The necessary reactants were heated together in the specified medium for the period indicated. Triethylamine (5% excess above the calculated amount) was used as the condensing agent in all cases except two (M5b, M19), where another condensing agent is given and three (M20, M21, M28a), where no condensing agent was required beyond the solvent used for the reaction. Merocyanine dye (M1-M32) separated either spontaneously or on cooling. The yield of crude, but washed, dye is given, followed by the yield after two recrystallizations from the solvent indicated. All of the dyes except M6 and M7 melted with decomposition.

The dyes appear as follows: M1, yellow crystals with blue reflex; M2, brownish needles with green reflex; M3, yellowish-orange flakes; M4, garnet crystals with green reflex; M5, red needles with blue reflex; M6, very pale yellow needles; M7, colorless crystals; M8, reddish-brown needles with blue and green reflex; M9, reddish-brown prisms with green reflex; M10, red needles with blue reflex; M11, orange-red needles with blue reflex; M12, orange crystals with blue reflex; M13, yellow-orange needles; M14, orange crystals; M15, lustrous yellow-orange plates; M16, orange needles with blue reflex; M17, red crystals with green reflex; M18, orange crystals; M19, red powder; M20, orange-yellow needles with blue reflex; M21, reddish-orange crystals; M22, orange crystals; M23, fine orange crystals; M24, brownish-golden plates; M25, orange-brown prisms with blue reflex; M26, garnet needles with blue reflex; M27, brownish-orange needles; M28, dark needles with blue reflex; M29, red crystals with golden reflex; M30, yellow-orange crystals; M31, minute blue-green crystals; M32, emerald green crystals.

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[COMMUNICATION NO. 1397 FROM THE KODAK RESEARCH LABORATORIES]

Color and Constitution. X.[1] Absorption of the Merocyanines[2]

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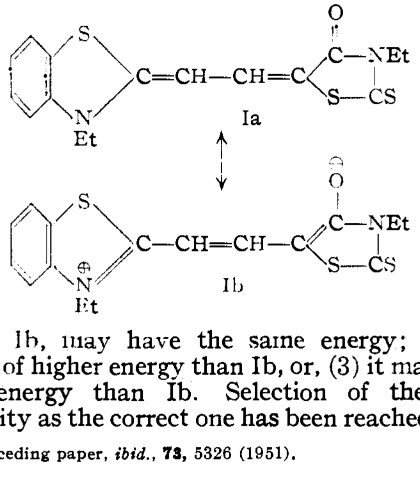
In a merocyanine an additional double bond enters *each* of the two rings of the dye in the dipolar resonance structure with $>\overset{\oplus}{N}=\overset{|}{C}(-\overset{|}{C}=\overset{|}{C})_n-\overset{\ominus}{O}$. Depending on the rings paired in the dye, stabilization thus acquired may be low, or high, or have any intermediate value. If such stabilization is low, the dye has low intrinsic polarity: it will show large $\lambda_{max.}$ deviations in all solvents and $\lambda_{max.}$ will tend to shift to longer wave lengths with increasing polarity of the solvent, especially for the higher vinylogs of a series. If the stabilization is moderate, the dye may show a negligible deviation in a solvent of moderate polarity such as methanol and $\lambda_{max.}$ will be relatively insensitive to change of solvent. If the stabilization is great, the dye has high intrinsic polarity and will show small deviations only in solvents of low polarity, and will exhibit extraordinary shifts of $\lambda_{max.}$ to *shorter* wave lengths with increasing polarity of the solvent, these shifts increasing with chain length. Thus the hypsochromic shifts $\lambda_{max.}$ pyridine → $\lambda_{max.}$ water for the series XII (n = 0, 1, 2, 3) are 365, 800, 1400 and 2200 Å., respectively.

(1) **Introduction.**—When the absorptions of the merocyanines first began to be examined between one and two decades ago, many of the relationships were incomprehensible. At that time a great quantity of data showing nonconvergence of the $\lambda_{max.}$ values of symmetrical[3] and certain unsymmetrical vinylogous cyanine series had been published,[4] but convergence in more highly unsymmetrical cyanine series had not then been noted,[5c] and was actually first observed in a vinylogous series of merocyanines, where it struck a puzzling new note. Also, just as the absorptions of many unsymmetrical cationic dyes could not be reconciled with those of structurally related symmetrical dyes until the introduction of the "deviation" concept,[5] so the absorptions of many merocyanines seemed anomalous when they were first compared with those of structurally related symmetrical cyanines.

The resonance theory has now been used successfully for interpreting the absorptions of ionized dyes such as the symmetrical[1] and unsymmetrical cyanines[5f] and *p*-dimethylaminostyryl derivatives.[5a,e] The merocyanines,[6] being un-ionized, present several special problems, but it will be shown that the resonance treatment gives a self-consistent qualitative account of their absorptions also.

(2) **Deviations in the Merocyanines.**—The key to the spectra of the merocyanines consists in regarding them, in each case, as a resonance hybrid between an uncharged and a dipolar structure, as illustrated by Ia↔Ib. In this dye a benzothiazole ring is linked to one derived from 3-ethylrhodanine; the resonance is of the amidic type $>N-\overset{|}{C}=O \longleftrightarrow >\overset{\oplus}{N}=\overset{|}{C}-\overset{\ominus}{O}$. Three possibilities arise: (1) the extreme resonance structures,


Ia

Ib

Ia and Ib, may have the same energy; (2) Ia may be of higher energy than Ib, or, (3) it may be of lower energy than Ib. Selection of the third possibility as the correct one has been reached in the

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† Deceased, October 15, 1951.

[1] Part IX, THIS JOURNAL, 73, 1087 (1951).

[2] Presented before the Organic Section of the American Chemical Society, March 28, 1949, at San Francisco, Calif.

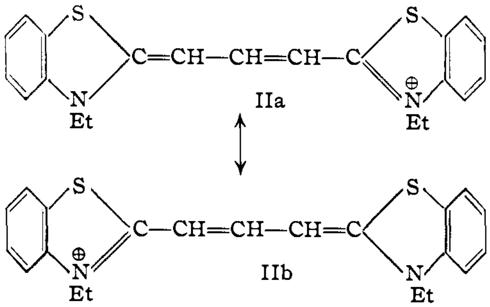
[3] N. I. Fisher and F. M. Hamer, *Proc. Roy. Soc.* (*London*), A154, 703 (1936).

[4] B. Beilenson, N. I. Fisher and F. M. Hamer, *ibid.*, A163, 138, (1937).

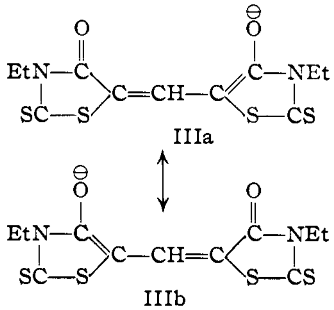
[5] (a) Part III, THIS JOURNAL, 63, 3203 (1941); (b) Part IV, *ibid.*, 63, 3214 (1941); (c) Part V, *ibid.*, 64, 199 (1942); (d) Part VI, *ibid.*, 67, 1869 (1945); (e) Part VII, *ibid.*, 67, 1875 (1945); (f) Part VIII, *ibid.*, 67, 1889 (1945).

[6] Preceding paper, *ibid.*, 73, 5326 (1951).

following way: the dye may be regarded as the structural hybrid between the thiacarbocyanine cation II, with its amidinium ion resonance, and the anion III. The latter, with carboxyl ion resonance, is that of a dye belonging to a group for which the name "oxonol" seems appropriate. Since II and III are symmetrical ions, the extreme resonance structures in each case are identical.


IIa

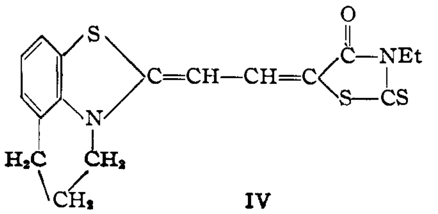
IIb


IIIa

IIIb

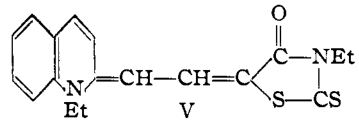
If Ia and Ib are not of the same energy under the conditions under which absorption is determined, then the dye would be expected to absorb at shorter wave length than that calculated by averaging the $\lambda_{max.}$ values of II and III, as a great many unsymmetrical dyes have already been found to do[5a–f]: in other words, I would be expected to show a "deviation" of a smaller or greater amount. Dyes II and III have $\lambda_{max.}$ in methyl alcohol of 5575 and 5320 Å., respectively, the mean being 5450 Å., so that I, with $\lambda_{max.}$ 5240 Å., absorbs at less than the mean by 210 Å., this amount being the "deviation." It thus appears that Ia and Ib are not equivalent energetically, though which structure has the lower and which the higher energy cannot be deduced from this result alone.

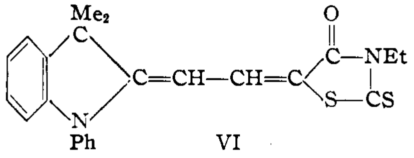
In evaluating the relative energies of uncharged and dipolar structures, it often happens that a dipolar structure is of higher energy because of charge separation. If this is tentatively assumed to be true of I, then a small increase in basicity of the N-ethylbenzothiazole ring should increase the stability (*i.e.*, lower the energy) of the positively charged form of the benzothiazole ring (in Ib) relative to the uncharged form (in Ia). The energy of Ib as a whole would be lowered relative to Ia in this modified dye, and the deviation would be reduced. It has previously been shown that one way of increasing the basicity of the N-ethylbenzothiazole ring is to replace ethyl by 3,4-trimethylene.[5e] Applied to I, this replacement gives IV, the deviation of which, calculated in similar fashion to that of I, is 160 Å. The assumption that Ib is of higher energy than Ia in methyl alcoholic solution thus seems justified.


IV

Confirmation of the above argument is provided by modifying the structure of I so as to *decrease* the basicity of the N-ethylbenzothiazole ring by replacing ethyl by benzyl, in one set of comparisons, and by ethoxycarbonylmethyl ($-CH_2COOEt$) in a second. These groups are known to decrease the basicity of the benzothiazole ring, ethoxycarbonylmethyl being the more effective group for the purpose.[5e] By raising the relative energy of the dipolar structure of the merocyanine I, these replacements would be expected to increase the deviation. Actually, these expectations were fully realized, for the deviation of the N-benzylbenzothiazole dye corresponding to I was 230 Å. and that of the N-CH_2COOEt derivative 280 Å.

It is not necessary to restrict modifications of I to small changes in basicity, though it was considered safer to do so to start with. A much greater increase in basicity of the basic nucleus of I is effected by replacing benzothiazole by 2-quinoline,[5e] giving V. This change would be expected to reduce the deviation markedly, and it does, for the deviation of V is only 30 Å. On the other hand, the 3,3-dimethyl-1-phenylpseudoindole ring is much less basic than benzothiazole,[5e] and its replacement of the latter in I to give VI should effect a considerable increase in the deviation. This is also realized in practice; the deviation of VI is 455 Å.


V


VI

The foregoing results are plotted in Fig. 1. The basic nuclei (1 to 22) and carbonyl-containing nuclei (23 to 32) combined in the merocyanines and other dyes described in this paper are numbered in this and subsequent figures to make it easier to identify a given dye in the experimental section. The nucleus numbers are given for each dye in Tables II, III and IV. Energy level diagrams of a roughly qualitative kind (that take into account the effect of the solvent, *cf.*, Section 7) are shown for each of the six merocyanines whose deviations are given. In each diagram the levels of the *structures* are shown at the left, and the levels of the ground and excited states (*g* and *e*, respectively) at the right. In the diagram for I, the level of Ib is shown higher than that of Ia. For the remaining diagrams, the energy of the dipolar extreme struc-

