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Shaping the Absorption and Fluorescence Bands of a Class of Efficient, Photoactive Chromophores: Synthesis and Properties of Some New 3*H*-Xanthen-3-ones

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SUMMARY

*An approach to the systematic design of absorption and fluorescence band shapes is developed from considerations of the solvatochromism and electronic perturbation of unsymmetrical chromophores. The predicted spectral shifting and line broadening has been demonstrated within a series of newly synthesized substituted 6-amino-3*H*-xanthen-3-ones* **1**. *A new method of presenting bandwidth data is developed which utilizes dipole strength-weighted moments of absorption bands.*

1. INTRODUCTION

The 3*H*-xanthen-3-ones (rhodols) **1** constitute a relatively little known class of xanthene dyes[1–3] which may be considered as hybrids of the ubiquitous rhodamines (**2**) and fluoresceins (**3**). Although this class of materials had been reported as early as 1894 in the German patent literature, its physical and chemical properties have not yet been systematically examined. These compounds attracted our attention because of our interest in new organic materials for use in laser and photovoltaic devices,[6] and, more specifically, because of the expected ease of modulating their properties via chemical substitutions. For example, one could expect to change the magnitude of the in-plane dipole transition of these materials in a given direction by

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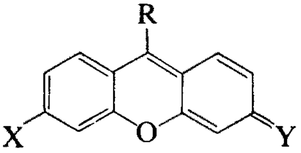


1: $X = NR_2$ $Y = O$
2: $X = NR_2$ $Y = {}^+NR_2$
3: $X = O^-$ $Y = O$

incorporation of electron-attracting or electron-donating substituents in the aromatic rings. In this way, it is expected that the shapes of the absorption and fluorescence bands could be systematically altered to optimize the lasing performance of these dyes. These ideas can be appreciated by noting the similarity of the rhodol chromophores to the structures of Brooker's merocyanines[4] for which Platt[5] has developed a useful theory to describe the changes in peak locations, widths and intensities as a function of electronic substitution.[7] In addition, it appeared feasible to modify other properties of these dyes, e.g. solubility, crystal packing, volatility and reduction potential, by means of suitably positioned polar or bulky groups.

In this communication we describe reliable methods for the preparation of several new series of 6-amino-3*H*-xanthen-3-ones including julolidinyl and sulfur analogs. In addition, we describe the application of Platt's theory to the shaping of absorption bands and the solvatochromic shifting of a series of these dyes. Preliminary studies have already dealt with the lasing properties of some of these materials.[8-10]

2. RESULTS AND DISCUSSION

2.1. Synthetic studies

In our initial studies we sought to improve and extend the earlier[1-3] procedures described for the synthesis of **1**. We found that the use of sulfuric acid or polyphosphoric acid proved to be more convenient and easier to control than zinc chloride as catalyst for the condensation reaction (eqn (1)). These mild conditions greatly reduce the oxidative side reactions that often occur in the classical methodology. Thus, good yields of dyes **6** were obtained from the reactions of 4-dimethylamino-2-hydroxy-2′-carboxybenzophenone[11] (**4a**) with various resorcinols **5**, as summarized in Table 1. The synthesis was extended to include the decarboxylated analogs **6b** by the use of 4-dimethylamino-2-hydroxybenzophenone (**4b**).

TABLE 1

Synthesis and Characterization of 3*H*-Xanthen-3-ones

Compound	R^1	R^2	R^4	M.p. (°C)	Yield[a] (%)	λ_{max}[b] (nm)	log ε[b]	Formula and mol. wt	Analysis (%)	
									Calculated	Found
6a	H	H	H	265–268	81	511	4·78	$C_{22}H_{19}NO_4 . 0{\cdot}5H_2O$[c] (370·4)	C, 73·11; H, 5·16; N, 3·70	C, 73·08; H, 5·40; N, 3·50
6a	CH_3	H	H	265–268	79	507	4·72	$C_{23}H_{19}NO_4 . CH_3OH$ (405·4)	C, 71·11; H, 5·68; N, 3·46	C, 71·11; H, 5·83, N, 3·49
6a	H	Cl	Cl	335–340	79	523	4·91	$C_{22}H_{15}Cl_2NO_4 . 1{\cdot}5H_2O$ (455·3)	C, 58·02; H, 3·96, N, 3·07; Cl, 15·60	C, 58·21; H, 3·82; N, 3·07; Cl, 15·33
6a	H	Cl	H	268–270[d]	96[d]	—	—	$C_{23}H_{18}ClNO_4$[e] (407·8)	C, 67·73; H, 4·41; N, 3·44; Cl, 8·71	C, 67·43, H, 4·68; N, 3·23, Cl, 8·96
6a	H	CH_3	CH_3	214–219	87	518	4·78	$C_{24}H_{21}NO_4 . 1{\cdot}25H_2O$ (409·9)	C, 70·33, H, 5·74; N, 3·42	C, 70·46; H, 5·97 N, 3·00
6b	H	H	H	239–240	57	518	4·88	$C_{21}H_{17}NO_2$ (315·4)	C, 80·00, H, 5·39; N, 4·44	C, 80·01; H, 5·55; N, 4·40
6b	CH_3	H	H	238–240	20	508[f]	4·69	$C_{22}H_{19}NO_2 . 0{\cdot}5H_2O$ (338·4)	C, 78·10; H, 5·92; N, 4·14	C, 78·43; H, 5·63; N, 4·00
6b	H	Cl	H	280–283	14	525[f]	4·90	$C_{21}H_{16}ClNO_2$ (349·8)	C, 72·10; H, 4·58, N, 4·00; Cl, 10·15	C, 71·96; H, 4·69, N, 4·04; Cl, 10·38
6b	H	Cl	Cl	301–305	23[g]	533	4·83	$C_{21}H_{15}Cl_2NO_2$ (384·2)	C, 65·64; H, 3·93, N, 3·65; Cl, 18·45	C, 65·95; H, 4·10; N, 3·45; Cl, 18·38
6b	H	CH_3	CH_3	272–274 (dec.)	84	524	4·81	$C_{23}H_{21}NO_2$ (343·4)	C, 80·46; H, 6·12; N, 4·08	C, 80·28; H, 6·19; N, 3·96
9	H	H	H	347–349 (dec)	54	529	4·87	$C_{26}H_{21}NO_4 . 1{\cdot}5H_2O$ (347·9)	C, 71·22, H, 5·52; N, 3·19	C, 71·14; H, 5·22; N, 3·13
6c	H	H	H	195–200	78	509	4·76	$C_{16}H_{15}NO_2 . 0{\cdot}25H_2O$ (257·8)	C, 74·56, H, 6·02, N, 5·43	C, 74·92; H, 6·22; N, 5·30
6c	H	Cl	Cl	287–290	9·3	524	4·91	$C_{16}H_{13}Cl_2NO_2$ (322·2)	C, 59·62; Cl, 22·05, H, 4·03; N, 4·34	C, 59·42; Cl, 22·26; H, 4·11, N, 4·29
6c	H	CH_3	CH_3	210–215	43	517	4·82	$C_{18}H_{19}NO_2$ (281·3)	C, 76·86, H, 6·76; N, 4·98	C, 77·05, H, 6·89, N, 4·79
6c	H	CH_2CO_2H	CH_3	253–257 (dec)	9·4	517[f]	4·63	$C_{19}H_{19}NO_4 . 0{\cdot}5CH_2Cl_2$ (367·8)	C, 63·67; H, 5·44; N, 3·80	C, 63·27; H, 5·50; N, 3·68
10[g]				253–255 (dec.)	16·5	541	4·92	$C_{21}H_{17}NOS$ (331·4)	C, 76·13; H, 5·13; N, 4·23; S, 9·66	C, 75·83; H, 5·44; N, 4·09; S, 9·37

