number of **3b** with χ_R and π_{azo}* (r: Correlation coefficienct).

after the usual work-up.

2b: Colorless crystals, 77%. Mp 230 °C. Found: C, 77.54; H, 6.95; N, 9.50%. Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.90; N, 9.58%. IR (Nujol) 3260 (C≡CH), 2100 (C≡C), and 1610 cm^{-1} (C=C); FAB-MS (*m/z*) 293 (M+1); ^1H NMR (DMSO-d_6) δ=2.97 (6H, s, Me), 3.06 (1H, s, C≡CH), 3.19 (6H, s, Me), 5.85 (1H, s, OH), 6.57 (2H, dd, *J*=2 and 8 Hz, ArH), 7.09 (2H, d, *J*=2 Hz, ArH), and 7.33 (2H, d, *J*=8 Hz, ArH).

2c: Pale yellow crystals, 75%. Mp 98—100 °C (lit, 98—99 °C).[20] IR (Nujol) 3400 (OH), 3300 (C≡CH), 2120 (C≡C), and 1580 cm^{-1} (C=C); EI-MS (*m/z*) 238 (M^+); ^1H NMR ($CDCl_3$) δ=2.91 (1H, s, C≡CH), 2.94 (1H, s, OH), 7.23—7.55 (6H, m, ArH), and 8.00—8.17 (2H, m, ArH).

2d: Colorless crystals, 89%. Mp 211—214 °C. IR (KBr) 3400 (OH), 3280 (C≡CH), and 1600 cm^{-1} (C=C); EI-MS (*m/z*) 398 (M^+); ^1H NMR ($CDCl_3$) δ=2.45 (1H, s, C≡CH), 3.20 (1H, s, OH), and 6.72—7.33 (14H, m, ArH).

Synthesis of Merocyanine Dyes: Bis[4-(dimethylamino)-phenyl]methylene System; General Method [Indandione Derivative (3a)]. 1,3-Indandione (50 mg, 0.17 mmol) was mixed with acetylenic alcohol (**2a**) (25 mg, 0.17 mmol) in EtOH (20 ml) at ambient temperature. The resulting violet solution was then heated under reflux for 1 h. After concentrating the reaction mixture under reduced pressure, green needles, thus obtained, were filtered and dried in vacuo while affording an analytically pure sample (55 mg, 76%). Mp 182—183 °C (decomp). Found: C, 79.67; H, 6.31; N, 6.31%. Calcd for $C_{28}H_{26}N_2O_2$: C, 79.59; H, 6.20; N, 6.63%. EI-MS (*m/z*) 422 (M^+); ^1H NMR ($CDCl_3$) δ=3.06 (6H, s, Me), 3.07 (6H, s, Me), 6.65 (2H, d, *J*=9 Hz, ArH), 6.74 (2H, *J*=9 Hz, ArH), 7.15—7.89 (9H, m, ArH and olefinic H), and 8.28 (1H, d, *J*=13 Hz, olefinic H). In the same method, **4a**, **7a**, and **8a** were prepared. The preparations of **5a** and **6a** were already reported.[8]

4a: Deep red crystals, 79%. Mp 269—271 °C (decomp). Found: C, 66.51; H, 6.28; N, 13.35%. Calcd for $C_{23}H_{24}O_3N_4 \cdot 1/2H_2O$: C, 66.81; H, 6.09; N, 13.35%. IR (KBr) 3170 (NH), 1715 (C=O), 1655 (C=O), and 1595 cm^{-1} (C=C); FAB-MS (*m/z*) 405 (M+1); ^1H NMR (DMSO-d_6) δ=3.02 (12H, s, NMe_2), 6.76 (2H, d, *J*=10 Hz, ArH), 6.81 (2H, d, *J*=10 Hz, ArH), 7.09 (2H, d, *J*=10, ArH), 7.28 (2H, d, *J*=10 Hz, ArH), 7.83 (1H, d, *J*=14 Hz, olefinic H), 8.20 (1H, d, *J*=14 Hz, olefinic H), and 10.88 (2H, s, NH).