TABLE I

DETAILS OF DYE SYNTHESES

Dye no.	Reactants, g.				Medium, ml.		Refluxed, min.	Yield, %	Solvent, ml./g.		M.p., °C.	Formula	Analyses, % Calcd.	Found
Merocyanine														
M86	QS1	3.9	KM1	1.6	EtOH	30	30	72, 36	MeOH	76	294–296	$C_{15}H_{12}N_2O_2$	N, 11.11	11.0
Merocarbocyanines														
M33	QS2	1.2	KM2	0.4	EtOH	20	20	85, 44	MeOH	150	191–193	$C_{23}H_{22}N_2OS_2$	S, 15.78	15.9
M34	QS3	1.8	R1	1.5	EtOH	25	20	75, 60	HOAc	150	248–250	$C_{18}H_{18}N_2O_3S_3$	S, 23.68	23.27
M35	QS4	1.8	R1	1.5	EtOH	25	20	87, 65	HOAc	150	241–242	$C_{21}H_{18}N_2OS_3$	S, 23.44	23.34
M36	QS5	0.3	R1	0.3	EtOH	15	20	70, 42	C_5H_5N–MeOH[a]		288–289	$C_{17}H_{16}N_2OS_2$	S, 26.70	26.70
M37	QS6	2.0	KM2	0.8[b]	Ac_2O	25	5	60, 40	HOAc	50	239–240	$C_{18}H_{18}N_2OS_2$	N, 8.19	8.17
M38	R2	2.4	KM2	2.2[c]	EtOH	15	30	11, 8	MeOH	1100	196–198	$C_{16}H_{16}N_2OS_2$	C, 60.70	60.47
													H, 5.10	5.07
M39	QS7	1.4	KM2	0.7	EtOH	15	20	89, 42	HOAc	26	190–192	$C_{19}H_{22}N_2OS_2$	N, 7.82	7.56
M40	QS8	1.25	KM2	0.4	EtOH	15	15	90, 50	HOAc	250	262–263	$C_{16}H_{16}N_2OS_2Se$	N, 7.09	6.85
M41	QS9	1.5	KM2	0.54[b]	Ac_2O	20	3	84, 54	HOAc	440	282–284	$C_{20}H_{18}N_2OS_3$	N, 7.04	7.03
M42	QS10	2.2	KM2	0.8	EtOH	20	15	82, 70	HOAc	18	233–235	$C_{16}H_{16}N_2O_2S_2$	N, 8.43	8.43
M43	QS11	1.3	R1	1.8	EtOH	15	15	53, 27	MeOH	80	165–166[d]	$C_{12}H_{16}N_2OS_3$	C, 47.96	47.81
													H, 5.37	5.45
M44	QS12	2.0	KM2	0.8[b]	HOAc	25	5	35, 20	HOAc	40	233–235	$C_{18}H_{18}N_2OS_2$	N, 8.19	8.11
M45	QS13	4.5	KM2	1.6[b]	HOAc	50	5	63, 33	HOAc	300	273–274	$C_{22}H_{20}N_2OS_2$	N, 7.14	6.83
M46	QS14	1.5	R1	1.5	EtOH	25	15	55, 33	HOAc	53	222–224	$C_{16}H_{20}N_2OS_3$	S, 27.30	27.40
M47	QS15	2.49	R1	3.06	C_5H_5N	10	10	29, 12	MeOH	80	178–179	$C_{14}H_{16}N_2OS_2$	C, 57.48	57.28
													H, 5.52	5.70
M48	QS16	5.0	R1	6.1	C_5H_5N	15	10	18, 10	MeOH	525	247–249	$C_{14}H_{16}N_2OS_2$	C, 57.48	57.34
													H, 5.52	5.36
M49	QS17	3.55	R1	3.1	EtOH	20	20	41, 30	MeOH	110	132–133	$C_{16}H_{22}N_2OS_3$	C, 54.18	54.08
													H, 6.26	6.20
M50	QS18	0.90	R1	1.0	EtOH	15	15	45, 26	MeOH	210	198–199	$C_{13}H_{16}N_2OS_3$	C, 49.95	49.9
													H, 5.16	5.4
M51	QS19	1.6	R1	1.0	C_5H_5N	15	30	67, 27	EtOH	40	183–184	$C_{18}H_{21}N_3OS_2$	C, 60.12	60.06
													H, 5.89	5.86
M52	QS2	2.4	KM1	0.8	EtOH	20	20	90, 70	MeOH	450	219–221	$C_{27}H_{22}N_2O_2$	C, 79.78	79.8
													H, 5.46	5.8
M53	QS2	2.4	KM3	0.8	EtOH	20	20	65, 37	MeOH	230	234–236	$C_{27}H_{23}N_3O$	C, 79.95	79.8
													H, 5.72	5.8
M54	QS2	2.4	KM4	0.73	EtOH	20	20	69, 34	MeOH	110	236–237	$C_{27}H_{21}NO_2$	C, 82.85	83.1
													H 5.41	5.5
M55	QS2	2.4	KM5	1.0	EtOH	20	20	88, 82	C_5H_5N–MeOH[a]		262–264	$C_{26}H_{27}N_3O_2S$	S, 7.20	7.1
M56	QS2	1.6	KM6	0.6	EtOH	20	15	85, 31	MeOH	400	218–219	$C_{28}H_{25}N_3O$	N, 10.02	9.98
M57	QS2	2.4	KM7	0.9	EtOH	20	20	88, 75	C_5H_5N–MeOH[a]		267–269	$C_{26}H_{27}N_3O_3$	N, 9.79	9.8
M58	QS2	2.4	KM8	0.73	EtOH	20	20	66, 31	MeOH	75	157–160[d]	$C_{23}H_{22}N_2O_2S$	S, 8.21	8.2
M59	QS2	4.8	KM9	1.6	EtOH	20	30	16, 12	EtOH	60	213–215	$C_{28}H_{25}N_2O$	C, 82.71	82.3
													H 6.45	6.7
M60	QS2	4.8	KM10	2.2	EtOH	20	30	30, 16	EtOH	120	199–200	$C_{29}H_{27}N_3OS$	C, 74.79	74.5
													H, 5.85	6.0
M61	QS20	4.5	KM1	1.6	EtOH	15	20	83, 65	MeOH	75	230–231	$C_{22}H_{20}N_2O_2$	C, 76.69	76.5
													H, 5.86	5.7
M62	QS20	4.5	KM3	1.6	EtOH	25	20	90, 35	C_5H_5N–MeOH[a]		244–246	$C_{22}H_{21}N_3O$	C, 76.91	77.1
													H, 6.17	6.2
p-Dimethylaminobenzylidene dyes														
B3	R8	3.0	KM5	4.0[c]	EtOH	50	180	80, 53	MeOH	430	212–214	$C_{17}H_{21}N_3O_2S$	C, 61.59	62.0
													H, 6.39	6.5
B4	R8	1.5	KM7	1.8[j]	HOAc	15	20	100, 82	MeOH	125	188–189	$C_{17}H_{21}N_3O_3$	C, 64.73	64.9
													H, 6.71	6.9
B7	R8	0.75	KM8	0.7[c]	EtOH	20	90	64, 36	MeOH	100	156–158[d]	$C_{14}H_{16}N_2O_2S$	N, 10.15	10.01
B8	R8	1.5	KM9	1.6[c]	EtOH	20	120	48, 17		[k]	153–154[d]	$C_{19}H_{20}N_2O$	C, 78.02	78.2
													H, 6.90	6.8
B10	R8	1.5	KM10	2.2[c]	EtOH	10	60	95, 49	HOAc	15	203–204	$C_{20}H_{21}N_3OS$	C, 68.35	68.3
													H, 6.02	5.8
p-Dimethylaminostyryl dye														
S5	QS17	3.5	R8	1.5[j]	Ac_2O	15	1.5	87, 48	EtOH	3	212–214	$C_{26}H_{34}N_2O_3S_2$	C, 64.15	64.2
													H, 7.04	6.7
Unsymmetrical carbocyanine dye														
U1	QS32	3.1	R9	2.0[c]	EtOH	15	240	60, 39	EtOH	10	187–188	$C_{23}H_{29}ClN_2O_4S$	C, 59.39	59.20
													H, 6.29	6.44
Symmetrical carbo- and dicarbocyanine dyes														
C2	QS32	3.1	R10	2.2[j]	C_5H_5N	15	90	61, 50	EtOH	45	222–223	$C_{21}H_{33}ClN_2O_4S_2$	C, 52.85	53.17
													H, 6.98	7.06
C3	QS33	3.36	R11	1.3[b]	Ac_2O	15	3	89, 30	EtOH	150	236–238	$C_{37}H_{35}ClN_2O_4$	C, 73.17	72.8
													H, 5.81	5.4
C4	QS25	1.0	QS34	0.65	EtOH	15	15	60,[l] 30	MeOH	30	189–191	$C_{29}H_{35}ClN_2O_4$	C, 68.13	68.17
													H, 6.90	7.01
C5	QS26	3.5	R11	1.3	EtOH	15	15	59, 36	MeOH	430	232–234	$C_{23}H_{23}IN_2Se_2$	I, 20.71	20.51
C19	QS30	4.7	R11	2.6[f]	$C_6H_{11}N$	30	900[m]	32, 4	MeOH	650	255–256	$C_{17}H_{19}IN_2$	I, 33.57	32.6

TABLE I (*Continued*)

Dye no.	Reactants, g.				Medium, ml.		Refluxed, min.	Yield, %	Solvent, ml./g.		M.p., °C.	Formula	Analyses, % Calcd.	Found
Symmetrical methine- and trimethine-oxonols														
01	R1	3.0	KM2	1.6	C_5H_5N	20	30	37,[n] 33	MeOH	10	181–183	$C_{17}H_{27}N_3O_2S_4$	C, 47.06 H, 6.28	47.10 6.08
02	R10	1.48	KM1	1.6[j]	C_5H_5N	10	15	95,[o] 40	MeOH	13	175–177	$C_{24}H_{17}N_6O_4$	N, 10.21	10.12
03	R10	3.0	KM3	3.2	C_5H_5N	20	6	73, 66	MeOH[p]		174–177	$C_{19}H_{14}N_4O_2$	C, 69.07 H, 4.27	69.14 4.28
05	R10	1.5	KM5	2.0[j]	C_5H_5N	30	15	100, 25	MeOH	100	183–185	$C_{17}H_{22}N_4O_4S_2$	C, 49.71 H 5.41	49.9 5.3
07	R10	1.5	KM7	0.9[j]	C_5H_5N	15	10	54, 10	EtOH	40	128–130[d]	$C_{17}H_{22}N_4O_6$	C, 53.94 H, 5.86	53.94 6.30
08	R12	2.9	KM8	2.6	C_5H_5N	20	120	22,[n] 12	EtOH[q]		146–148	$C_{17}H_{27}N_3O_4S_2$	S, 15.98	16.01
09	R13	3.2	KM9	6.4	$C_5H_{11}N$	10	900[r]	17, 12	EtOH	200	182–184	$C_{21}H_{20}N_2O_2$	C, 75.86 H, 6.07	75.6 5.7
010	R13	3.2	KM10	8.8	$C_5H_{11}N$	10	900[r]	57, 13	EtOH	250	202–203	$C_{23}H_{22}N_4O_2S_2$	C, 61.31 H, 4.93	61.7 5.2
012	R14	1.7	KM1	1.6	C_5H_5N	10	10	68,[o] 34	MeOH	50	161–164	$C_{26}H_{19}N_3O_4$	N, 9.61	9.37
Merocarbocyanines														
M63	QS20	4.5	KM4	1.5	EtOH	15	3	80, 43	MeOH	120	210–211	$C_{22}H_{19}NO_2$	C, 80.19 H, 5.82	79.9 5.7
M64	QS20	4.5	KM5	2.0	EtOH	15	20	78, 73	C_5H_5N-MeOH[a]		275–276	$C_{21}H_{25}N_3O_2S$	C, 65.75 H, 6.57	65.8 6.7
M65[e]	QS20	1.0	KM6	0.4	EtOH	15	15	75, 25	MeOH	25	182–184	$C_{23}H_{23}N_3O$	C, 77.27 H, 6.49	76.90 6.06
M66	QS20	4.5	KM7	1.84	EtOH	10	20	87, 81	C_5H_5N-MeOH[a]		272–274	$C_{21}H_{25}N_3O_3$	C, 68.63 H, 6.83	68.8 6.8
M67	QS20	2.25	KM8	0.73	EtOH	20	20	89, 43	MeOH	260	189–190[d]	$C_{18}H_{20}N_2O_2S$	C, 65.81 H, 6.14	66.1 6.4
M68	QS20	4.5	KM9	1.6	EtOH	10	20	29, 3[f]	EtOH	5	172–174	$C_{23}H_{24}N_2O$	C, 80.17 H, 7.03	80.3 6.7
M69	QS20	4.5	KM10	2.2	EtOH	10	20	72, 55	C_5H_5N-MeOH[a]		202–203	$C_{24}H_{25}N_3OS$	C, 71.43 H, 6.25	71.4 5.8
M70	QS20	4.5	KM2	1.6	EtOH	15	20	70, 61	C_5H_5N-MeOH[a]		211–212	$C_{18}H_{20}N_2OS_2$	C, 62.71 H, 5.85	62.8 5.8
M71	QS21	3.0	R7	3.0	EtOH	25	30	76, 24	MeOH	150	220–222	$C_{22}H_{18}N_2O_2$	N, 8.19	8.2
M72	QS22	3.0	R7	3.0	EtOH	25	15	91, 74	C_5H_5N-MeOH[a]		154–156	$C_{22}H_{18}N_2O_2$	C, 77.14 H, 5.30	77.3 5.6
M73	QS23	3.0	R7	3.0	EtOH	15	20	93, 14	C_5H_5N-MeOH[a]		252–254	$C_{17}H_{14}N_2O_2$	C, 73.35 H, 5.07	73.7 5.1
M82	QS7	2.1	KM5	1.0	EtOH	10	25	25, 16	C_5H_5N-MeOH[a]		312–313	$C_{22}H_{27}N_3O_2S$	C, 66.45 H, 6.85	66.2 7.0
Merodicarbocyanines														
M74	QS24	4.0	KM2	3.2	EtOH	25	15	84, 16[g]	HOAc	50	177–179	$C_{25}H_{24}N_2OS_2$	C, 69.39 H, 5.6	69.6 5.9
M75	QS25	2.5	KM2	0.8	EtOH	20	15	89, 68	C_5H_5N-MeOH[a]		176–178	$C_{21}H_{24}N_2OS_2$	S, 16.69	16.57
M76	QS26	1.8	R3	0.8	EtOH	20	15	80, 35	C_5H_5N-MeOH[a]		237–239	$C_{18}H_{18}N_2OS_2Se$	C, 51.25 H, 4.30	51.44 4.47
M77	QS27	2.0	R3	1.7	EtOH	20	15	86, 22[h]	C_5H_5N-MeOH[a]		272–275	$C_{20}H_{18}N_2OS_3$	N, 7.04	7.03
M78	QS28	1.15	KM2	0.4	EtOH	10	10	55, 16	Me_2CO	1000	256–258	$C_{18}H_{18}N_2O_2S_2$	C, 60.29 H, 5.06	60.25 5.05
M79	QS11	2.6	R3	1.65	EtOH	20	15	62, 37	MeOH	300	166–168	$C_{14}H_{18}N_2OS_3$	S, 29.47	29.34
M80	QS29	1.5	R3	0.8	EtOH	20	15	78, 28	C_5H_5N-MeOH[a]		253–255	$C_{20}H_{20}N_2OS_2$	S, 17.41	17.59
M81	QS22	1.5	R3	0.8	EtOH	20	15	78, 16	C_5H_5N-MeOH[a]		210–213	$C_{20}H_{20}N_2OS_2$	S, 17.41	17.17
M83	QS25	2.43	KM5	1.0	EtOH	20	90[i]	31, 21	C_5H_5N-MeOH[a]		302–303	$C_{24}H_{29}N_3O_2S$	C, 68.05 H, 6.90	68.01 6.98
M84	QS19	3.2	R4	3.6	EtOH	20	60	12, 7	C_5H_5N	100	304–305	$C_{23}H_{28}N_4O_3$	C, 67.61 H, 6.91	67.2 6.9
M87	QS30	2.35	R5	3.3	EtOH	20	15	10, 3	MeOH	140	227–229	$C_{19}H_{16}N_2O_2$	C, 74.98 H, 5.30	74.4 5.1
Merotricarbocyanines														
M85	QS31	1.28	KM5	0.5	EtOH	20	60[i]	18, 9	EtOH	550	190–192	$C_{26}H_{31}N_3O_2S$	C, 69.45 H, 6.95	69.34 7.03
M88	QS30	18.8	R6	28.8	EtOH	60	30	1.9, 0.7	MeOH	1600	201–203	$C_{21}H_{18}N_2O_2$	N, 8.49	8.3
p-Dimethylaminobenzylidene dye														
B2	R8	1.5	KM3	1.6	HOAc	13	30	52, 46	HOAc	10	216–217	$C_{18}H_{17}N_3O$	C, 74.21 H, 5.88	74.3 5.9

[a] The dye was dissolved in pyridine and pptd. with MeOH. [b] Plus one mol. of fused NaOAc. [c] Plus piperidine as catalyst. [d] Without decomposition. [e] Prepared by J. D. Kendall and J. R. Majer, *J. Chem. Soc.*, 687 (1948). [f] After four recrystallizations from EtOH and one from ligroin (b.p. 90–120°). [g] After four recrystallizations from EtOH and one from HOAc. [h] After five recrystallizations. [i] At room temperature. [j] No condensing agent used in addition to the medium. [k] From benzene–ligroin, b.p. 60–90° (1:10). [l] After conversion to perchlorate. [m] Heated at 100°. [n] As the triethylamine salt. [o] As the pyridine salt. [p] Dissolved as the triethylamine salt and pptd. with concd. HCl. [q] Dissolved in EtOH (10 ml./g.) and added 5 volumes of ether. [r] Heated at 120°.