[a] Sulfuric acid catalyst.

[b] Spectra were determined in methanol unless noted otherwise.

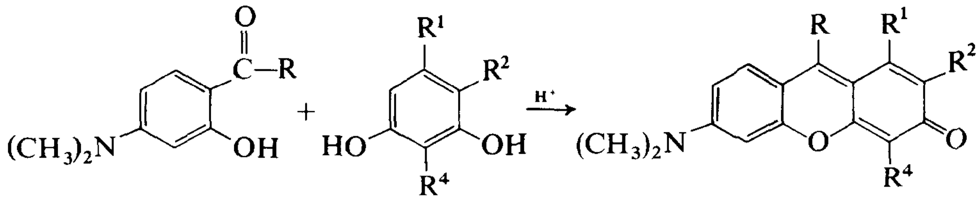
[c] Methyl ester, m.p. 262–265°C.

[d] Bisulfate salt.

[e] Methyl ester, m.p. 299–305°C

[f] Ethanol.

[g] Polyphosphoric acid catalyst

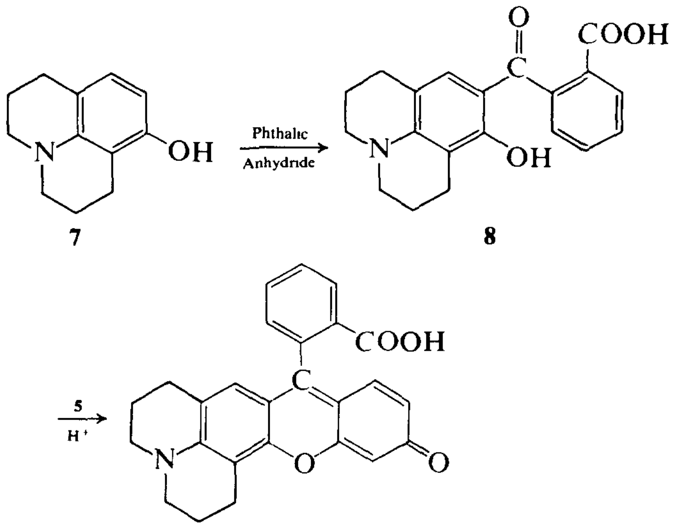


4 **5** **6** (1)

4a: $R = o\text{-}C_6H_4CO_2H$
4b: $R = C_6H_5$
4c: $R = CH_3$

6a: $R = o\text{-}C_6H_4CO_2H$
6b: $R = C_6H_5$
6c: $R = CH_3$

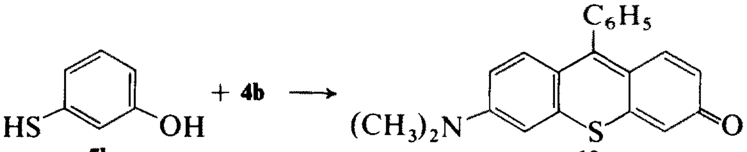
This useful intermediate was prepared from **4a** via decarboxylation using a copper salt–quinoline procedure.[12] Similarly, 4-dimethylamino-2-hydroxyacetophenone (**4c**) was prepared from the acetate of *m*-dimethylaminophenol by a Fries rearrangement and used to prepare a series of 9-methylxanthen-3-ones **6c**. Finally, the julolidinyl analog **9** was prepared from **8** by a similar route.



7 **8** **9**

We then investigated the feasibility of incorporation of the sulfur atom into these dyes. Monothioresorcinol[13] was reacted with **4b** in polyphosphoric acid with the expectation that either 9-phenyl-3*H*-xanthene-3-thione (**1**; $X = NR_2$, $Y = S$) or the 10-thia analog **10** would be formed. (When this reaction was attempted in 50% sulfuric acid we obtained **6b** (R^1, R^2, $R^4 = H$). A control experiment verified the suspicion that thioresorcinol was converted to resorcinol under the reaction conditions.) The structure of the product obtained using polyphosphoric acid is believed to be **10** because both the product and **6b** showed a strong carbonyl absorption at

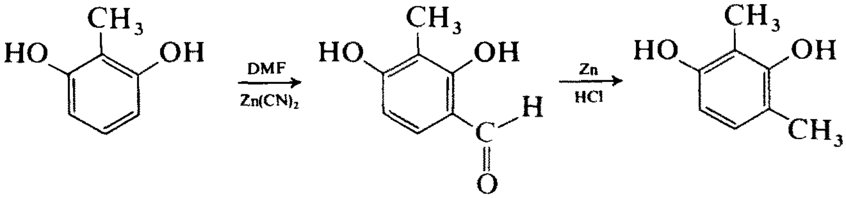
1590 cm^{-1} in the infrared spectrum and elemental analysis revealed the presence of one sulfur atom. (A much weaker absorption at 1645 cm^{-1} which is present in all of the 9-aryl systems was absent in **10**. We believe this band is an overtone due to Fermi resonance. The relatively small shift in the visible spectrum (23 nm) relative to the oxo analog is also consistent with **10**.) The mass spectrum of **10** showed a fragmentation pattern very similar to that of the oxygen analog (see below).



5b **10**

2.2. Resorcinols

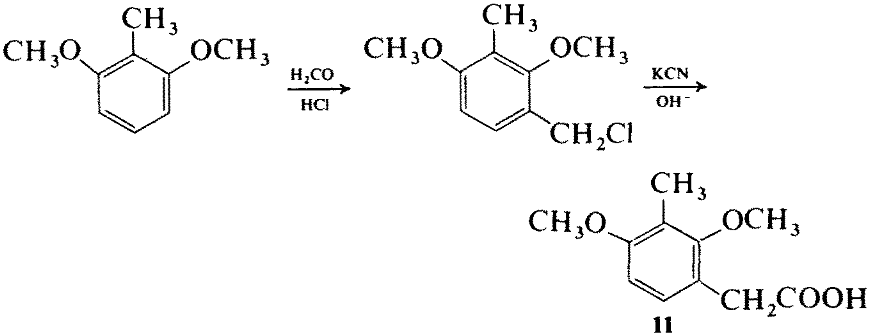
2,4-Dimethylresorcinol (**5**; $R^2, R^4 = CH_3$) was synthesized by a modification of the procedure of Robinson and Shah[14] starting from commercially available 2-methylresorcinol (eqn (2)).