7a: Reddish brown crystals, 45%. Mp 277—278 °C (decomp). Found: C, 82.64; H, 6.62; N, 5.87%. Calcd for $C_{33}H_{30}N_2O \cdot 1/2H_2O$: C, 82.64; H, 6.51; N, 5.84%. IR (KBr) 1650 (C=O) and 1605 cm^{-1} (C=C); EI-MS (*m/z*) 470 (M^+); ^1H NMR ($CDCl_3$) δ=2.99 (6H, s, Me), 3.09 (6H, s, Me), 6.65 (2H, d, *J*=9 Hz, ArH), 6.81 (2H, d, *J*=9 Hz, ArH), and 6.68—8.42 (14H, m, ArH and olefinic H).

8a: Reddish-orange crystals, 80%. Mp 159—160 °C (decomp). Found: C, 76.49; H, 7.56; N, 7.40%. Calcd for $C_{24}H_{28}N_2O_2$: C, 76.56; H, 7.50; N, 7.44%. IR (KBr) 1650 (C=O) and 1605 cm^{-1} (C=C); EI-MS (*m/z*) 376 (M^+). ^1H NMR ($CDCl_3$) δ=2.19 (3H, s, Me), 2.43 (3H, s, Me), 3.00 (6H, s, Me) 3.04 (6H, s, Me), 6.61 (2H, d, *J*=9 Hz, ArH), 6.73 (2H, d, *J*=9 Hz, ArH), 6.89 (1H, d, *J*=11 Hz, olefinic H), 7.15 (2H, d, *J*=9 Hz, ArH), 7.30 (2H, d, *J*=9 Hz, ArH), and 7.37 (1H, d, *J*=11 Hz, olefinic H).

3,6-Bis(dimethylamino)fluorenylidene System: General Method [Indandione Derivative (3b)]. To a stirred solution of acetylenic alcohol (**2b**) (0.20 g, 0.68 mmol) in EtOH (40 ml) was added 1,3-indandione (0.11 g, 0.68 mmol) at ambient temperature. After stirring for 3 h, the reaction mixture was concentrated in vacuo to give crystals, which were recrystallized from dichloromethane. Compound **3b** was obtained as deep green crystals (0.24 g, 84%). Mp 240 °C. Found: C, 79.59; H, 5.89; N, 6.58%. Calcd for $C_{28}H_{24}N_2O_2$: C, 79.98; H, 5.75; N, 6.66%. IR (Nujol) 1710, 1660 (C–O), and 1600 cm^{-1} (C=C); EI-MS (*m/z*) 420 (M^+); ^1H NMR ($CDCl_3$) δ=3.10 (6H, s, Me), 3.11 (6H, s, Me), 6.40—6.60 (2H, m, ArH), 6.80—6.90 (2H, m, ArH), 7.60—8.00 (6H, m, ArH), 8.24 (1H, d, *J*=14 Hz, olefinic H), and 8.55 (1H, d, *J*=14 Hz, olefinic H). In the similar method, barbituric and thiobarbituric acid derivatives (**4b** and **5b**) were prepared.

4b: Deep bluish-violet crystals, 88%. Mp 305 °C. Found: C, 65.70; H, 5.43; N, 13.39%. Calcd for $C_{23}H_{22}N_4O_3 \cdot H_2O$: C, 65.70; H, 5.75; N, 13.33%. IR (Nujol) 1730, 1625 (C=O), and 1603 cm^{-1} (C=C); FAB-MS (*m/z*) 403 (M+1); ^1H NMR (DMSO-d_6) δ=3.11 (12H, s, Me), 6.59 (1H, d, *J*=9 Hz, ArH), 6.63 (1H, d, *J*=9 Hz, ArH), 7.25 (2H, d, *J*=9 Hz, ArH), 7.46 (1H, d, *J*=9 Hz, ArH), 7.73 (1H, d, *J*=9 Hz, ArH), 8.19 (1H, d, *J*=14 Hz, olefinic H), 8.84 (1H, d, *J*=14 Hz, olefinic H), 11.00 (1H, s, NH), and 11.06 (1H, s, NH).

5b: Deep blue crystals, 74%. Mp >330 °C. Found: 63.33; H, 5.35; N, 12.85%. Calcd for $C_{23}H_{22}N_4O_2 \cdot H_2O$: C, 63.28; H, 5.35; N, 12.85%. IR (Nujol) 1680, 1640 (C=O), and 1605 cm^{-1} (C=C); FAB-MS (*m/z*) 419 (M+1); ^1H NMR (DMSO-d_6) δ=3.14 (12H, s, Me), 6.58 (1H, d, *J*=9 Hz, ArH), 8.20 (1H, d, *J*=14 Hz, olefinic H), 8.81 (1H, d, *J*=14 Hz, olefinic H), 12.10 (1H, s, NH), and 12.17 (1H, s, NH). In the cases of malononitrile, anthrone, acetylacetone, and 3-(dicyanomethylene)-1-indanone derivatives (**6b—9b**), appropriate heating for several hours was necessary due to the low reactivities of the reactants.