The dyes appear as follows: M33, brownish-red crystals with a blue reflex; M34, scarlet powder; M35, reddish needles with a blue reflex; M36, reddish crystals with a blue reflex; M37, dark bluish-gray crystals; M38, amber crystals; M39, reddish crystals with a blue reflex; M40, purplish needles with a blue reflex; M41, dark needles with blue and green reflexes; M42, orange-red prisms with a bluish reflex; M43, reddish-brown crystals; M44, dark purplish-blue crystals; M45, dark crystals with a greenish reflex; M46, bronze needles; M47, reddish crystals with a blue reflex; M48, dark purplish needles; M49, reddish crystals with a bluish reflex; M50, garnet crystals with a brilliant metallic reflex, M51, red needles; M52, deep yellow crystals with a greenish reflex; M53, beautiful red prisms; M54, beautiful golden scales with a greenish reflex; M55, beautiful orange crystals with a blue reflex; M56, red crystals; M57, deep yellow needles; M58, beautiful orange crystals; M59, orange flakes; M60, orange needles with a blue reflex; M61, orange crystals; M62, orange-scarlet crystals; M63, dark reddish-brown crystals with a bluish reflex; M64, bright orange crystals; M65, reddish-orange crystals; M66, bright yellow crystals; M67, reddish crystals; M68, orange powder; M69, red needles; M70, reddish-brown crystals; M71, reddish plates; M72, blue-gray needles with a blue reflex; M73, dark crystals with a bluish reflex; M74, dark greenish-brown crystals; M75, steely-gray needles; M76, dark crystals with a lustrous blue reflex; M77, dull greenish powder; M78, blue crystals; M79, metallic blue crystals; M80, dark crystals with bluish reflex; M81, lustrous greenish-blue crystals; M82, orange crystals with a golden reflex; M83, dark crystals with a lustrous blue reflex; M84, red needles with a blue reflex; M85, bluish crystals with a brilliant blue reflex; M86, yellow-cream crystals; M87, dark glittering crystals; M88, very dark greenish crystals.

B2, red crystals; B3, compact crystals with blue reflex; B4, orange crystals; B7, orange plates; B8, yellow-orange crystals; B10, orange crystals; S5, dark red crystals with a blue reflex; U1, yellow crystals; C2, orange crystals with a blue reflex; C3, green crystals; C4, green crystals; C5, lustrous greenish-bronze needles; C19, greenish needles; 01, garnet needles with a blue reflex; 02, yellowish crystals; 03, yellow felt of crystals; 05, brownish needles with a blue reflex; 07, buff crystals; 08, buff crystals; 09, red crystals; 010, cream-colored crystals; 012, purplish crystals with a blue reflex.

TABLE II

OPTICAL DATA

Dye no.	Dye name	Nuclei	$\lambda_{max.}$ obsd., MeOH, Å.	$\lambda_{max.}$ calcd., Å.	Deviation, Å.	Proportional deviation
	Merocarbocyanine dyes					
M33	3-Et-5-[(3,3-diMe-1-Ph-2(3H)-indolylindene)-ethylidene]-rhodanine (VI)	1 + 23	4980	5435	455	70[a] 79.1[b]
M34	5-[(3-Ethoxycarbonylmethyl-2(3H)-benzothiazolylidene)-ethylidene]-3-Et-rhodanine	2 + 23	5180	5460	280	
M35	5-[(3-Benzyl-2(3H)-benzothiazolylidene)-ethylidene]-3-Et-rhodanine	3 + 23	5240	5470	230	
M8	3-Et-5-[(3-Et-2(3H)-benzothiazolylidene)-ethylidene]-rhodanine (I)	4 + 23	5260	5450	210	32.3[a]
M36	3-Et-5-[(3,4-trimethylene-2(3H)-benzothiazolylidene)-ethylidene]-rhodanine (IV)	5 + 23	5280	5440	160	
M37	3-Et-5-[(1-Et-2(1H)-quinolylidene)-ethylidene]-rhodanine (V)	6 + 23	5650	5680	30	4.6[a]
M38	3-Et-5-(1,2-diMe-3-indolylmethylene)-rhodanine	7 + 23	4460	5110	650	100[a]
M39	3-Et-5-[(1-Et-3,3-diMe-2(3H)-indolylidene)-ethylidene]-rhodanine	8 + 23	5035	5395	360	55.4[a]
M40	3-Et-5-[(3-Et-2(3H)-benzoselenazolylidene)-ethylidene]-rhodanine	9 + 23	5260	5510	250	38.4[a]
M41	3-Et-5-[(1-Et-2(1H)-naphtho[1,2]thiazolylidene)-ethylidene]-rhodanine	10 + 23	5450	5635	185	28.5[a]
M42	3-Et-5-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-rhodanine	11 + 23	4900	5075	175	26.9[a]
M43	3-Et-5-[(3-Et-2(3H)-thiazolinylidene)-ethylidene]-rhodanine	12 + 23	4830	4885	55	8.5[a]
M44	3-Et-5-[(1-Et-4(1H)-quinolylidene)-ethylidene]-rhodanine	13 + 23	6160	6185	25	3.8[a]
M45	3-Et-5-[(4-Et-3(4H)-benzo[f]quinolylidene)-ethylidene]-rhodanine	14 + 23	5810	5830	20	3.1[a]
M46	3-Et-5[(3-Et-4,5,6,7-tetrahydrobenzothiazolylidene)-ethylidene]-rhodanine	15 + 23	5465	5510	45	6.9[a]
M47	3-Et-5-[(1-Et-2(1H)-pyridylidene)-ethylidene]-rhodanine	16 + 23	5405	5470	65	10[a]
M48	3-Et-5-[(1-Et-4(1H)-pyridylidene)-ethylidene]-rhodanine	17 + 23	5650	5675	25	3.8[a]
M49	3-Et-[(3-Et-hexahydrobenzothiazolylidene)-ethylidene]-rhodanine	18 + 23	4850	4925	75	11.4[a]
M50	3-Et-5-[(3-Et-4-Me-2(3H)-thiazolylidene)-ethylidene]-rhodanine	19 + 23	5395	5440	45	6.9[a]
M51	5-[(1,3-DiEt-2(3H)-benzimidazolylidene)-ethylidene]-3-Et-rhodanine	20 + 23	5125	5135	10	1.5[a]
M52	4-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-3-Ph-5(4H)-isoxazoline	1 + 24	4855	4900	45	7.8[b]
M53	4-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-1-Ph-5-pyrazolone	1 + 25	4840	4930	90	15.6[b]
M54	2-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-1,3-indandione	1 + 26	4955	5075	120	20.8[b]
M55	5-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-1,3-diEt-2-thiobarbituric acid	1 + 27	4940	5070	130	23.6[b]
M56	4-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-3-Me-1-Ph-5-pyrazolone	1 + 28	4795	4960	165	28.7[b]
M57	5-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-1,3-diEt-barbituric acid	1 + 29	4665	4875	210	36.5[b]
	p-Dimethylaminobenzylidene dyes					
B1	4-*p*-Me$_2$N-benzylidene-3-Ph-5(4H)-isoxazolone[c]	24	4800	5160	360	32.1[b]
B2	4-*p*-Me$_2$N-benzylidene-1-Ph-4-pyrazolone	25	4800	5185	385	34.4[b]
B3	5-*p*-Me$_2$N-benzylidene-1,3-diEt-2-thiobarbituric acid	27	4900	5325	425	37.9[b]
B4	5-*p*-Me$_2$N-benzylidene-1,3-diEt-barbituric acid	29	4660	5130	470	42.0[b]
B5	2-*p*-Me$_2$N-benzylidene-1,3-indandione[d]	26	4810	5330	520	46.4[b]
B6	4-*p*-Me$_2$N-benzylidene-3-Me-1-Ph-5-pyrazolone[e]	28	4670	5215	545	48.6[b]
B7	5-*p*-Me$_2$N-benzylidene-3-Et-2-thio-2,4-oxazolidinedione	30	4370	5260	890	79.5[b]
B8	3-*p*-Me$_2$N-benzylidene-1-Et-oxindole	31	4360	5370	1010	90.2[b]
B9	5-*p*-Me$_2$N-benzylidene-3-Et-rhodanine[f] (VII)	23	4660	5690	1030	92.0[b]
B10	5-*p*-Me$_2$N-benzylidene-3-Et-1-Ph-2-thiohydantoin	32	4560	5680	1120	100[b]

TABLE II (*Continued*)

Dye no.	Dye name	Nucleus	$\lambda_{max.}$ obsd., MeOH, Å.	$\lambda_{max.}$ calcd., Å.	Deviation, Å.	Proportional deviation
	p-Dimethylaminostyryl dyes					
S1	3-*p*-Me$_2$N-benzylidene-1,2-diMe-pseudoindolium ClO$_4$	7	5480	5480	0	0[a]
S2	2-*p*-Me$_2$N-styryl-3,3-diMe-1-Ph-pseudoindolium ClO$_4$	1	5630	5810	180	13.7[a]
S3	2-*p*-Me$_2$N-styryl-3,3-diMe-1-Et-pseudoindolium I	8	5460	5760	300	22.9[a]
S4	2-*p*-Me$_2$N-styryl-3-Et-thiazolinium I	12	4790	5255	465	35.5[a]
S5	2-*p*-Me$_2$N-styryl-3-Et-hexahydrobenzothiazolium *p*-toluenesulfonate	18	4820	5295	475	36.3[a]
S6	2-*p*-Me$_2$N-styryl-3-Et-benzoxazolinium I	11	4960	5440	480	36.6[a]
S7	2-*p*-Me$_2$N-styryl-3-Et-benzoselenazolium I	9	5360	5880	520	38.9[a]
S8	2-*p*-Me$_2$N-styryl-3-Et-benzothiazolium I	4	5240	5820	580	44.3[a]
S9	2-*p*-Me$_2$N-styryl-1-Et-naphtho[1,2]thiazolium I	10	5310	6005	695	53.0[a]
S10	2-*p*-Me$_2$N-styryl-1-Et-quinolinium I	6	5250	6050	800	61.0[a]
S11	3-*p*-Me$_2$N-styryl-4-Et-benzo[f]quinolinium I	14	5200	6200	1000	76.4[a]
S12	2-*p*-Me$_2$N-styryl-3-Et-4-Me-thiazolium I	19	4800	5810	1010	77.0[a]
S13	2-*p*-Me$_2$N-styryl-3-Et-4,5,6,7-tetrahydrobenzothiazolium I	15	4810	5880	1070	82.5[a]
S14	4-*p*-Me$_2$N-styryl-1-Et-quinolinium I	13	5460	6555	1095	83.5[a]
S15	2-*p*-Me$_2$N-styryl-1-Et-pyridinium I	16	4610	5840	1230	94[a]
S16	4-*p*-Me$_2$N-styryl-1-Et-pyridinium I	17	4775	6045	1270	97[a]
S17	2-*p*-Me$_2$N-styryl-1,3-diEt-benzimidazolium I	20	4195	5505	1310	100[a]
	Unsymmetrical carbocyanine dye					
U1	3-Et-2′,5′-diMe-1′-Ph-hexahydrothia-3′-pyrrolocarbocyanine ClO$_4$		4205	4505	300	32.6[a]
	Merocarbocyanine dyes					
M58	5-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-3-Et-2-thio-2,4-oxazolidinedione	1 + 30	4680	5000	320	55.5[b]
M59	3-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-1-Et-oxindole	1 + 31	4570	5120	550	95.5[b]
M60	5-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-3-Et-1-Ph-2-thiohydantoin (XIII)	1 + 32	4850	5425	575	100[b]
M61	3-Ph-4-[(1,3,3-triMe-2(3H)-indolylidene)-ethylidene]-5-(4H)-isoxazolone (XIV)	21 + 24	4780	4850	70	
M62	1-Ph-4-[(1,3,3-tri-Me-2(3H)-indolylidene)-ethylidene]-5-pyrazolone	21 + 25	4800	4880	80	
M63	2-[(1,3,3-TriMe-2(3H)-indolylidene)-ethylidene]-1,3-indandione	21 + 26	4920	5025	105	
M64	1,3-DiEt-2-thio-5-[(1,3,3-triMe-2(3H)-indolylidene)-ethylidene]-barbituric acid	21 + 27	4900	5020	120	
M65	3-Me-1-Ph-4-[(1,3,3-triMe-2(3H)-indolylidene)-ethylidene]-5-pyrazolone	21 + 28	4760	4910	150	
M66	1,3-DiEt-5-[(1,3,3-triMe-2(3H)-indolylidene)-ethylidene]-barbituric acid	21 + 29	4650	4825	175	
M67	3-Et-2-thio-5-[(1,3,3-triMe-2(3H)-indolylidene)-ethylidene]-2,4-oxazolidinedione	21 + 30	4740	4955	215	
M68	1-Et-3-[(1,3,3-triMe-2(3H)-indolylidene)-ethylidene]-oxindole	21 + 31	4560	5065	505	
M69	3-Et-1-Ph-2-thio-5-[(1,3,3-triMe-2(3H)-indolylidene)-ethylidene]-hydantoin	21 + 32	4900	5375	475	
M70	3-Et-5-[(1,3,3-triMe-2(3H)-indolylidene)-ethylidene]-rhodanine	21 + 23	5000	5385	385	
M71	4-[(1-Et-2(1H)-quinolylidene)-ethylidene]-3-Ph-5(4H)-isoxazolone (X)	6 + 24	5025	5150	125	
M72	4-[(1-Et-4(1H)-quinolylidene)-ethylidene]-3-Ph-5(4H)-isoxazolone (XI)	13 + 24	5425	5650	225	
M73	4-[(1-Me-4(1H)-pyridylidene)-ethylidene]-3-Ph-5(4H)-isoxazolone (XII, *n* = 1)	22 + 24	4700	5140	440	
	Merodicarbocyanine dyes					
M74	3-Et-5-[(3,3-diMe-1-Ph-2(3H)-indolylidene)-2-butenylidene]-rhodanine	1 + 23	5460	6315	855	
M75	3-Et-5-[(1-Et-3,3-diMe-2(3H)-indolylidene)-2-butenylidene]-rhodanine (XV)	8 + 23	5660	6270	610	
M76	3-Et-5-[(3-Et-2(3H)-benzoselenazolylidene)-2-butylidene]-rhodanine	9 + 23	6010	6385	375	
M31	3-Et-5-[(3-Et-2(3H)-benzothiazolylidene)-2-butenylidene]-rhodanine	4 + 23	6050	6315	265	
M77	3-Et-5-[(1-Et-2(1H)-naphtho[1,2]thiazolylidene)-2-butenylidene]-rhodanine	10 + 23	6310	6505	195	
M78	3-Et-5-[(3-Et-2(3H)-benzoxazolylidene)-2-butylidene]-rhodanine	11 + 23	5790	5965	175	
M79	3-Et-5-[(3-Et-2(3H)-thiazolinylidene)-2-butenylidene]-rhodanine	12 + 23	5700	5790	90	
M80	3-Et-5-[(1-Et-2(1H)-quinolylidene)-2-butenylidene]-rhodanine	6 + 23	6630	6600	−30	
M81	3-Et-5-[(1-Et-4(1H)-quinolylidene)-2-butenylidene]-rhodanine	13 + 23	7160	7130	−30	

[a] In Fig. 4. [b] In Fig. 7. [c] A. Wahl and A. Meyer, *Compt. rend.*, **146**, 639 (1908). [d] E. Noelting and H. Blum, *Ber.*, **34**, 2467 (1901). [e] W. Dmowska and S. Weil, *Roczniki Chem.*, **8**, 170 (1938) [*C. A.*, **33**, 592 (1939)]. [f] R. Andreasch and A. Zipser, *Monatsh.*, **26**, 1191 (1905).

ture is indicated by the symbol ⊕⊖. Of the six dyes, the separation of the levels of the structures is least for V, where these levels are very close together, becoming progressively greater on proceeding, in order, to the dyes above V in the figure. The fundamental concepts of resonance theory dictate that the interaction between the levels of the extreme structures is greatest where these levels are closest together, *i.e.*, in V, so that that part of the separation of the *g* and *e* levels which is the result of this interaction is greatest in V. Nevertheless, the *total* separation of the *g* and *e* levels, the transition energy, is least for V and greatest for VI because of the dominant effect of the greater separation of the levels of the *structures* in the upper dyes in the figure.