(2)

Preparation of the acetic acid derivative **6c** ($R^2 = CH_2CO_2H$, $R^4 = CH_3$) necessitated a synthesis of a resorcinol with methyl and carboxymethyl substituents. The dimethyl ether **11** was prepared according to eqn (3).

Since mechanistic speculations on the source of dye formation led us to believe that prior demethylation was not necessary, **11** was treated directly

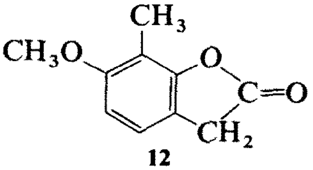


(3)

11

with the acetophenone **4c** in the presence of sulfuric acid. The expected dye was obtained, but in low yield, together with a volatile side product peculiar to this system and to which we assign structure **12**. (This substance (60 mg) had m.p. 135–7°C; NMR δ 2·6 (s, 3H), 3·70 (s, 2H), 3·83 (3H), 6·6 (d, $J=8$ Hz), 7·4 (d, $J=8$ Hz); IR (Nujol), 1799 cm^{-1}. $C_{10}H_{10}O_3$ (mol. wt 178·2). Calc.: C, 67·41; H, 5·66. Found: C, 67·19; H, 5·61%.)

In general, therefore, it may not be necessary to deprotect alkoxy groups or related derivatives.



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2.3. Characterization

All the dyes gave elemental analyses consistent with the assigned structures, although in many cases solvents were incorporated in the dye crystals despite repeated attempts to dry them at elevated temperatures. It is probable that these solvents are incorporated in empty lattice sites.

For example, 2-chloro-9-phenyl-3*H*-xanthen-3-one crystallized with methylene chloride so that the centrosymmetrical sheets of dye molecules were found by X-ray crystallography to contain rotationally disordered methylene chloride molecules in a stoichiometric 1:1 composition. One of the hydrogen atoms of methylene chloride appears to be hydrogen-bonded to the carbonyl oxygen (O···C distance = 2·83 Å), and the remaining hydrogen and chlorine atoms are randomly disordered. The partial quinoidal character of the 3*H*-xanthen-3-one system was also confirmed by this analysis.[15]

Mass spectral data taken at 70 eV provided further confirmation of these structures. The unsolvated molecular ion was usually the base peak except in carboxylated systems which showed base peaks at $M^+ - 44$ or $M^+ - 45$. Chlorinated systems showed the expected isotopic clusters. In addition, a major fragmentation pathway (10–50% relative intensity) for most dyes included $M^+ - 29$.

Proton magnetic resonance spectral data of selected compounds are listed in Table 2. These absorptions further support the assigned structures.

Finally, the data (Table 1) for the absorption spectra in the visible region provide strong support for the assigned structures[3–7] showing intense peaks from 507 to 538 nm and molar extinction coefficients greater than 5×10^4.

TABLE 2
PMR Spectral Data for Dyes at 60 MHz with Tetramethylsilane as Internal Standard

Compound	R^1	R^2	R^4	*PMR spectrum: δ-value, multiplicity, relative intensity*
6b[a]	H	H	H	3·14, s, 6; 6·9–7·6, m, 11
6a[a,b]	H	H	H	3·13, s, 6; 3·65, s, 3; 6·4–8·4, m, 10
6c[a]	H	H	H	2·50, s, 3; 3·05, s, 6; 6·2–7·7, m, 6
6c[a]	H	CH_3	CH_3	2·23, s, 6; 2·57, s, 3; 3·08, s, 6; 6·5–7·3, m, 4
6c[c]	H	Cl	Cl	3·10, s, 3; 3·53, s, 6; 7·1–8·4, m, 4

[a] In $CDCl_3$.
[b] Methyl ester.
[c] In CF_3CO_2H.

2.4. Shaping of the absorption and fluorescence bands of 3*H*-xanthen-3-ones

The importance of band shapes in lasing dyes can be appreciated from a consideration of the absorption and fluorescence spectra of Rhodamine B, shown in Fig. 1. Lasing action cannot occur in the main $0' \rightarrow 0''$ fluorescence peak because this would involve lasing to a highly populated lower energy level. Instead, lasing occurs to the weak shoulder of the fluorescence band, i.e. $0' \rightarrow 1''$ with respect to the dominant aromatic breathing vibration energy (*ca.* $1200\,cm^{-1}$). The greater part of the transition strength of the fluorescence band is thus wasted and actually competes with lasing action through spontaneous fluorescence in the $0' \rightarrow 0''$ component.

On this basis, we sought to devise dipolar merocyanine dyes which would follow the behavior outlined by Platt.[5] He was able to systematize essentially all of Brooker's observations[4] through a theory which assigned spectroscopically devised basicity values to the end-groups of extended chain chromophores. Using Platt's table of end-group wavelength contributions and basicities (b_L or b_R), one constructs the absorption wavelength (in nanometers) of a hypothetical electronically balanced dye:

$$\lambda_{\text{isoenergetic}} = \lambda_L + \lambda_R + 49N$$

where N is the number of carbon atoms in the unsaturated chain linking the end-groups. Then, transferring to energy units (kiloKaysers (kK) or $1000\,cm^{-1}$):[5]