6b: Deep green crystals, 78%. Mp 300—305 °C. Found: C, 77.53; H, 5.97; N, 16.38%. Calcd for $C_{22}H_{20}N_4$: C, 77.62; H, 5.92; N, 16.46%. IR (Nujol) 2210 (C≡N) and 1605 cm^{-1} (C=C); EI-MS (*m/z*) 340 (M^+); ^1H NMR ($CDCl_3$) δ=3.14 (12H, s, Me), 6.40—6.60 (2H, m, ArH), 6.83 (2H, d, *J*=2 Hz, ArH), 6.90 (1H, d, *J*=13 Hz, olefinic H), 7.49 (2H, d, *J*=8 Hz, ArH), and 8.34 (1H, d, *J*=13 Hz, olefinic H).

7b: Deep reddish-violet crystals, 35%. Mp 289—292 °C. IR (Nujol) 1660 (C=O) and 1600 cm^{-1} (C=C); FAB-MS (*m/z*) 469 (M+1); ^1H NMR ($CDCl_3$) δ=3.09 (6H, s, Me), 3.15 (6H, s, Me), 6.50—7.10 (4H, m, ArH and olefinic H), 7.35—7.70 (6H, m, ArH and olefinic H), and 7.90—8.45 (6H, m, ArH and olefinic H).

8b: Brown crystals, 28%. Mp 210 °C. Found: C, 76.72; H, 6.68; N, 8.01%. Calcd for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48%. EI-MS (*m/z*) 374 (M^+); IR (Nujol) 1640 (C=O) and 1610 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=2.48 (6H, s, Me), 3.10 (6H, s, Me), 3.12 (6H, s, Me), 6.50—6.65 (2H, m, ArH), 6.85—7.10 (3H, m, ArH and olefinic H), 7.40—7.80 (2H, m, ArH), and 8.29 (1H, d, *J*=13 Hz, olefinic H).

9b: Deep green crystals, 84%. Mp 274—278 °C. IR (Nujol) 2230 (C=N), 1700 (C=O), and 1600 cm^{-1} (C=C); EI-MS (*m/z*) 468 (M^+); ^1H NMR (DMSO-d_6) δ=3.46 (12H, s, NMe_2), 6.49 (2H, dd, *J*=2, 9 Hz, ArH), 7.16 (2H, d, *J*=9 Hz, ArH), 7.68—7.82 (5H, m, ArH), 8.45—8.55 (2H, m, ArH and olefinic H), and 8.97 (1H, d, *J*=14 Hz, olefinic H).

Thioxanthenylidene System: General Method [Indandione Derivative (3c)]. 1,3-Indandione (0.12 g, 0.84 mmol) was added to a stirred solution of acetylenic alcohol (**2c**) (0.20 g, 0.84 mmol) in EtOH. After stirring for 30 min, the reaction

mixture was heated under reflux for 3 h and then evaporated under reduced pressure to give deep reddish-violet crystals, which after recrystallization from dichloromethane yielded 0.13 g (43%). Mp 232 °C. IR (Nujol) 1720, 1690 (C=O), and 1600 cm^{-1} (C=C); EI-MS (*m/z*) 366 (M^+); ^1H NMR ($CDCl_3$) δ=7.37—8.00 (13H, m, ArH and olefinic H) and 8.33 (1H, d, *J*=12 Hz, olefinic H).

4c: Reddish-violet crystals, 38%. Mp 328—329 °C. Found: C, 64.72; H, 3.59; N, 7.85%. Calcd for $C_{19}H_{12}N_2O_3 \cdot 0.3H_2O$: C, 64.51; H, 3.59; N, 7.92%. IR (Nujol) 1640 (C=O) and 1560 cm^{-1} (C=C); FAB-MS (*m/z*) 349 (M+1); ^1H NMR (DMSO-d_6) δ=7.45—7.88 (8H, m, ArH), 8.02 (1H, d, *J*=12 Hz, olefinic H), 8.30 (1H, d, *J*=12 Hz, olefinic H), and 11.15 (2H, s, NH).