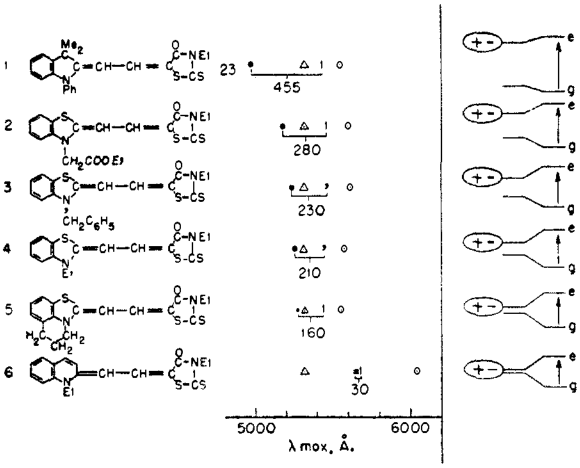


Fig. 1.—Deviations of a series of merocarbocyanines derived from 3-ethylrhodanine; the absorptions were determined in methyl alcohol: ● represents $\lambda_{max.}$ of the merocarbocyanine; ⊙, $\lambda_{max.}$ of the related *sym*, carbocyanine; ⚠, $\lambda_{max.}$ of the *sym*-oxonol (III); | indicates the average between ⊙ and ⚠. The deviation is shown by ⊤.

In the diagrams, the level *e* of the first excited state is shown somewhat higher than that of the appropriate dipolar structure. This may not be correct,[7] but for the present purpose the important thing is to stress the correlation between increased transition energy, *g*→*e*, with increased separation between the levels of the extreme structures.

(3) **Deviation and Chain Length.**—In several groups of unsymmetrical dyes that were previously examined, deviation was found to increase with chain length in a vinylogous series.[5c,d] This generalization is also found to hold for vinylogous series of merocyanines, as may be seen in Fig. 2. For the dyes in the upper part of the figure for which the deviation where $n = 1$ is already considerable, the increase in deviation to where $n = 2$ is very great. However, where the deviation for $n = 1$ is not particularly great, that for $n = 2$ shows no great increase, and in fact the benzoxazole derivatives have deviations of 175 Å. for both chain lengths (*cf.*, Section 9). The 2-quinoline derivative with a very small deviation (30 Å.) where $n = 1$ shows a small negative deviation (−25 Å.) for $n = 2$, but this is not very large, and both values may be treated as close to zero. Similar remarks apply to the 4-quinoline derivatives. It is striking that although the 2- and 4-quinoline derivatives give greatly different deviations in the *p*-dimethylaminostyryl series,[5e] in Fig. 2 both sets of deviations are very small. This is a further illustration of the "Sensitivity Rule" already described[5a,8] and which will be referred to again in the next section.

TABLE III

OPTICAL DATA

Dye no.	Dye name	Nuclei	$\lambda_{max.}$ obsd., MeOH, Å.
	Michler's Hydrol Blue ClO_4		6060
	Symmetrical carbo-[a] and dicarbocyanine dyes		
C1	1,1′,3,3,3′,3′-HexaMe-indocarbocy·I[b]	21 + 21	5450
C2	3,3′-DiEt-hexahydrothiacarbocy·ClO_4	18 + 18	4525
C3	3,3,3′,3′-TetraMe-1,1′-diPh-indodicarbocy·ClO_4	1 + 1	6500
C4	1,1′-DiEt-3,3,3′,3′-tetraMe-indodicarbocy·ClO_4	8 + 8	6410
C5	3,3′-DiEt-selenadicarbocy·I	9 + 9	6660
C6	3,3′-DiEt-thiadicarbocy·I[c]	4 + 4	6500
C7	3,3′-DiEt-4,5;4′,5′-dibenzothiadicarbocy·I[d]	10 + 10	6880
C8	3,3′-DiEt-oxadicarbocy·I[e]	11 + 11	5800
C9	3,3′-DiEt-thiazolinodicarbocy·I[f]	12 + 12	5450
C10	1,1′-DiEt-2,2′-dicarbocy·I[g]	6 + 6	7075
C11	1,1′-DiEt-4,4′-dicarbocy·I[g]	13 + 13	8130
	Symmetrical methine- and trimethineoxonol dyes[h]		
O1	Bis-[3-Et-rhodanine-(5)]-methineoxonol, NEt_3 salt (III)	23 + 23	5320
O2	Bis-[3-Ph-5(4H)-isoxazolone(4)]-methineoxonol, pyridine salt	24 + 24	4255
O3	Bis-[1-Ph-5-pyrazolone-(4)]-methineoxonol	25 + 25	4310
O4	Bis-[1,3-indandione-(2)]-methineoxonol[i]	26 + 26	4600
O5	Bis-[1,3-diEt-2-thiobarbituric acid-(5)]-methineoxonol	27 + 27	4590
O6	Bis-[3-Me-1-Ph-5-pyrazolone-(4)]-methineoxonol[j]	28 + 28	4370
O7	Bis-[1,3-diEt-barbituric acid-(5)]-methineoxonol	29 + 29	4200
O8	Bis-[3-Et-2-thio-2,4-oxazolidinedione-(5)]-methineoxonol, NEt_3 salt	30 + 30	4455
O9	Bis-[1-Et-oxindole-(3)]-methineoxonol	31 + 31	4685
O10	Bis-[3-Et-1-Ph-2-thiohydantoin-(5)]-methineoxonol	32 + 32	5300
O11	Bis-[3-Et-rhodanine-(5)]-trimethineoxonol,[k] NEt_3 salt	23 + 23	6130

[a] For $\lambda_{max.}$ in MeOH of other carbocyanines used, see Part VII.[5e] [b] W. König, *Ber.*, **57**, 685 (1924). [c] T. Ogata, *Proc. Imp. Acad., Tokyo*, 9, 602 (1933). [d] Z. P. Sytnik and B. S. Shteĭngardt, *J. Applied Chem. U.S.S.R.*, 9, 1842 (1936). [e] F. M. Hamer and R. J. Rathbone, *J. Chem. Soc.*, 595 (1945). [f] F. M. Hamer, R. J. Rathbone and B. S. Winton, *ibid.*, 1434 (1947). [g] T. Ogata, *Proc. Imp. Acad., Tokyo*, **8**, 421 (1932). [h] The absorptions of the oxonol dyes were determined in the presence of sufficient piperidine for complete dissociation. [i] G. Errera, *Gazz. chim. ital.*, **32**, 330 (1902). [j] Knorr, *Ann.*, **238**, 184 (1887). [k] F. M. Hamer and B. S. Winton, *J. Chem. Soc.*, 1126 (1949).

The deviations (Δλ) in Fig. 2 where $n = 1$ are plotted against the values for $n = 2$ in Fig. 3. All the points except the first are seen to lie close to a straight line the slope of which is 2.43, and with an intercept on the *x* axis of almost exactly 100 Å. It follows that for a dye with a deviation of at least 175 Å. where $n = 1$, the deviation for $n = 2$ is given very closely by

$$\Delta\lambda_{n=2} = 2.43\,(\Delta\lambda_{n=1} - 100\ \text{Å.})$$

(4) **Relative Basicities of a Series of Nuclei in Three Series of Dyes.**—From the argument given in Section (2) it follows that the order of decreasing deviation for dyes of a given chain length, in the series shown in Fig. 2, would be the order of increasing basicity of the variable (basic) nuclei. These nuclei have already been arranged in order of basicity in two different series, the one a

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(7) W. E. Moffitt, *Proc. Phys. Soc.*, **A63**, 700 (1950).

(8) L. G. S. Brooker, *Rev. Mod. Physics*, **14**, 275 (1942).

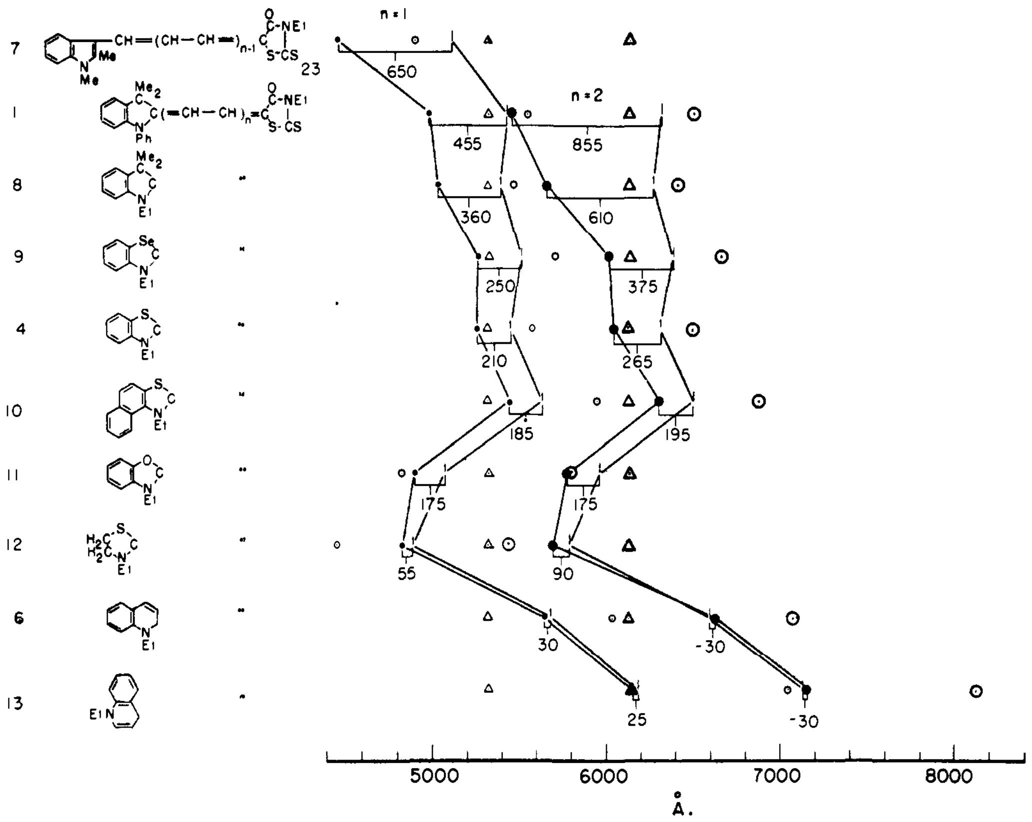


Fig. 2.—Deviations of vinylogous series of merocyanines derived from 3-ethylrhodanine; the absorptions were determined in methyl alcohol: ● represents $\lambda_{\max.}$ of the merocyanine; ⊙, $\lambda_{\max.}$ of the related cyanine; △, $\lambda_{\max.}$ of the related oxonol (III, or its higher vinylog); | indicates the average between ⊙ and △. Deviations are shown by ⊤. The heavier symbols are for $n = 2$.

group of *p*-dimethylaminostyryl dyes and the other a series of unsymmetrical carbocyanines in which 2,5-dimethyl-1-phenylpyrrole was the constant nucleus.[5e] It is clearly of interest to see whether the results obtained in Fig. 2 agree with these earlier determinations. The three methods are compared in Fig. 4, data being plotted for seventeen basic nuclei, *i.e.*, several in addition to those given in Fig. 2.

In Fig. 4 the relative deviations obtained in the two earlier series are given in Columns 1 and 2 and those obtained with merocarbocyanines derived from 3-ethylrhodanine in Column 3. (The deviations in Column 1 are now based on absorptions in methyl alcohol, whereas in the earlier comparisons[5e] the measurements were in nitromethane, chosen because of the instability of Michler's Hydrol Blue perchlorate in methyl alcohol. In spite of instability it is possible to determine $\lambda_{\max.}$ for this dye in methanol (it is 6060 Å.), thus making it possible to use one solvent throughout Fig. 4. The deviations now plotted in Column 1 are in good agreement with those previously obtained using nitromethane; in fact there is somewhat less intersection of the lines between Columns 1 and 2 in Fig. 4 than in Fig. 3 of the earlier reference.[5e])

In Columns 1 and 2, the highest deviations are given by the dyes with the most basic nucleus, whereas in Column 3 the highest deviation is associated with the least basic nucleus. It is therefore necessary to plot the deviations in Column 3 in the opposite direction to those in Columns 1 and 2 in order that the three series shall correspond.

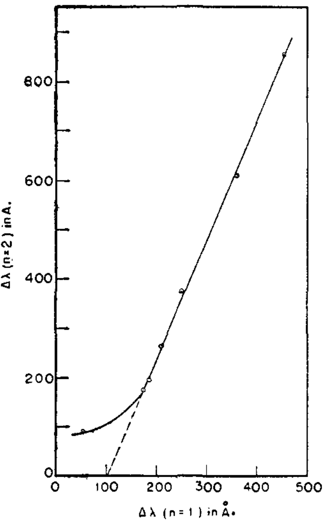


Fig. 3.—Deviations (Δλ) for merocyanines with $n = 1$ plotted against deviations where $n = 2$ (Fig. 2).