$$\nu_{\text{iso}} = 10^4/\lambda_{\text{iso}}$$

and

$$\nu^2 = \{\nu_{\text{iso}}^2 + (b_L - b_R)^2\}$$

It was this second-order energy perturbation on the symmetrical

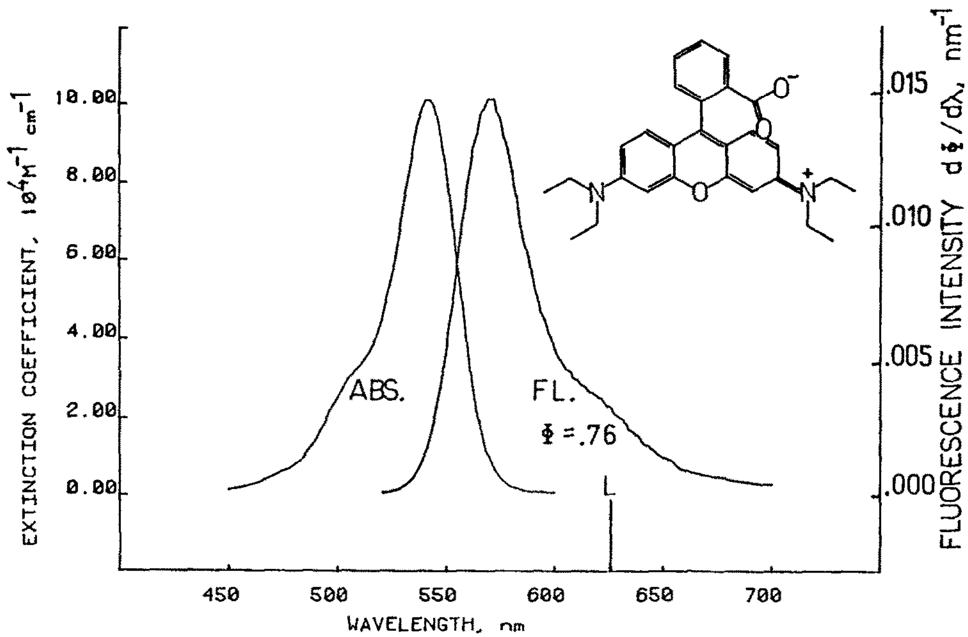
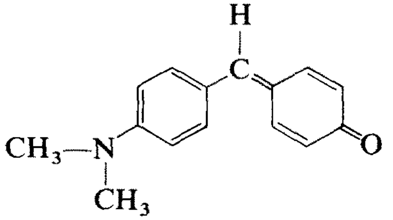


Fig. 1. Absorption and fluorescence quantum yield spectra of the familiar laser dye Rhodamine B in ethanol. The absorption and fluorescence spectra show full mirror-image shape, along with the sharpness and strength characteristic of ionic, cyanine-like dyes. Unfortunately, this shape is not optimal for lasing action, since lasing cannot occur in the strong central peak (0′ → 0″) of the fluorescence band. Instead, best lasing (vertical bar) occurs well out in the weak vibrational shoulder. The spontaneous fluorescence in the main band competes with lasing action, and has the effect of increasing the power threshold for initiating laser action and of decreasing the available band of wavelengths over which lasing action is possible.

chromophore which eluded Brooker in his study of the wavelength deviations of merocyanine dyes.

It is not possible to predict the absorption peaks of our new dyes from Platt's work, since the requisite cyclized groups were not tabulated. The nearest molecule subject to prediction would be the quinone methide shown below.



$$\lambda_{\text{iso}} = 277 + 49 + 316 = 642\,\text{nm}\ (15{\cdot}576\,\text{kK})$$

$$b_L = -4{\cdot}3\,\text{kK} \quad b_R = +0{\cdot}1\,\text{kK in } CH_3OH$$

$$\nu_{CH_3OH} = (15{\cdot}576^2 + [-4{\cdot}3 - 0{\cdot}1]^2)^{1/2} = 16{\cdot}18_6\,\text{kK} \rightarrow 618\,\text{nm}$$

The point of greatest value from Platt's consideration was the prediction that the absorption bandwidth would increase as the absorption peak was blue-shifted through an increasing basicity difference. His qualitative line-broadening equation is

$$\Delta v(\mathrm{kK}) = 1{\cdot}0 + 0{\cdot}2|\Delta b|$$

giving

$$\Delta \nu = 1{\cdot}88\,\mathrm{kK}$$

for the above dye. We inferred from this that we could modify the basicities of end-groups (+ for electron-donor substituents), and that the mirror-image quality of the fluorescence band would lead to a corresponding increase in the fluorescence bandwidth.

Platt's treatment ignores the presence or absence of partially resolved vibrational fine structure in the absorption spectrum. Under these conditions the overall band broadening appears first as an intensity shift from the $0' \leftarrow 0''$ band to the $1' \leftarrow 0''$ satellite and then in a continued broadening of an unresolved vibrational envelope. These changes can be seen from the spectra shown in Fig. 2 as the substituents are changed from electron-withdrawing ($R^2, R^4 = Cl$) to electron-donating ($R^2, R^4 = CH_3$).

Among the three materials featured in Fig. 2, the dimethyl substituents produce the best absorption band shape for lasing action with low starting threshold and high efficiency. The isoenergetic state (in CH_3OH) lies closest to the monochloro-substituted dye and thus that material represents little or no improvement over Rhodamine B as a laser material.

We have felt the need for a unified measurement of bandwidth, one which would not change abruptly and arbitrarily at some level of partial resolution of the vibrational structures of absorption and fluorescence bands. This need is satisfied by calculating dipole strength-weighted moments for the absorption band in frequency space. One must calculate in frequency space to keep continuity with the familiar aromatic interval of 1200–$1300\,\mathrm{cm}^{-1}$, but this is rendered somewhat awkward by instruments giving wavelength presentation of digitized data. We will report separately on the digitized processing for obtaining dipole strength-weighted band moments from data collected at equal wavelength intervals.[10] For the moment, it suffices to give the resulting equations and to tabulate the moments for the three dyes of Fig. 2.

The first band moment is just the dipole strength:

$$D = \text{constant} \times \int_{\text{band}} \varepsilon \frac{d\nu}{\nu} = \text{constant} \times \int \varepsilon \frac{d\lambda}{\lambda} \simeq \text{constant} \times \Delta\lambda \sum_{\text{band}} \frac{\varepsilon}{\lambda}$$

where $\Delta\lambda$ is the wavelength interval of digitization, and constant = 9·185 × 10^{-39} esu^2 cm^2/(mol/liter)$^{-1}$ cm^{-1}. We find it convenient to retain the units of molar extinction coefficient and calculate

$$I_1 = \Delta\lambda \sum_{\text{band}} \frac{\varepsilon}{\lambda}$$

The magnitude of this integral is of the order of 4000 (mol/liter)$^{-1}$ cm^{-1} for many commercial dyes, 6000–8000 (mol/liter)$^{-1}$ cm^{-1} for the present materials and up to 18 000 (mol/liter)$^{-1}$ cm^{-1} for extended dicarbocyanine dyes. It is a useful parameter in its own right for comparing the integrated absorptions of chromophores in familiar units.