5c: Brown crystals, 85%. Mp >300 °C. Found: C, 61.95; H, 3.34; N, 7.20%. Calcd for $C_{19}H_{12}N_2O_2S_2 \cdot 0.2H_2O$: C, 62.01; H, 3.40; N, 7.61%. IR (Nujol) 1640 (C=O) and 1560 cm^{-1} (C=C); FAB-MS (*m/z*) 365 (M+1); ^1H NMR (DMSO-d_6) δ=6.98—7.63 (8H, m, ArH), 8.03 (1H, d, *J*=12 Hz, olefinic H), 8.33 (1H, d, *J*=12 Hz, olefinic H), and 12.25 (2H, m, NH).

6c: Brown crystals, 92%. Mp 290 °C. Found: C, 75.01; H, 3.83; N, 9.34%. Calcd for $C_{18}H_{10}N_2S$: C, 75.49; H, 3.52; N, 9.79%. IR (Nujol) 2240 (C≡N) and 1580 cm^{-1} (C=C); EI-MS (*m/z*) 286 (M^+); ^1H NMR ($CDCl_3$) δ=6.70 (1H, d, *J*=14 Hz, olefinic H), 7.26—7.57 (8H, m, ArH), and 7.81 (1H, d, *J*=14 Hz, olefinic H). Other derivatives, such as anthrone or acetylacetone, could not be prepared, even upon changing the reaction conditions: i.e., raising the reaction temperature by using alcohols with higher boiling points or prolonging the reaction time.

10-(9-Xanthenylidene)-9(10*H*)-anthrylidene System; General Method [Indandione Derivative (3d)]: 1,3-Indandione (37 mg, 0.25 mmol) was added to acetylenic alcohol (**2d**) (0.10 g, 0.25 mmol) in EtOH and the reaction mixture was heated under reflux for 24 h. Reddish-violet crystals were obtained after evaporating the solvent, adding ether, and recrystallizing the resulting crystals (42 mg, 32%). Mp >340 °C. IR (Nujol) 1630 (C=O) and 1590 cm^{-1} (C=C); FAB-MS (*m/z*) 526 (M+1); ^1H NMR ($CDCl_3$) δ=6.64 (2H, d, *J*=9 Hz, ArH), 7.26—7.79 (15H, m, ArH and olefinic H), and 8.70—8.92 (6H, m, ArH and olefinic H).

4d: Violet crystals, 35%. Mp >340 °C. Found: C, 74.40; H, 4.13; N, 5.00%. Calcd for $C_{33}H_{20}N_2O_4 \cdot 1.3H_2O$: C, 74.51; H, 4.28; N, 5.27%. IR (KBr) 1710, 1620 (C=O), and 1595 cm^{-1} (C=C); FAB-MS (*m/z*) 509 (M+1); ^1H NMR (DMSO-d_6) δ=6.69 (2H, d, *J*=9 Hz, ArH), 7.35—7.94 (12H, m, ArH and olefinic H), 8.66 (2H, d, *J*=9 Hz, ArH), 8.75 (1H, dd, *J*=2 and 9 Hz, ArH), 9.16 (1H, d, *J*=2 Hz, ArH), 10.44 (1H, s, NH), and 11.00 (1H, s, NH).

5d: Reddish-violet crystals, 57%. Mp >340 °C. Found: C, 72.49; H, 3.86; N, 4.97%. Calcd for $C_{33}H_{20}N_2O_3S \cdot 1.3H_2O$: C, 72.49; H, 4.16; N, 5.11%. IR (KBr) 1630 (C=O) and 1595 cm^{-1} (C=C); FAB-MS (*m/z*) 524 (M+1); ^1H NMR (DMSO-d_6) δ=6.77—7.00 (2H, m, ArH), 7.29—8.04 (12H, m, ArH and olefinic H), 8.66 (2H, d, *J*=9 Hz, ArH), 8.84 (1H, dd, *J*=2 and 9 Hz, ArH), 9.25 (1H, s, ArH), and 11.54 (2H, s, NH). Other derivatives such as malononitrile, anthrone, or acetylacetone derivatives could not be isolated.

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