For the most part, agreement between the three columns is good. For less basic and moderately basic nuclei, the order is the same except for nuclei of two types. Benzoxazole and particularly thiazoline have smaller deviations in Column 3 and therefore appear to be of higher basicity there than they do in the other columns, though the anomaly with

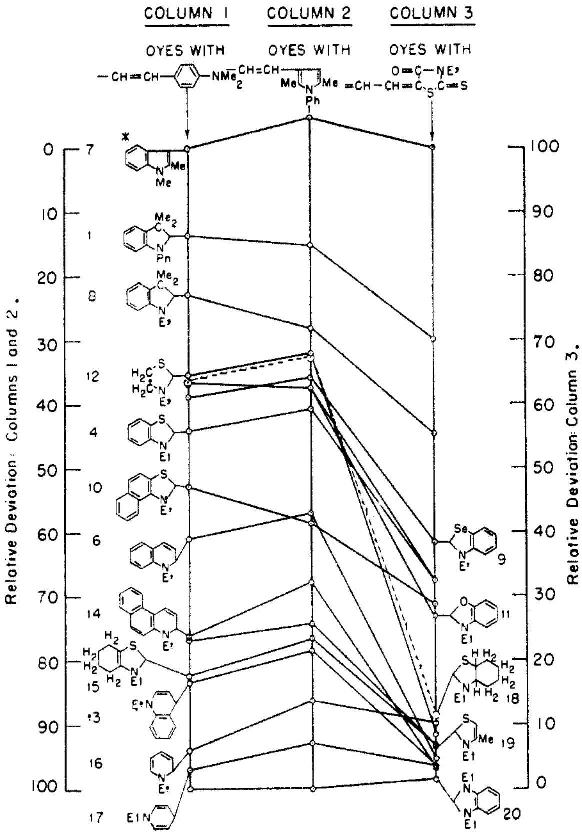


Fig. 4.—Order of basicity of nuclei, a comparison of three methods. Relative deviations are plotted. In Columns 1 and 2, the 1,3-diethylbenzimidazole derivatives have the highest deviations, expressed as 100 arbitrary units in each column. In Column 3, the merocarbocyanine from 1,2-dimethylindole has the highest deviation which is also expressed as 100 arbitrary units. One unit of relative deviation in Column 1 is 13.1 Å.; in Column 2, 9.2 Å.; and in Column 3, 6.5 Å. All absorptions are in methyl alcohol. The indole derivatives have one —CH= group fewer in the chain between the nuclei than the remaining dyes.

benzoxazole is not great. It was at first thought that the thiazolinomerocarbocyanine might be especially heavily stabilized by solvent molecules because of the fact that in the thiazoline ring the polar atoms are relatively exposed, and solvent stabilization (*cf.* Section 7) would result in an increase in stability of the dipolar extreme structure with a consequent reduction of the deviation. In order to test this hypothesis, the merocarbocyanine containing the hexahydrobenzothiazole ring was examined, for this nucleus, though formally a thiazoline, is much bulkier than the unsubstituted thiazoline, and might be expected to show less solvent stabilization. However, the deviation figures for N-ethylhexahydrobenzothiazole derivatives were in all three columns extremely close to those for N-ethylthiazoline, so that the anomaly remains unexplained.

Toward the bottom of Column 3 a number of the more strongly basic nuclei are clustered together, none having a deviation of more than 12 units. This behavior is easily understood in terms of the "Sensitivity Rule" already enunciated,[5a,8] which says that a small change in the energetic asym-

Table IV

Optical Data: Absorptions in Solvents Other than MeOH

Dye no.	Nuclei	λmax. obsd., C_5H_5N, Å.	λmax. calcd., Å.	Deviation, Å.
M33	1 + 23	4980	5525	545
M37	6 + 23	5700	5775	75
M40	9 + 23	5265	5575	310
M42	11 + 23	4980	5160	180
M60	1 + 32	4850	5525	675
M60	1 + 32	5000[a]	5475	475
M61	21 + 24	4865	4950	85
M61	21 + 24	4775[a]	4875	100
M71	6 + 24	5320	5265	−55
M72	13 + 24	5850	5790	−60
M73	22 + 24	5150	5265	115
M87	22 + 24	6100	6250	150

Dye no.	Dye name	Nuclei	Solvent	λmax. obsd., Å.
	Merocyanine dye			
M1	XIX, *n* = 0	4 + 23	C_5H_5N	4320
M1		4 + 23	50% C_5H_5N	4320
	Merocarbocyanine dyes			
M8	XIX, *n* = 1	4 + 23	C_5H_5N	5280
M8		4 + 23	50% C_5H_5N	5395
M82	1,3-DiEt-5-[(1-Et-3,3-diMe-2-(3H)-indolylidene)-ethylidene]-2-thiobarbituric acid (XVIII, *n* = 1)	8 + 27	C_5H_5N	4950
		8 + 27	40% C_5H_5N	4980
	Merodicarbocyanine dyes			
M31	XIX, *n* = 2	4 + 23	C_5H_5N	6050
M31		4 + 23	40% C_5H_5N	6330
M83	1,3-DiEt-5-[(1-Et-3,3-diME-2(3H)-indolylidene)-2-butenylidene]-2-thiobarbituric acid (XVI; XVIII, *n* = 2)	8 + 27	C_5H_5N	5950
M83		8 + 27	40% C_5H_5N	5935
M83		8 + 27	75% EtOH	5895
M83		8 + 27	$C_6H_{11}Ph$	5845
M75		8 + 23	75% EtOH	5880
M75		8 + 23	$C_6H_{11}Ph$	5475
M84	1,3-diEt-5-[(1,3-diEt-2(3H)-benzimidazolylidene)-2-butenylidene]-barbituric acid (XVII)	20 + 29	25% EtOH	4265
M84		20 + 29	$C_6H_{11}Ph$	5550
	Merotricarbocyanine dyes			
M32	XIX, *n* = 3	4 + 23	C_5H_5N	6350
M32		4 + 23	50% C_5H_5N	7330
M85	1,3-DiEt-5-[(1-Et-3,3-diMe-2-(3H)-indolylidene)-2,4-hexadienylidene]-2-thiobarbituric acid (XVIII, *n* = 3)	8 + 27	C_5H_5N	6975
		8 + 27	40% C_5H_5N	6925
	Symmetrical carbo- and dicarbocyanine dyes			
C1		21 + 21	C_5H_5N	5520
C12	3,3,3′,3′-TetraMe-1,1′-diPh-indocarbocy·ClO_4	1 + 1	C_5H_5N	5650
		1 + 1	10% C_5H_5N	5600
C13	1,1′-DiEt-2,2′-carbocy·Br	5 + 6	C_5H_5N	6150
C14	3,3′-DiEt-selenacarbocy·I	9 + 9	C_5H_5N	5750
C15	3,3′-DiEt-oxacarbocy·I	11 + 11	C_5H_5N	4920
C16	1,1′-DiEt-4,4′-carbocy·I	13 + 13	C_5H_5N	7200
C17	1,1′,3,3,3′,3′-HexaMe-indocarbocy·I	21 + 21	C_5H_5N	5520
		21 + 21	10% C_5H_5N	5450
C18	1,1′-DiMe-4,4′-pyrido-carbocy·I	22 + 22	C_5H_5N	6150
C19	1,1′-DiMe-4,4′-pyridodi-carbocy·I	22 + 22	C_5H_5N	7200
	Methine- and trimethineoxonol dyes[b]			
01		23 + 23	C_5H_5N	5400
02		24 + 24	C_5H_5N	4380
02		24 + 24	20% C_5H_5N	4300
010		32 + 32	C_5H_5N	5400
010		32 + 32	20% C_5H_5N	5350
012	Bis-[3-Ph-5(4H)-isoxazolone-(4)]-trimethineoxonol, pyridine salt	24 + 24	C_5H_5N	5300

[a] In 10% pyridine. [b] The absorptions of the oxonol dyes were determined in the presence of sufficient piperidine for complete dissociation.

metry of the extreme structures produces a small effect on the deviation of an energetically symmetrical or nearly symmetrical dye, but a much greater effect on the deviation of a highly unsymmetrical dye. Thus, the strongly basic nuclei are well differentiated in Columns 1 and 2, where the unsymmetrical dyes containing them have large deviations and are therefore highly unsymmetrical, but are ill differentiated in Column 3, where they have small deviations, the dyes being energetically much more nearly symmetrical.

(5) Relative "Acidities" of a Series of Nuclei.—Just as it is possible to arrange basic nuclei in order of basicity by a comparison of the deviations that they give when combined into merocarbocyanines, so it is possible to arrange a series of carbonyl-containing nuclei, as they occur in merocyanines, in order of relative electron-attracting power, or "acidity." The results of such a comparison are shown in the left-hand column of Fig. 5, where the deviations are compared for a series of merocarbocyanines derived from a variety of cyclic ketomethylene compounds and having 3,3-dimethyl-1-phenylpseudoindole as the constant nucleus. This feebly basic ring was deliberately chosen; it was felt that it would give a satisfactory differentiation between the variable acidic nuclei. The deviations range from 45 to 575 Å.

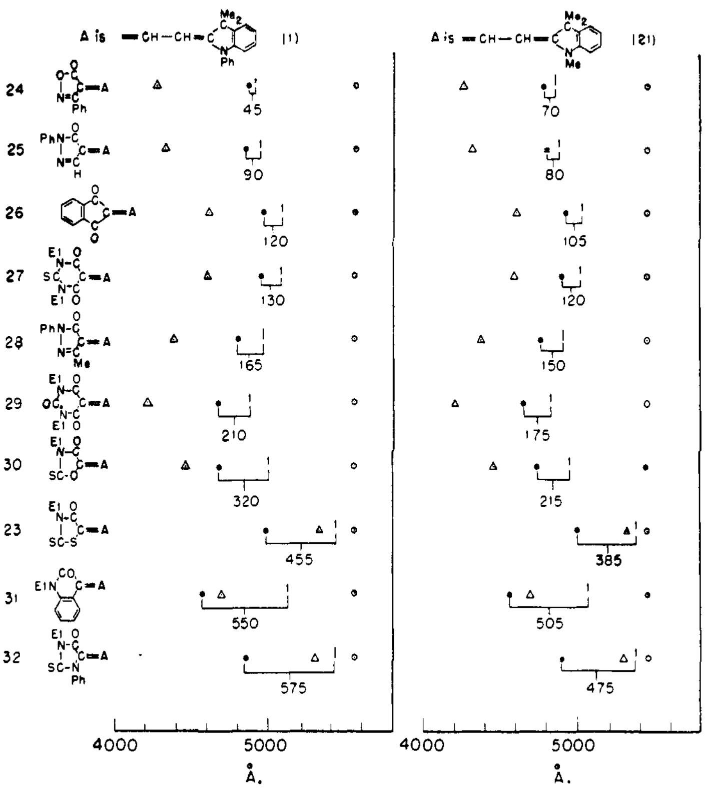
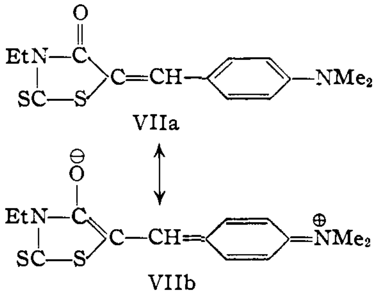


Fig. 5.—Order of acidity for ten carbonyl-containing nuclei. Values of $\lambda_{max.}$ in methyl alcohol are as follows: ●, merocyanine; ⊙, *sym*-carbocyanine; △, *sym*-oxonol; |, average between ⊙ and △; ⊤ indicates deviation, the magnitude being given in Å.

Considering the feeble basicity of the 3,3-dimethyl-1-phenylpseudoindole nucleus, there can be little doubt that all, or nearly all, of the deviations of derivatives of this nucleus shown in Fig. 5 are the result of the lower energy, in each case, of the uncharged extreme structure of the merocarbocyanine. But where the deviation is small, the possibility exists that the carbonyl-containing nucleus is so strongly acidic that the dipolar structure of the merocyanine is somewhat lower in energy than the uncharged structure. That these interpretations are apparently correct follows from an examination of the set of deviations in the right-hand column of Fig. 5. In these, the carbonyl-containing nuclei are kept as before, but the basic nucleus is replaced by the slightly more basic 1,3,3-trimethylpseudoindole nucleus. If a deviation in the left-hand column of the figure is the result of the uncharged extreme resonance structure having lower energy, then the corresponding dye in the right-hand column should have a somewhat smaller deviation. This relationship is seen actually to hold for all the carbonyl-containing nuclei except the topmost one, where the deviation is increased. But in any case the deviations in both columns establish the order of *increasing* deviation as the order of *decreasing* acidity of the carbonyl-containing nuclei.

It is of interest to see whether the order found in Fig. 5 agrees with that obtained from a study of *p*-dimethylaminobenzylidene derivatives such as VII. These dyes, obtained by condensing the appropriate keto-methylene compounds with *p*-dimethylaminobenzaldehyde, are the structural hybrids between Michler's Hydrol Blue and oxonols such as III. The absorptions of dyes of this type show very large deviations (Fig. 6), which is unquestionably the result of the appreciably lower energy of the uncharged structures, such as VIIa, relative to polar structures, such as VIIb. The latter are unstable for two reasons: their polar nature and the quinonoidal state of the benzene ring. If this assumption is correct, then the high energy of VIIb should be lowered by replacing the 3-ethylrhodanine ring by one of higher acidity, the deviation being reduced. The deviations of these benzylidene dyes should therefore serve for the arrangement of the acidic nuclei in order of increasing acidity. The data given in Fig. 6 show that the order actually obtained in this way closely follows that obtained in Fig. 5. The two sets of results are compared in Fig. 7, and although the agree-



VIIa

VIIb

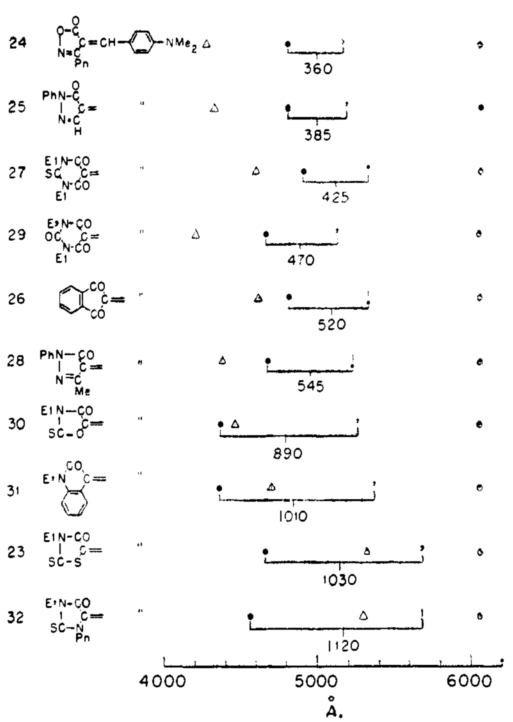


Fig. 6.—Deviations of *p*-dimethylaminobenzylidene dyes. Values of $\lambda_{max.}$ in methyl alcohol are shown as follows: ●, *p*-dimethylaminobenzylidene compound (*e.g.*, VII); ⊙, Michler's Hydrol Blue perchlorate; ▲, symmetrical oxonol; |, arithmetic mean between ⊙ and ▲. Deviations are shown by ⊤, the magnitude being given in Å.

ment is not perfect, it is as good as can reasonably be expected from comparisons of this nature.