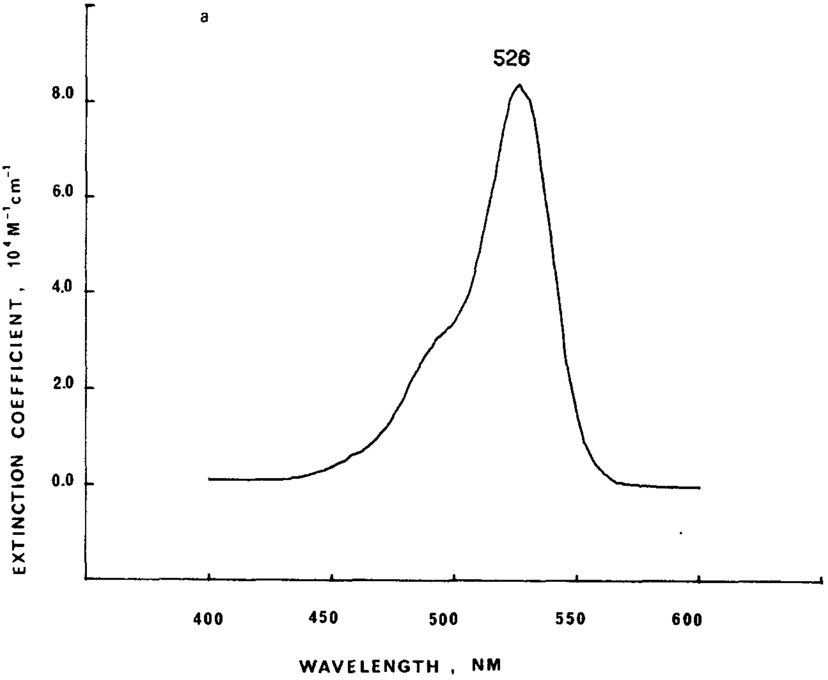
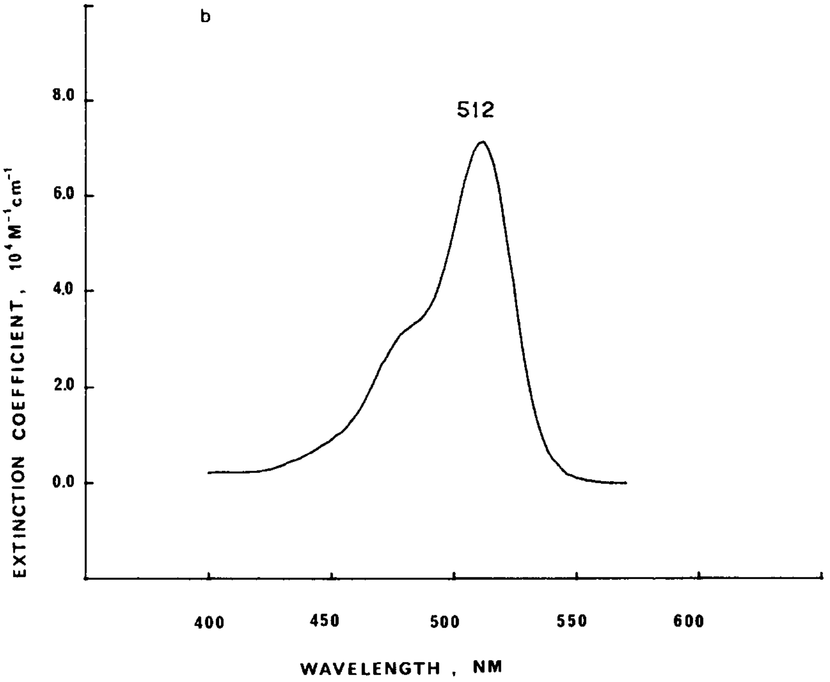


Fig. 2. Absorption spectra of three of the tunable cyclized merocyanine dyes **6a** developed in this investigation. As the substituents on the chromophore are changed from electron-withdrawing (*a*) $R^2 = R^4 = Cl$ to (*b*) $R^2 = R^4 = H$ to electron-donating (*c*) $R^2 = R^4 = CH_3$, intensity is transferred to the (1 → 0″) vibrational shoulder of the absorption band, and a corresponding change occurs in the intensity ratio of the vibrational shoulder to the main (0 → 0″) peak of the absorption band. This type of band shaping has long been known in the photographic merocyanine sensitizing dyes, but has not been systematically applied to the design of laser dyes.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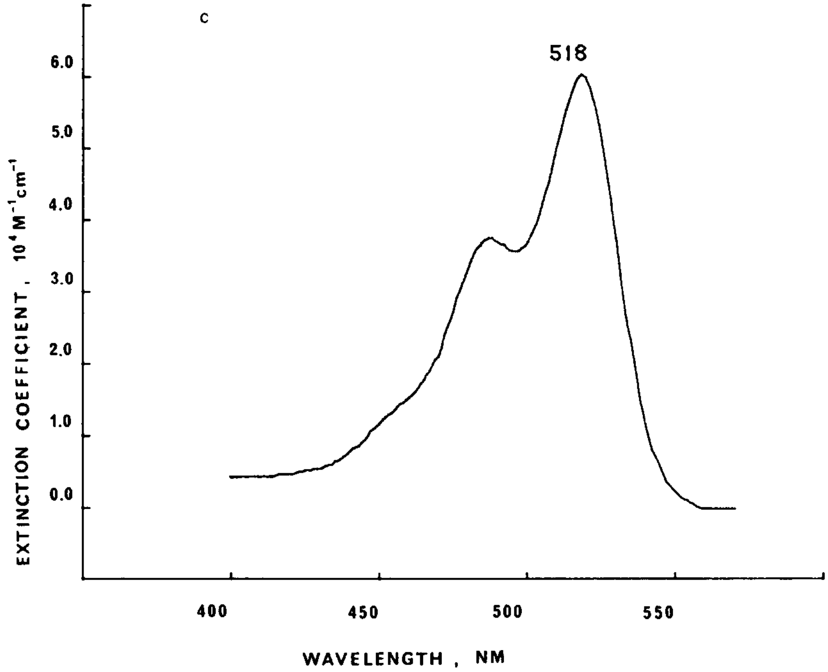
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EXTINCTION COEFFICIENT, $10^4 M^{-1}cm^{-1}$
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500
550
WAVELENGTH , NM

Fig. 2—*contd.*

The second moment is the dipole strength-weighted band center:

$$\bar{\nu} = \frac{\int \varepsilon \, \mathrm{d}\nu}{\int \varepsilon \frac{\mathrm{d}\nu}{\nu}} = \frac{\int \varepsilon \frac{\mathrm{d}\lambda}{\lambda^2}}{\int \varepsilon \frac{\mathrm{d}\lambda}{\lambda}} = \frac{I_2}{I_1}$$

where $I_2 = \Delta\lambda \sum (\varepsilon/\lambda^2)$.

This value of $\bar{\nu}$ is generally greater than $\nu_{\max}$, the frequency of the absorption band peak. The difference $(\bar{\nu} - \nu_{\max})$ is one measure of the broadening and skewing of the band, but has the property of changing discontinuously as vibrational intensities shift.

The third moment, the dipole strength-weighted bandwidth, is of the greatest interest as a critical test of band shape modification. It is calculated as

$$\overline{\Delta\nu^2} = \frac{\int (\nu - \bar{\nu})^2 \frac{\mathrm{d}D}{\mathrm{d}\nu} \, \mathrm{d}\nu}{\int \varepsilon \frac{\mathrm{d}\nu}{\nu}} = \frac{I_3}{I_1} - \left(\frac{I_2}{I_1}\right)^2$$

where $I_3 = \Delta\lambda \sum (\varepsilon/\lambda^3)$.