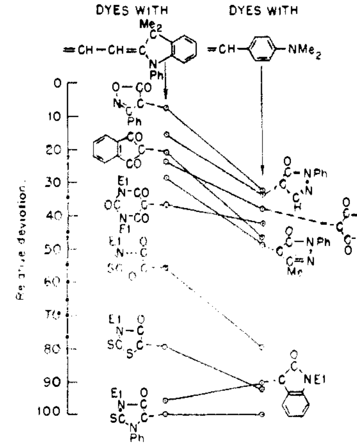
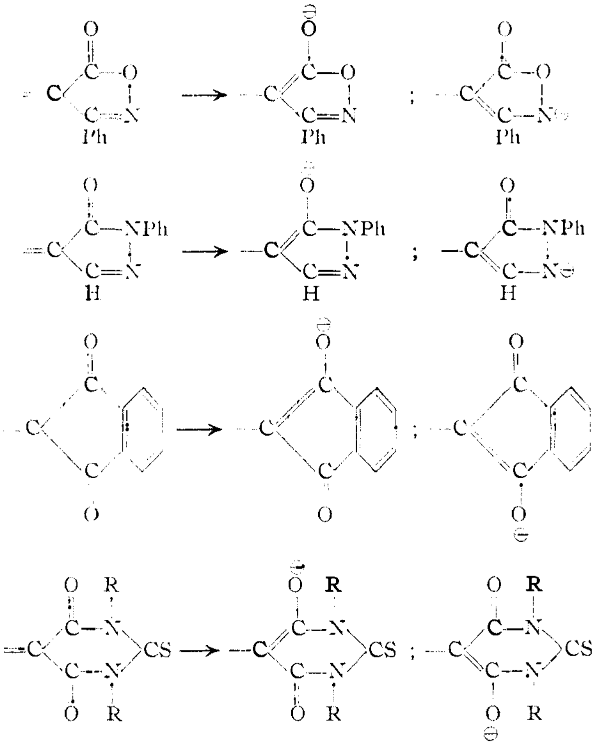


Fig. 7.—Order of acidity of nuclei, a comparison of two methods. In each series the highest deviation is taken as 100 arbitrary units. For dyes from Fig. 5 one unit of relative deviation equals 5.75 Å., and for dyes from Fig. 6 one unit equals 11.2 Å.

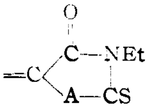
(6) Resonance Interpretation of the Relative Acidities of a Series of Nuclei.—In attempting to account for the order of acidity of the nuclei in Figs. 5, 6 and 7, one broad principle stands out. The ten nuclei may be divided into two groups, in one of which the negative charge may be located with considerable plausibility on either of two atoms, in the charged way of writing the ring, as shown below:

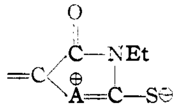


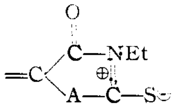
For indandione and the barbituric and thiobarbituric acids, the two atoms that can assume the negative charge are both oxygen and are identically linked, though in isoxazolone and pyrazolone, one atom is oxygen and the other nitrogen. It is highly significant that the possibility of sharing the charge between predominantly two atoms is restricted to the six most strongly acidic nuclei; the conclusion is inescapable that the additional stabilization that accrues from this possibility is responsible for the high acidity of the nuclei.

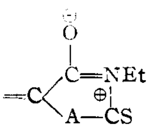
For the four less acidic nuclei, it is not possible to locate the negative charge on an atom other than the carbonyl oxygen, hence the low position of the nuclei on the list.

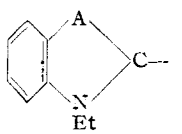
Another comparison concerns the relative positions of the three nuclei of the type VIII (A = O, S or NPh) which may be accounted for as follows: In the basic nuclei IX (A = O, S or NPh) the order of increasing basicity is undoubtedly


VIII


VIIIa


VIIIb


VIIIc


IX

O < S < NPh,[5e,9] which may be accounted for in terms of the increasing stability of the charged

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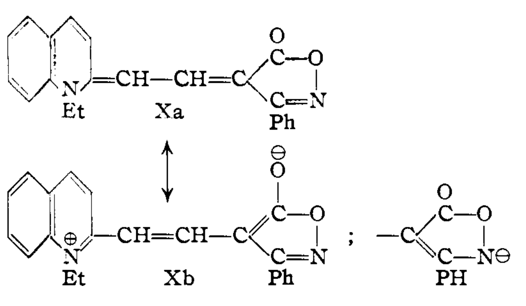
(9) It seems safe to assume that the basicity of the 1-ethyl-3-phenylbenzimidazole nucleus will not be lower than that of N-ethylbenzothiazole.

groupings $-\overset{\oplus}{O}=\ <-\overset{\oplus}{S}=\ <-\overset{\oplus}{N}Ph=$ relative to the uncharged groupings. Applied to VIII, this conclusion points to contributions of the type of VIIIa in the same order, but in VIIIa the negativity of the thiocarbonyl sulfur is partly drained off, so that this atom is less able to polarize as in VIIIb. But the more the >NEt group is polarized as in VIIIb the less it can polarize as in VIIIc, which contribution would normally hinder the carbonyl oxygen from accepting an electron by polarization of the main chromophoric chain of the dye. The end result of these balances is that the nucleus with the most basic value of A, the thiohydantoin, will show the lowest acidity of the three, while that with the least basic A grouping, the thioöxazolidinedione, will be the most acidic.

In a third comparison, the higher acidity of the 1,3-diethyl-2-thiobarbituric acid nucleus relative to 1,3-diethylbarbituric acid follows from the higher acidity of >C=S relative to >C=O.

(7) Polarity and Solvatochromism of the Merocyanines.—If one of the more highly acidic nuclei in Fig. 7, such as that from 3-phenylisoxazolone, were combined with a strongly basic nucleus, as 2-quinoline, the resulting dye (X) would have an uncommonly high contribution from the dipolar structure (Xb) and might even show a deviation in methyl alcohol because of the appreciably lower energy of this structure. Experiment confirms this deduction, the deviation for X being 125 Å. (Fig. 8). Furthermore, replacement of the 2-quinoline nucleus in X by the still more basic 4-quinoline and 4-pyridine nuclei, in XI and XII (n = 1), respectively, increases the deviation still further (to 225 and 440 Å., respectively) (Fig. 8).



Dyes X, XI and XII (n = 1), which show deviations in methyl alcohol because of the lower energy of the dipolar structures, are thus strongly polar merocyanines which contrast sharply with the weakly polar merocyanines already described (*e.g.*, those showing appreciable deviations in Figs. 1 and 2 which deviate because of the lower energy of the uncharged structures). Some of these weakly polar dyes are included in the upper part of Fig. 8. Between the two extreme types in this figure there is V, with its small deviation; this dye constitutes a moderately polar intermediate type.

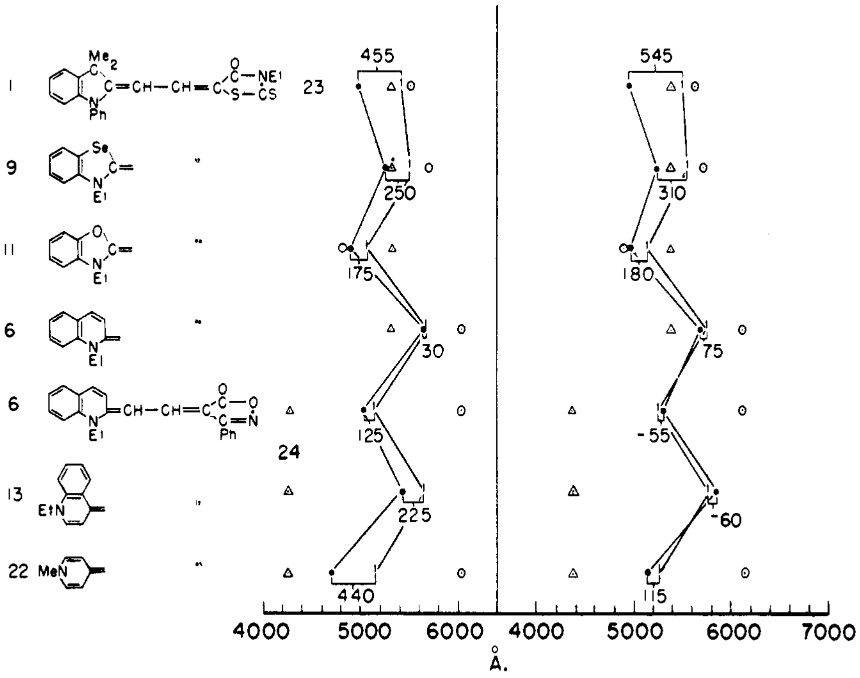
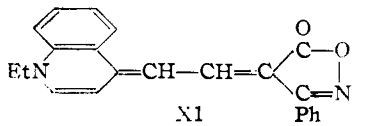
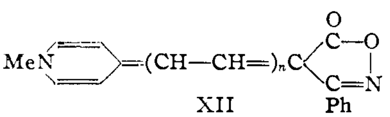


Fig. 8.—Deviations of merocarbocyanines. In the comparisons on the left, values of $\lambda_{max.}$ in methyl alcohol are shown as follows: ●, merocarbocyanine; ⊙, symmetrical carbocyanine; △, symmetrical oxonol; |, arithmetic mean between ⊙ and △. Deviations in Å. are shown by ⊤. In the comparisons on the right, the absorption and deviations are for pyridine solutions. The $\lambda_{max.}$ values for 1,1′-diethyl-4,4′-carbocyanine iodide are not shown; they are 7050 and 7200 Å. for methyl alcohol and pyridine, respectively.


XI


XII

The essential correctness of the above classification is confirmed in the following way: the methyl alcoholic absorptions summarized in the left-hand part of Fig. 8 were redetermined in a less polar solvent, anhydrous pyridine. The higher the polarity of the solvent the greater will be its ability to form electrostatically oriented dipole layers around the polar atoms of the dye molecule, especially if these atoms are well exposed and there are several of them. For all merocyanines the solvent dipole layers will effectively stabilize the dipolar contributing structure. In passing from a solvent of moderate polarity such as methyl alcohol to one of lower polarity, pyridine, the solvent

TABLE V

OPTICAL DATA FOR FIGURE 9

% C_5H_5N	0	10	20	30	40	50	60	70	80	90	95	100
M86 A. 4-(1-Me-4(1H)-pyridylidene)-3-Ph-5(4H)-isoxazolone (XII, n = 0)												
$\lambda_{max.}$, Å.	3635	3700		3750		3800	3810		3880	3920		4000
$\epsilon_{max.} \times 10^{-4}$	2.8	2.91		2.97		3.17	3.24		3.4	3.44		3.5
M52 B. 4-[(1-Me-4(1H)-pyridylidene)-ethylidene]-3-Ph-5(4H)-isoxazolone (XII, n = 1)												
$\lambda_{max.}$, Å.	4350	4500	4575	4625	4675	4700	4750	4800	4895	4975	5150	
$\epsilon_{max.} \times 10^{-4}$	3.48	3.72	3.89	3.97	4.14	4.39	4.54	4.79	5.25	5.91	7.58	
M87 C. 4-[(1-Me-4(1H)-pyridylidene)-2-butenylidene]-3-Ph-5(4H)-isoxazolone (XII, n = 2)												
$\lambda_{max.}$, Å.	4700	4950	5080	5150	5220	5300	5380	5450	5600	5800	5920	6100
$\epsilon_{max.} \times 10^{-4}$	3.77	4.11	4.34	4.4	4.62	4.86	5.25	5.55	6.3	7.58	8.87	11.8
M88 D. 4-[(1-Me-4(1H)-pyridylidene)-2,4-hexadienylidene]-3-Ph-5(4H)-isoxazolone (XII, n = 3)												
$\lambda_{max.}$, Å.	4875	5150	5250	5375	5475	5525	5650	5800	5950	6385	6725	7100
$\epsilon_{max.} \times 10^{-4}$	3.0	3.1	3.14	3.46	3.5	3.56	3.59	3.91	4.16	4.42	5.1	9.37
M61 E. 3-Ph-4-[(1,3,3-triMe-2(3H)-indolylidene)-ethylidene]-5-(4H)-isoxazolone (XIV)												
$\lambda_{max.}$, Å.		4780				4850						4865
$\epsilon_{max.} \times 10^{-4}$		6.80				7.38						7.54
M60 F. 5-[(3,3-DiMe-1-Ph-2(3H)-indolylidene)-ethylidene]-3-Et-1-Ph-2-thiohydantoin (XIII)												
$\lambda_{max.}$, Å.			5020	5020	5020	5000	4980	4980	4920	4900		4850
$\epsilon_{max.} \times 10^{-4}$			7.26	7.26	7.17	7.03	7.03	6.95	6.7	6.55		6.75

stabilization of the dipolar structure of the merocyanine will be reduced. For weakly polar merocyanines, this should result in a further increase in the asymmetry of the extreme structures and an increase in deviation, whereas for a strongly polar merocyanine the asymmetry of the extreme structures should be reduced, and likewise the deviation.

The deviations plotted in the right-hand part of Fig. 8 for pyridine solutions show that these predictions are realized in practice. The two extreme types of merocyanines are sharply differentiated, the deviation of the least polar representative in the series being increased from 455 to 545 Å., while that of the most polar dye is reduced from 440 to 115 Å. Intermediate types are less affected by the change; for instance, the deviation of V in both methyl alcohol and pyridine is not great.

Other things being equal, a merocyanine having little or no deviation is deeper in color than one with a considerable deviation, and it is important to realize that a steady increase in intrinsic polarity from the most weakly polar to the most strongly polar merocyanine is not accompanied by a progressive fall in deviation and deepening of color. A minimum deviation and maximum depth of color in any given solvent is reached when the uncharged and dipolar extreme structures have the same energy; on *either* side of this "equator" a deviation is encountered, with lightening of color.