Values of these parameters are listed in Table 3.

The same effects of band shifting and band broadening may be demonstrated for a single dye in this class by varying the solvent. There are a few merocyanines which shift hardly at all with change of solvent but many others which show extreme solvent sensitivity. Brooker[4] took advantage of the complete miscibility of two extreme solvents, water and pyridine, to construct a solvent scale; and Platt further systematized this scale. Here we present a solvent series on a single dye (**6b**; $R^2 = R^4 = CH_3$) in Table 4. Spectra from this series are shown in Fig. 3.

The spectra of Tables 3 and 4 and Figs 2 and 3 exhibit the result of a dye with appropriate band shape for lasing in a convenient solvent, in this case

TABLE 3

Absorption Band Parameters for Selected Dyes in Methanol Solvent with Trace NH_3

Dye	$\lambda_{\max}$ (*nm*)	$\nu_{\max}$ (*cm*$^{-1}$)	$10^{35} \times D$ (*esu*^{2} *cm*^{2})	$\bar{\nu}$ (*cm*$^{-1}$)	$(\bar{\nu} - \nu_{\max})$ (*cm*$^{-1}$)	$(\overline{\Delta\nu^2})^{1/2}$ (*cm*$^{-1}$)
6a: $R^2 = R^4 = Cl$	526	19 011	6·71	19 519	508	973
6a: $R^2 = R^4 = H$	512	19 531	6·35	20 261	730	1 159
6a: $R^2 = R^4 = CH_3$	518	19 305	6·36	20 332	1 027	1 376
Rhodamine B (control)	541	18 484	7·61	18 869	385	832

TABLE 4

Absorption Spectra of the Dye 6-Dimethylamino-2,4-dimethyl-9-phenyl-3*H*-xanthene-3-one in Water–Pyridine Mixtures and Other Solvents

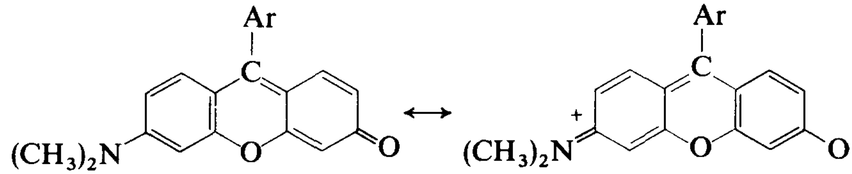
Solvent[a]	λ_{max} (*nm*)	ν_{max} (*cm*$^{-1}$)	$10^{35} \times D$ (*esu*^{2} *cm*^{2})	$\bar{\nu}$ (*cm*$^{-1}$)	$(\bar{\nu} - \nu_{max})$ (*cm*$^{-1}$)	$(\overline{\Delta\nu^2})^{1/2}$ (*cm*$^{-1}$)
100% H_2O	—	(aggregates)				
80% H_2O, 20% Py	534	18 727	6·14	19 441	714	1 032
60% H_2O, 40% Py	533	18 762	6·03	19 500	738	1 035
40% H_2O, 60% Py	534	18 727	5·89	19 548	821	1 062
20% H_2O, 80% Py	531	18 832	5·87	19 791	959	1 182
10% H_2O, 90% Py	530	18 868	5·42	19 983	1 115	1 236
5% H_2O, 95% Py	529	18 904	5·52	20 184	1 280	1 344
100% Py	493	20 284	6·35	20 598	314[b]	1 729
100% CH_3OH	525·5	19 029	6·71	20 088	1 059	1 331

[a] Py, pyridine.

[b] The discontinuity in $(\bar{\nu} - \nu_{max})$ which occurs as the intensity of the 1′ ← 0″ satellite rises above that of the 0′ ← 0″ origin band should be noted. No such discontinuity occurs in the dipole strength-weighted parameter $(\overline{\Delta\nu^2})^{1/2}$.

methanol. Methanol lies closer to pyridine (a poor laser solvent) than to water in the Brooker–Platt solvent series,[4–6] and the elevation of the vibrational satellite of the dimethyl dye has proceeded to a satisfactory level in methanol.

To convey some physical feeling for the factors working in the band-shaping process, we need to consider the resonance structure appropriate to these dyes:



Platt has pointed out that in the isoenergetic case these two structures contribute equally to the ground state (S_0) *and* to the first excited state (S_1). Thus there is very little change in the equilibrium bond distances of an isoenergetic molecule/solvent system in the optical transition $S_1 \rightarrow S_0$. By contrast, molecule/solvent systems perturbed out of the isoenergetic condition have an unequal contribution from the two resonance structures. If the contributions are, for example, 60% of the non-dipolar form and 40% of the dipolar form in the ground state S_0, the contributions will be reversed to 40% non-dipolar and 60% dipolar in the first excited state S_1. This leads to a considerable change in bond lengths and an increase in the

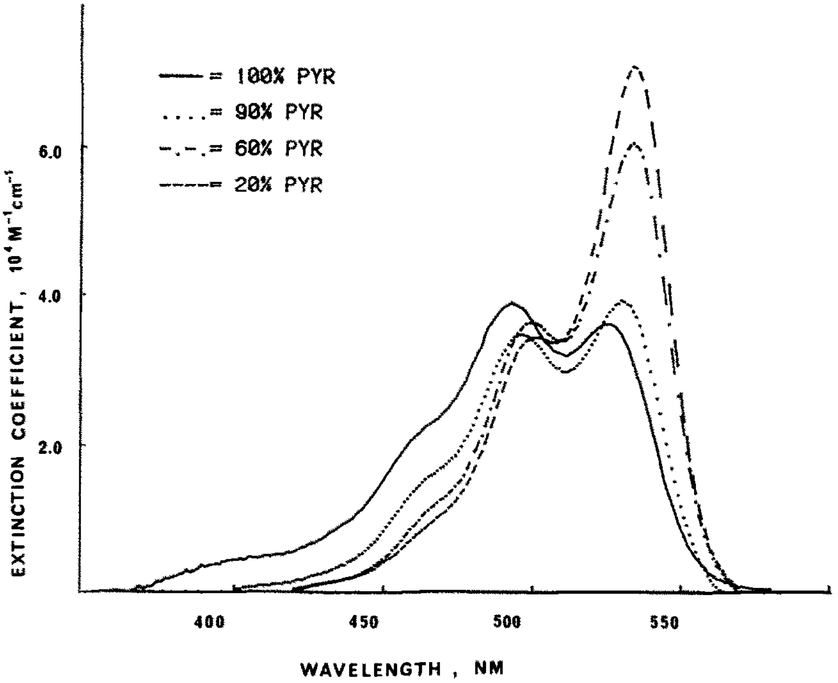


Fig. 3. Solvent sensitivity or 'solvatochromism' exhibited by a single dye (**6b**) in a succession of pyridine (Py)–water mixtures. The four spectra shown here are representative samples from the more extensive solvent series listed in Table 3. Dye **6b** is similar to **6a** ($R^2 = R^4 = CH_3$) in Fig. 2(*c*) above, having 2,4-dimethyl substituents on the chromophore, but it also has a central 9-phenyl group rather than a 9-(*o*-carboxyphenyl) group. The *o*-carboxyl group hinders torsion of the central phenyl ring and improves both fluorescence quantum yield and lasing action. Both the dye shown here and the dye of Fig. 2(*c*) have favorable band shapes for lasing action in methanol, one of the preferred laser solvents. Methanol falls at an intermediate position in Platt's pyridine–water solvent system scale, somewhat closer to 100% pyridine than to 100% water.

Franck–Condon overlap integrals for vibrational satellite transitions such as $1' \leftarrow 0''$ and $2' \leftarrow 0''$. In the case of extreme dissymmetry in either sense, the absorption spectrum begins to resemble the spectrum of a polyene. The ideal for a laser material lies somewhere between the isoenergetic and polyenoid cases.

3. EXPERIMENTAL

Infrared spectra were determined in Nujol mulls on a Perkin–Elmer Model 727B spectrometer. Proton magnetic resonance spectra were obtained in $CDCl_3$ on a Varian Model T-60 spectrometer; integrated relative intensities were consistent with assigned structures.

Absorption spectra were obtained on a Cary Model 17D spectrometer which was interfaced to a Tektronix Model 4052 minicomputer through an Adam–Smith type 310 interface. This arrangement provided for storage of $A(\lambda)$ data on tape and allowed for convenient calculation and tabulation of dipole strength-weighted parameters. A Tektronix Model 4662 interactive digital platen was used to obtain hard copy. Mass spectra (70 eV) were obtained on a Hewlett–Packard 5985 GC/MS instrument. Elemental analyses were performed by G. Robertson Inc., Florham Park, NJ, USA. Samples were dried *in vacuo* at 111°C for 72 h over P_2O_5.

3.1. 4-Dimethylamino-2-hydroxy-2′-carboxybenzophenone (4a)

A mixture of *m*-dimethylaminophenol (68·5 g, 0·50 mol) and phthalic anhydride (74 g, 0·50 mol) in 300 ml of toluene was refluxed for 6 h. The crude product was removed by filtration and was washed with 50 ml of cold toluene and 50 ml of cold methanol. After crystallization from a 2:1 mixture of methanol and ethanol there was obtained 85 g (60%) of crystals, m.p. 187–190°C.

$C_{16}H_{15}NO_4$ (mol. wt 285·3). Calc.: C, 67·36; H, 5·26; N, 4·91.
Found: C, 67·46; H, 5·31; N, 4·64%.

3.2. 8-Hydroxy-9-*o*-carboxybenzoyljulolidine (8)

This was prepared in a similar manner and had m.p. 201–203°C.

$C_{20}H_{19}NO_4 . 0{\cdot}25H_2O$ (mol. wt 341·9).
Calc.: C, 70·28; H, 5·71; N, 4·04.
Found: C, 70·18; H, 6·09; N, 3·83%.

3.3. 4-Dimethylamino-2-hydroxybenzophenone (4b)

The acid **4a** (2·85 g, 0·010 mol) was dissolved in 100 ml of water containing 1·06 g (0·010 mol) of sodium carbonate. The filtered solution was treated with 0·800 g (0·003 mol) of copper sulfate dissolved in 30 ml of water and the precipitated salt removed by filtration, washed with water and dried *in vacuo*. A mixture of the copper salt (1·5 g, 0·004 mol) **4a** (15 g, 0·052 mol) and copper carbonate (1·5 g, 0·006 mol) in 105 ml of quinoline was heated at 180–190°C for 6–8 h. Most of the quinoline was removed by distillation under reduced pressure at 100°C. The residue was taken up in ether and filtered to remove an insoluble residue. The ether solution was washed with dilute HCl until neutral, followed by sodium carbonate solution, and finally with water. The dried ether extract was evaporated to give 8·0 g (58·4%) yellow needles, m.p. 90–92°C; NMR: δ 3·03 (s), 6·23 (m, 2H), 7·55 (m, 6H); *m/e* 241 (M^+).

$C_{15}H_{15}NO_2$ (mol. wt 241·3). Calc.: C, 74·68; H, 6·22; N, 5·81.
Found: C, 74·48; H, 6·43; N, 5·61%.

3.4. 4-Dimethylamino-2-hydroxyacetophenone (4c)

A mixture of 27·4 g (0·20 mol) of *m*-dimethylaminophenol and 20·4 g (0·20 mol) of acetic anhydride which contained a drop of conc. H_2SO_4 was refluxed for 0·5 h. The resulting solution was poured into water and after addition of a few milliliters of ethanol and three drops of conc. HCl the solution was heated at reflux for 0·25 h. The solvents were removed by rotary evaporation and the residue was dissolved in ether. The ether was washed with water, dried (Na_2SO_4) and partially evaporated. Addition of petroleum ether (b.p. 60–80°C) gave the acetate ester as white plates, m.p. 39–40°C (Lit.[16] m.p. 36·5°C).

A solution of 59·6 g (0·33 mol) of the acetate in 150 ml of 1,2-dichloroethane was added dropwise to a stirred slurry of 53·2 g (0·398 mol) of aluminum chloride in 150 ml of 1,2-dichloroethane. The reaction temperature rose to *ca.* 40°C during the addition. The mixture was heated at 80°C for 4·5 h and stirred at 25°C for 17 h. Addition of ice and water was followed by 500 ml of 1·2 M-HCl. The organic phase was washed with brine, then water, and dried. The crude yellow product crystallized from methylene chloride–petroleum ether (b.p. 30–60°C) to give 9·8 g (16%) of ketone **4c**, m.p. 120–123°C; NMR: δ 2·46 (s), 3·03 (s), 6·2 (m, 2H), 7·58 (d, $J = 9$ Hz).

$C_{10}H_{13}NO_2$ (mol. wt 179·2). Calc.: C, 67·04; H, 7·26; N, 7·82.
Found: C, 67·05; H, 7·38; N, 7·74%.