Since the deviation of XII (n = 1) was reduced in going from moderately polar methyl alcohol to less polar pyridine, it was thought that by proceeding to strongly polar aqueous pyridine (9 vol. water to 1 vol. pyridine) the deviation would be increased. This was found to be true; in this solvent mixture the deviation reached the high value of 675 Å. In these determinations with XII (n = 1) there was a marked net shift of $\lambda_{max.}$ to shorter wave lengths with increasing polarity of the solvent. The dye has $\lambda_{max.}$ 5150 Å. in anhydrous pyridine, 4700 Å. in methyl alcohol and 4500 Å. in aqueous pyridine.

It should be mentioned that after we had prepared strongly polar merocyanines such as XII (n = 1) and had arrived at the present explanation of their behavior, our attention was called by the late Dr. S. E. Sheppard to the interesting and penetrating speculations of Förster, in which it was suggested that in un-ionized dyes, characterized by a heavy contribution of a dipolar structure, the absorption would be shifted to shorter wave lengths with increasing polarity of the solvent.[10] At the time of Förster's paper it was not known how to construct molecules having the properties he described; in fact, Sheppard doubted whether such exceedingly polar molecules could be realized in practice,[11] though he later modified his doubts.[12]

The results described above for XII (n = 1) suggested the determination of the absorptions not only in pure pyridine and in pure water, but in mixtures of the two. Values of $\lambda_{max.}$ and $\epsilon_{max.}$ so obtained are plotted in Fig. 9, B, the figures on the curves showing the parts, by volume, of pyridine in 100 parts of solvent. Similar curves were plotted for the lower vinylog of the dye (XII, n = 0; Fig. 9, A) and for the higher vinylogs (XII, n = 2 and 3; Fig. 9, C and D, respectively).

Even for the dye with the shortest chain (XII, n = 0), the effect of change of solvent on the absorption is considerable, $\lambda_{max.}$ water being 3635 Å. and $\lambda_{max.}$ pyridine 4000 Å., but for the dyes with longer chain lengths the shifts reach an unprecedented magnitude. These strongly polar dyes are extraordinarily sensitive to change in polarity of the solvent. For XII (n = 1), going from water to

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[10] Th. Förster, *Z. Elektrochem.*, **45**, 572 (1939).

[11] S. E. Sheppard, P. T. Newsome and H. R. Brigham, THIS JOURNAL, **64**, 2934 (1942).

[12] S. E. Sheppard and P. T. Newsome, *ibid.*, **64**, 2941 (1942).

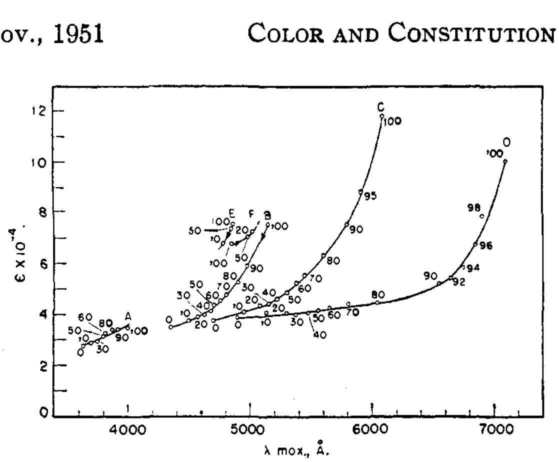
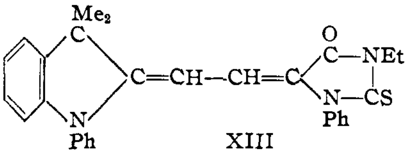


Fig. 9.—Curves A, B, C, D and plots of $\epsilon_{max.}$ against $\lambda_{max.}$ for the vinylogous series XII (n = 0, 1, 2, 3), respectively, in pyridine and water and mixtures of the two. Figures on the curves indicate parts by volume of pyridine in 100 volumes of solvent. Curves E and F pertain to XIV and XIII, respectively.

anhydrous pyridine produces a shift in $\lambda_{max.}$ of 800 Å., the corresponding figures for XII (n = 2 and 3) being 1400 and 2200 Å., respectively.

Each of the curves A, B, C and D in Fig. 9 may be regarded as the trace of the absorption maxima of a continuous series of dyes showing progressively increasing asymmetry of the extreme structures, produced, not by structural changes, as are, for example, the series of merocyanines shown in Figs. 1 and 5, but by *progressive change in the environment* of a single molecular species. Since the dyes are closest to energetic equivalence of the extreme structures in pure pyridine, it follows from the hyperbolic nature of the curves for the three dyes of longer chain length that the most conspicuous effect of introducing the next energetic asymmetry (*i.e.*, going from pure to 95% pyridine) is to reduce $\epsilon_{max.}$, though $\lambda_{max.}$ is also affected. Further down the curves the effect on $\epsilon_{max.}$ of increasing the asymmetry is considerably less until, in going from water containing 10% pyridine to pure water, there is very little further change in $\epsilon_{max.}$, though $\lambda_{max.}$ is still sensitively affected. These results have an obvious bearing on the relation between asymmetry of the extreme structures and light absorption not only for merocyanines but for dyes in general.

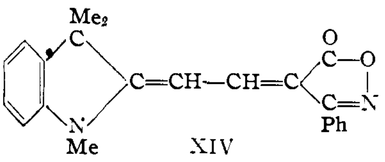
The behavior of the dyes XII may be contrasted with that of the very weakly polar XIII. This dye has the large deviation in methyl alcohol of 575 Å.,



XIII

and although the deviation is affected by change in the polarity of the solvent, as would be expected of a weakly polar dye, the changes are not very great (Fig. 10). The polarity of this dye is low, and any added solvent stabilization is rather low too.

The moderately polar dye XIV, in which a weakly basic nucleus is linked to one that is strongly acidic, shows only a small deviation in methyl alcohol, and is relatively insensitive to changes in environment (Fig. 10), as might have been expected from the "Sensitivity Rule" already referred to.



XIV

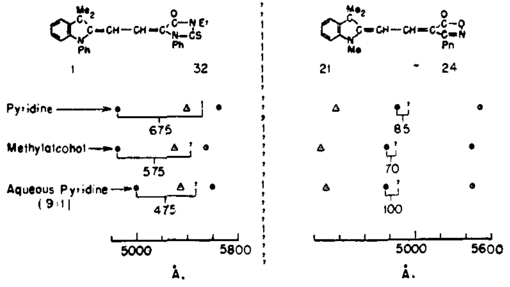


Fig. 10.—Deviations of XIII and XIV in various solvents; ● indicates $\lambda_{max.}$ of the merocarbocyanine; ⊙, $\lambda_{max.}$ of the related symmetrical carbocyanine; △, of the related symmetrical oxonol and |, the arithmetic mean between ⊙ and △. Deviations, ⊤, are given in Å.

For comparison with the relatively strongly polar dyes XII, values of $\lambda_{max.}$ and $\epsilon_{max.}$ for XIII and XIV are plotted in Fig. 9. With increasing polarity of the solvent, the feebly polar XIII (curve F) shows what has until now been regarded as "normal" behavior for un-ionized dyes, *i.e.*, $\lambda_{max.}$ shifts to *longer* wave lengths with increasing polarity of the solvent (indicated by the direction of the arrow heads on the curves). The description of this behavior as "normal" follows from the fact that in un-ionized dyes that have been encountered in the past, the non-polar contributing structure was usually of lower energy than the polar structure. Reversal of the usual behavior by dyes such as XII, which are characterized by low-energy dipolar structures, has been infrequent until now, though a wide variety of dyes that behave in this way are now seen to be available. Furthermore, such dyes are apparently no less stable than less polar merocyanines.

It is interesting that the amount of the "reversed" solvatochromic shift shown by dyes such as XII, is so very much greater than the "normal" shift shown by a dye such as XIII. This is because in the solvent stabilization of a feebly polar dye such as XIII, the solvent in effect stabilizes a dipolar structure which is of much less significance to the resonance than the uncharged structure, whereas in the dyes XII the solvent stabilizes a structure which is equally as important as, or even more important than, the second extreme structure.

It is sometimes helpful to distinguish between the *intrinsic* polarity of a merocyanine, assessed by considering the relative energies of the extreme structures unperturbed by outside influences, and the *effective* (or *conditioned*) polarity, which is the intrinsic polarity modified by the solvent or other environmental stabilization. Deviations, or the degree of convergence (*cf.* Section 9) determined in some very weakly polar solvent, will give a rough estimate of the intrinsic polarity, while the effective polarity of the dye will always be higher in solvents of higher polarity. The difference between intrinsic and effective polarity will be greater the higher the intrinsic polarity, at least, for the dyes studied in the present paper.

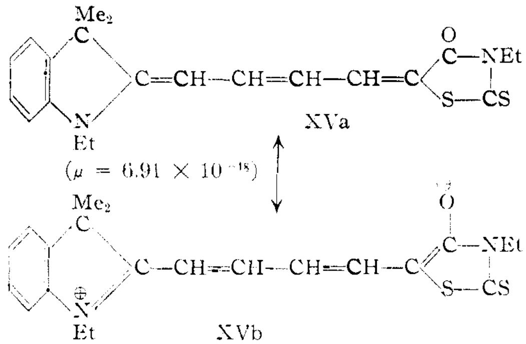
Dye VI, with its deviation in weakly polar pyridine of 545 Å. (Fig. 8), has low intrinsic polarity, and although the deviation is reduced to 455 Å. in methyl alcohol, the effective polarity of the dye in this solvent is still much lower than that required for energetic equivalence of the extreme structures.

In a comparison of un-ionized dyes, one with a 20% contribution of a dipolar structure, although weakly polar in an absolute sense, would nevertheless be strongly polar compared with a dye for which the corresponding contribution was only 10%. In the present comparisons the criterion of deviation shows that dyes such as V and XIV receive contributions of around 50% from their dipolar structures when dissolved in solvents of moderate polarity. The dyes XII must receive contributions well in excess of this figure, perhaps 80%, in solvents of moderate or high polarity.

The effect on the absorption of heating solutions of merocyanines may be understood according to the principle that increase in temperature generally lowers the dielectric constant of a solvent and tends specifically to disrupt the oriented solvent dipoles around the solute. When in a given solvent a dye deviates because of predominant non-polarity, heating the solution tends to increase the deviation and lighten the color, but if the dye deviates because of predominant polarity, heating lessens the deviation and deepens the color. Temperature effects are generally more marked with dyes of the second category; thus, XII ($n = 2$) gives a solution in ethyl alcohol which is crimson at 0° but violet at the boiling point.

(8) **Dipole Moments.**—When the analysis of absorption relationships had made it clear that merocyanines could be constructed that were weakly polar or strongly polar or of virtually any intermediate value, three representative dyes, XV, XVI and XVII, were prepared which, from their nuclei, would be expected to be weakly polar, moderately polar and strongly polar, respectively. Increasing polarity of the dyes in the order XV, XVI, XVII may be explained in a rough comparative way by noting that for one principal dipolar contributing structure for XV (XVb) there are two such structures for XVI (XVIb) and four for XVII (XVIIb).

Absorption data for the three dyes in solvents of different polarities agreed with the above designations. Dye XV showed the "normal" bathochromic shift with increasing polarity of the solvent, having $\lambda_{\text{max.}}$ 5475 Å. in feebly polar phenylcyclohexane, and $\lambda_{\text{max.}}$ 5880 Å. in strongly polar aqueous ethanol (1:3); XVI was relatively little affected by solvent changes, having $\lambda_{\text{max.}}$ 5845 Å. in phenylcyclohexane and $\lambda_{\text{max.}}$ 5895 Å. in aqueous ethanol; and XVII showed strong inversion of the "normal" behavior, with $\lambda_{\text{max.}}$ 5550 Å. in phenylcyclohexane and $\lambda_{\text{max.}}$ 4265 Å. in aqueous ethanol.

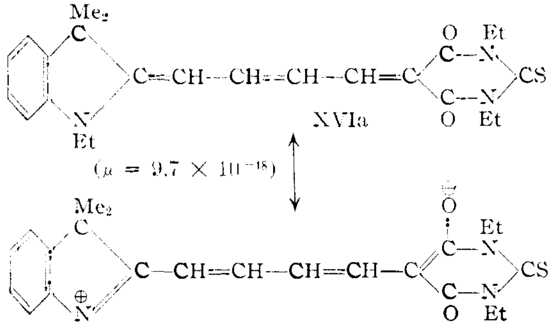


XVa

($\mu = 6.91 \times 10^{-18}$)

XVb

(1 dipolar structure)

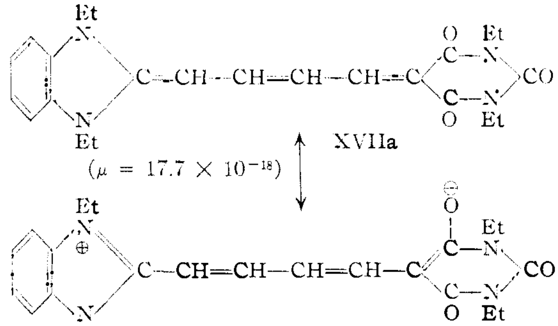


XVIa

($\mu = 9.7 \times 10^{-18}$)

XVIb

(2 dipolar structures)



XVIIa

($\mu = 17.7 \times 10^{-18}$)

XVIIb

(4 dipolar structures)

Dipole moment determinations for the three dyes were carried out through the kindness of Dr. C. P. Smyth, who reported results which fully confirmed our predictions. The figures given show that XV had the lowest dipole moment of the three, while that of XVII was the "largest yet observed for a molecule other than that of a salt or a zwitterion."[13]

(9) **Convergence and Non-convergence of the Merocyanines.**—These characteristics of vinylogous series may in many cases be controlled by a judicious choice of solvent. It may be seen from Fig. 9 that the vinylene shifts in the series XII are non-convergent for $\lambda_{\text{max.}}$ values in pyridine but strongly convergent for $\lambda_{\text{max.}}$ values in water. The data are plotted in Fig. 11 in a way that makes the relationship clearer.

The four curves in Fig. 11 are remarkably similar in shape, but the slope at any point in one of them is less than the slope in the corresponding part of the curve for the dye with the next higher chain length. The slopes are greatest in the neighborhood

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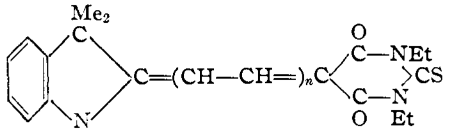
[13] L. M. Kushner and C. P. Smyth, THIS JOURNAL, **71**, 1401 (1949).

of the pure solvents, pyridine and water; in these regions the $\lambda_{\max.}$ values of the absorptions are especially sensitive to a small change in composition of the solvent, and this sensitivity increases regularly with n. There is little doubt that $\lambda_{\max.}$ determinations with XII (n = 2 or 3) could be used for estimating water (or other strongly polar substance) in pyridine (or other relatively non-polar liquid). It remains to be seen whether the convergence–non-convergence pattern brought out in Fig. 11 applies to vinylogous series in general, and not merely to one group of merocyanines, but this seems a possibility.