3.5. 2,4-Dihydroxy-3-methylbenzaldehyde

Phosphoryl chloride (18·4 g, 0·12 mol) was added dropwise to 45 g (0·061 mol) of dimethylformamide with stirring and cooling to 0°C. 2-Methylresorcinol (12·4 g, 0·10 mol) was added in small portions while maintaining the temperature at 0°C. The resulting solution was allowed to warm to 25°C slowly followed by heating on a steam bath for 3 h. The reaction was quenched by pouring on to 500 g of an ice–water mixture. The product was extracted into methylene chloride, and the combined extracts were washed with water, dried (Na_2SO_4) and evaporated to yield a yellow oil. Crystallization from hot water or 20% ethanol gave 9·2 g (61%) of beige-colored crystals, m.p. 154–155°C; NMR (DMSO-d_6): δ 2·00 (s, CH_3), 6·6 (d, $J = 9$ Hz), 7·5 (d, $J = 9$ Hz), 9·7 (s).

$C_8H_8O_3$ (mol.wt 152·1). Calc.: C, 63·16; H, 5·26.
Found: C, 63·05; H, 5·26%.

3.6. 2,4-Dimethylresorcinol

The aldehyde (10·0 g, 0·066 mol) was added over 1 h to a refluxing slurry of the amalgam prepared from 110 g of zinc dust, 1% aqueous $HgCl_2$ solution, 200 ml of 10% hydrochloric acid and 60 ml of ethanol. Ethanol (50 ml) and hydrochloric acid (50 ml) were added and the resulting mixture was heated for 3 h. The aqueous ethanol was decanted and the solids were rinsed with ethanol. The combined extracts were evaporated to about one-third of the original volume followed by ether extraction (× 4). The combined ether extracts were dried and evaporated to give 5 g (56%) of a solid, m.p. 107–108°C after crystallization from chloroform and petroleum ether (two early reports[17,18] give m.p.s of 146°C and 149–150°C for 2,4-dimethylresorcinol). NMR: δ 2·13 (s), 6·28 (d, $J = 8$ Hz), 6·78 (d, $J = 8$ Hz).

$C_8H_{10}O_2$ (mol.wt 138·2). Calc.: C, 69·54; H, 7·30.
Found: C, 69·56; H, 7·24%.

3.7. 2,4-Dimethoxy-3-methylphenylacetic acid

Chloromethylation of 2,6-dimethoxytoluene[19]

A stream of hydrogen chloride was passed into a warm (55–60°C) solution of 39 ml of 37% formaldehyde (0·52 mol) in 60 ml of dioxane. A solution of 30·4 g (0·20 mol) of 2,6-dimethoxytoluene in 20 ml of dioxane was added while maintaining the temperature between 55 and 60°C and a constant flow of HCl. The reaction mixture was cooled and poured into ice–water mixture followed by ether extraction (× 4). The extracts were washed with water until neutral, dried and evaporated. The residual oil was distilled to give two major fractions: b.p. 110–112°C (0·5 mm), 10 g (25%); b.p. 130–140°C (0·5 mm). The lower-boiling component is believed to be 2,4-dimethoxy-3-methylchloromethylbenzene; NMR: δ 2·13 (s), 3·80 (s), 4·63 (s), 6·6 (d, $J = 8$ Hz), 7·2 (d, $J = 8$ Hz).

$C_{10}H_{13}ClO_2$ (mol.wt 200·7). Calc.: C, 59·85; H, 6·48; Cl, 17·70.
Found: C, 60·05; H, 6·24; Cl, 18·01%.

2,4-Dimethoxy-3-methylphenylacetonitrile

A slurry containing 10 g (0·05 mol) of the chloride described above, 3·3 g (0·067 mol) of sodium cyanide and 0·45 g of sodium iodide in 80 ml of acetone was heated at reflux for 24 h. The salts were removed by filtration and washed with acetone. The combined extracts were evaporated to give an oil which was dissolved in ether and washed with water. The dried ether solution was evaporated to give 5·0 g (52%) of needles, m.p. 50°C after crystallization from petroleum ether; IR (Nujol), 2252 cm^{-1}; NMR: δ 2·16 (s), 3·5 (s), 3·76 (s), 3·83 (s), 6·6 (d, $J = 8$ Hz), 7·2 (d, $J = 8$ Hz).

$C_{11}H_{13}NO_2$ (mol. wt 191·2). Calc.: C, 69·11; H, 6·80; N, 7·33.
Found: C, 69·11; H, 6·50; N, 7·16%.

2,4-Dimethoxy-3-methylphenylacetic acid

Hydrolysis of the nitrile (5 g) was accomplished by heating for 5 h with potassium hydroxide (4 g) in 20 ml of ethanol. Evaporation of the ethanol followed by acidification with HCl gave the free acid **11** (3·5 g), m.p. 143–145°C after crystallization from chloroform–petroleum ether. NMR: δ 2·16 (s), 3·63 (s), 3·72 (s), 3·8 (s), 6·6 (d, $J = 8$ Hz), 7·1 (d, $J = 8$ Hz), 9·8 (bs).

$C_{11}H_{14}O_4$ (mol. wt 210·2). Calc.: C, 62·85; H, 6·66.
Found: C, 62·95; H, 6·57%.

3.8. Condensation reactions

Sulfuric acid: preparation of **6a** *($R^1, R^2, R^4 = H$) . H_2SO_4*

A suspension of 2·85 g (0·010 mol) of **4a** and 1·5 g (0·014 mol) of resorcinol in 50 ml of 50% H_2SO_4 was heated to 120–130°C. After 5 h the reaction mixture was cooled and filtered. The orange precipitate was washed with ice-cold water, dried and crystallized from chloroform; yield 3·8 g (81%), m.p. 210–215°C. The bisulfate was purified by chromatography on silica gel by gradient elution with methanol–benzene (8–15%).

$C_{22}H_{19}NO_8S . 0{\cdot}5H_2O$ (mol. wt 466·5).
Calc.: C, 56·65; H, 4·29; N, 3·00.
Found: C, 57·17; H, 4·72; N, 2·61%.

The free base was obtained by treatment of the salt with 5% Na_2CO_3 solution, filtration and neutralization with acetic acid. The base was removed by filtration, washed with water and crystallized from methanol, m.p. 265–268°C.

Phosphoric acid: preparation of 2,4-dichloro-6-dimethylamino-9-methyl-3H-xanthen-3-one

A mixture of 1·7 g (0·010 mol) of **4c** and 1·94 g (0·011 mol) of 2,4-dichlororesorcinol[20] and 22 g of polyphosphoric acid was heated to 120–130°C for 5–6 h. The reaction was quenched with ice–water followed by basification with NaOH and water. The dried extracts were evaporated to yield a tarry mass. Crystallization from CH_2Cl_2 served to purify the dye; yield 0·30 g (9·4%).

Methyl esters were prepared by heating the appropriate dye in methanolic HCl for 5 h. Evaporation of the solvent gave a residue that was taken up in chloroform, washed with aq. Na_2CO_3 and water. The dried extracts were evaporated and the residue was crystallized from benzene–methanol.

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