The non-convergence of the $\lambda_{\max.}$ values for the dyes XII in pure pyridine, which would normally indicate approximate energetic equivalence of the extreme structures, stands in apparent contradiction to the existence of deviations in this solvent, 115 Å. for XII, $n = 1$ (Fig. 8) and 150 Å. where $n = 2$. However, the deviation for $n = 2$ does not greatly exceed that for $n = 1$, and such relative constancy of the deviations for successive vinylogs assures non-convergence of the series as effectively as the absence of deviations. The situation with XII does not seem to be uncommon with the merocyanines, for other examples where the deviation of a dye with $n = 2$ is not very much greater than that with $n = 1$ are seen in Fig. 2.

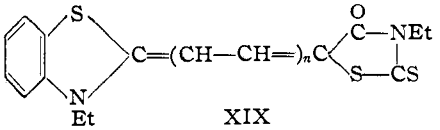
It seems likely that although the series XII is non-convergent in pyridine, the dipolar structures nevertheless dominate, for the absorptions respond sensitively and continuously to added asymmetry of the structures produced by adding water to the solvent.

On the other hand, members of the series XVIII are relatively insensitive to changes of solvent, behavior typical of dyes of intrinsically moderate polarity. For n = 1, 2 and 3, the values of $\lambda_{\max.}$ in pyridine are 4950, 5950 and 6975 Å., respectively, and 4980, 5935 and 6925 Å. in the same order in highly aqueous pyridine (2 vol. pyridine to 3 vol. water). In neither solvent is there any marked convergence. It seems likely that the extreme structures of these dyes in pyridine solution are much nearer the *iso-energetic* point (*cf.* following paper) than are those of XII in the same solvent.



XVIII

The vinylogs XIX are typical of a rather weakly polar series. For n = 0, 1, 2 and 3, the $\lambda_{\max.}$ values in anhydrous pyridine are 4320, 5280, 6050 and 6350 Å., respectively, the values showing marked convergence. In 50% aqueous pyridine, the maxima lie at 4320, 5395, 6330 and 7330 Å., respectively, and are practically non-convergent.



XIX

Convergence of a series is thus partly a function of the intrinsic polarity of the vinylogs and partly of the polarity of the solvent. It is favored by solvents that promote high asymmetry of the extreme structures, and is strongly dependent upon the choice of solvent when the vinylogs are either intrinsically weakly polar or strongly polar.

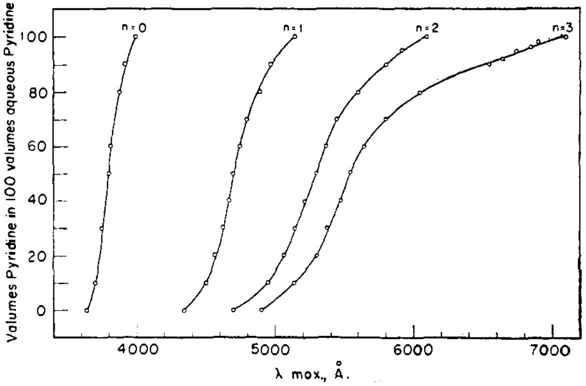
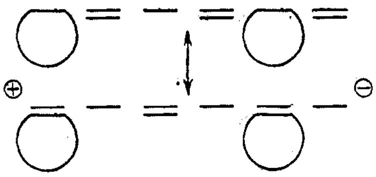


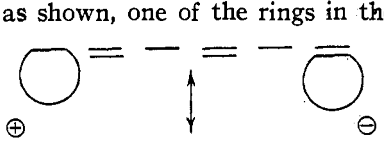
Fig. 11.—Plot of $\lambda_{\max.}$ for the dyes XII (n = 0, 1, 2, 3) against percentage by volume of pyridine–water mixtures.

(10) **Relation of the Merocyanines to Certain Other Un-ionized Compounds.**—The considerable depth of color shown by many merocyanines is a result of the fact that in the amidic resonance that characterizes them, the dipolar structure enjoys unusually high stability (for un-ionized dyes as a class). This is because *each* of the ring systems in a merocyanine acquires an extra double bond in the dipolar structure, and with it additional stabilization.

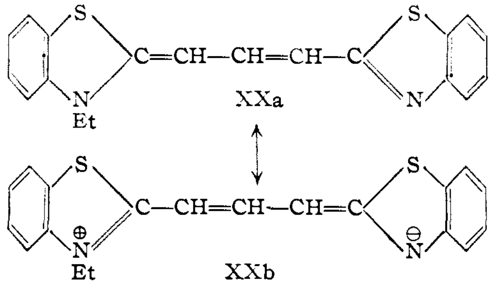
Thus, there are six linkages between the auxochromic atoms of a merocarbocyanine such as I, half of them single and half double bonds, as shown. In the uncharged structure, two single bonds of these six are included in ring systems; these become double bonds in the dipolar structure, the rings thereby acquiring additional stabilization the amount of which varies from dye to dye.



If in another type of un-ionized dye the rings are disposed as shown, one of the rings in the dipolar structure gains a double bond, but the gain in stabilization is offset by a loss in the second ring, which loses a double bond. In such a system, the dipolar structure will not, in general, acquire the additional stabilization characteristic of the merocyanines. In spite of this handicap, however, it is possible to select the rings so that the dye absorbs

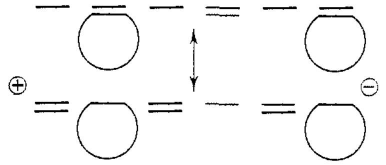


at relatively long wave lengths. Anhydronium bases of cyanines (*e.g.*, XX) illustrate this general

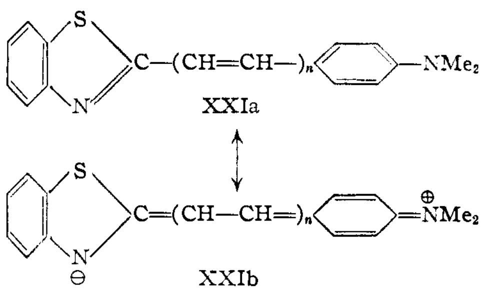

XXa
XXb

type, and deeply colored bases of this class have been described.[14] Another example is phenol blue.[5b]

In a third type of un-ionized dye, the conjugated chain passes through two rings as shown:

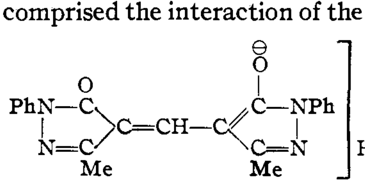


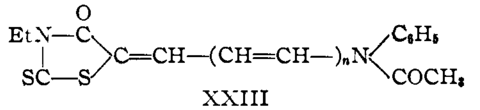
Here the polar structure *loses* stabilization in each ring; it is therefore especially high in energy, and such compounds tend to absorb at short wave lengths and to form strongly convergent series. They are illustrated by bases such as XXI.[5a]


XXIa
XXIb

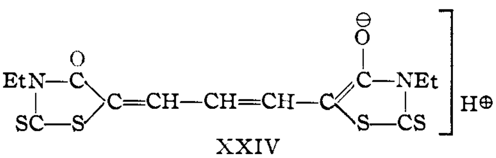
The merocyanines as a class clearly tend to be more polar than types such as XX and XXI. However, a classical uncharged formula may be written for even extremely polar merocyanines, hence they would appear to be less polar than "meso-ionic" compounds.[15,16]

(11) **Symmetrical Oxonols.**—The absorptions of a number of monomethine oxonols and of one trimethineoxonol were required for the calculation of merocyanine deviations. Certain monomethine oxonols have been known for a long time, that from 3-methyl-1-phenyl-5-pyrazolone (XXII), for instance, was prepared by several methods, one of which comprised the interaction of the pyrazolone with ethyl orthoformate.[17] This method proved satisfactory for other highly acidic nuclei, but failed with nuclei of lower acidity, so that relatively strong ionization of the methylene hydrogen seems to be a necessary condition for the reaction. An alternative method which gave some of the desired dyes comprised interaction of acetanilidomethylene intermediates such as XXIII ($n = 0$) with a further equivalent of keto-methylene compound[18]; intermediates such as XXIII ($n = 0$) were prepared by the reaction of the keto-methylene compound with diphenylformamidine,[19] with subsequent acetylation. A simpler method for preparing the oxonols, and one which is successful even when applied to keto-methylene compounds of low acidity, consists in the condensation of the keto-methylene compound with the very reactive diethoxymethylacetate.[20]


XXII


XXIII

The trimethineoxonol (XXIV) was prepared by the condensation of XXIII ($n = 1$) with 3-ethylrhodanine in pyridine solution using triethylamine as condensing agent.[18] The necessary intermediate (XXIII), $n = 1$) was obtained by condensing 3-ethylrhodanine with β-anilinoacrolein anil hydrochloride in acetic anhydride solution.


XXIV

Oxonols are conveniently named by a method similar to that used for the cyanines in the fourth edition of Beilstein's Handbuch. Thus, XXII becomes bis-[3-methyl-1-phenyl-5-pyrazolone-(4)]-methineoxonol and XXIV, bis-[3-ethylrhodanine-(5)]-trimethineoxonol.

Acknowledgments.—We wish to thank Mr. Don Ketchum and his department for the microanalyses, and Mr. E. E. Richardson, Mrs. Betty Colwell and Mr. E. M. Long for the absorptions.

Experimental

The melting points are corrected; all dyes melted with decomposition except when otherwise noted.

Quaternary salts used are:

QS1*	1-Methyl-4-phenylmercaptopyridinium *p*-toluenesulfonate
QS2	2-(2-Acetanilidovinyl)-3,3-dimethyl-1-phenylpseudoindolium perchlorate
QS3	3-Ethoxycarbonylmethyl-2-methylbenzothiazolium iodide
QS4	3-Benzyl-2-methylbenzothiazolium iodide
QS5	2-Methyl-3,4-trimethylenebenzothiazolium iodide
QS6	2-(2-Anilinovinyl)-1-ethylquinolinium iodide
QS7*	2-(2-Anilinovinyl)-1-ethyl-3,3-dimethylpseudoindolium iodide

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(14) Part I, THIS JOURNAL, **62**, 1116 (1940).

(15) W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, 307 (1949).

(16) W. Baker, *Endeavour*, **9**, 35 (1950).

(17) L. Claisen, *Ann.*, **297**, 37 (1887).

(18) L. G. S. Brooker and G. H. Keyes, U. S. Patent 2,241,238 (1941).

(19) *E.g.*, F. B. Dains and S. I. Davis, *Kansas Univ. Sci. Bull.*, **15** 265 (1924).

(20) S. G. Dent, Jr., and L. G. S. Brooker, U. S. Patent 2,533,206 (1950).

QS8*	2-(2-Acetanilidovinyl)-3-ethylbenzoselenazolium iodide
QS9*	2-(2-Anilinovinyl)-1-ethylnaphtho[1,2]thiazolium iodide
QS10	2-(2-Acetanilidovinyl)-3-ethylbenzoxazolium iodide
QS11	3-Ethyl-2-methylthiazolinium iodide
QS12	4-(2-Anilinovinyl)-1-ethylquinolinium iodide
QS13*	3-(2-Anilinovinyl)-4-ethylbenzo[f]quinolinium iodide
QS14	3-Ethyl-2-methyl-4,5,6,7-tetrahydrobenzothiazolium iodide
QS15	1-Ethyl-2-picolinium iodide
QS16	1-Ethyl-4-picolinium iodide
QS17*	3-Ethyl-2-methylhexahydrobenzothiazolium *p*-toluenesulfonate
QS18	3-Ethyl-2,4-dimethylthiazolium iodide
QS19	1,3-Diethyl-2-methylbenzimidazolium iodide
QS20	2-(2-Acetanilidovinyl)-1,3,3-trimethylpseudoindolium iodide
QS21	1-Ethylquinaldinium *p*-toluenesulfonate
QS22	1-Ethyllepidinium iodide
QS23	1-Methyl-4-picolinium *p*-toluenesulfonate
QS24*	2-(4-Methoxy-1,3-butadienyl)-3,3-dimethyl-1-phenylpseudoindolium perchlorate
QS25*	2-(4-Acetanilido-1,3-butadienyl)-1-ethyl-3,3-dimethylpseudoindolium iodide
QS26	3-Ethyl-2-methylbenzoselenazolium iodide
QS27	1-Ethyl-2-methylnaphtho[1,2]thiazolium *p*-toluenesulfonate
QS28	2-(4-Acetanilido-1,3-butadienyl)-3-ethylbenzoxazolium iodide
QS29	1-Ethylquinaldinium iodide
QS30	1-Methyl-4-picolinium iodide
QS31*	2-(6-Acetanilido-1,3,5-hexatrienyl)-1-ethyl-3,3-dimethylpseudoindolium iodide
QS32	3-Ethyl-2-methylhexahydrobenzothiazolium iodide
QS33	2,3,3-Trimethyl-1-phenylpseudoindolium perchlorate
QS34	1-Ethyl-2,3,3-trimethylpseudoindolium iodide

Keto-methylene compounds used are:

KM1	3-Phenyl-5(4H)-isoxazolone
KM2	3-Ethylrhodanine
KM3	1-Phenyl-5-pyrazolone
KM4	1,3-Indandione
KM5	1,3-Diethyl-2-thiobarbituric acid
KM6	3-Methyl-1-phenyl-5-pyrazolone
KM7	1,3-Diethylbarbituric acid
KM8	3-Ethyl-2-thio-2,4-oxazolidinedione
KM9	1-Ethyloxindole
KM10	3-Ethyl-1-phenyl-2-thiohydantoin

Other **reactants** are:

R1*	5-Acetanilidomethylene-3-ethylrhodanine
R2	1,2-Dimethyl-3-indolealdehyde
R3	5-(3-Acetanilidoallylidene)-3-ethylrhodanine
R4*	5-(3-Acetanilidoallylidene)-1,3-diethylbarbituric acid
R5*	4-(3-Acetanilidoallylidene)-3-phenyl-5(4H)-isoxazolone
R6*	4-(5-Acetanilido-2,4-pentadienylidene)-3-phenyl-5(4H)-isoxazolone
R7*	4-Acetanilidomethylene-3-phenyl-5(4H)-isoxazolone
R8	*p*-Dimethylaminobenzaldehyde
R9	2,5-Dimethyl-1-phenyl-3-pyrrolecarboxaldehyde
R10	Ethyl orthoformate
R11	β-Anilinoacrolein anil hydrochloride
R12*	5-Acetanilidomethylene-3-ethyl-2-thio-2,4-oxazolidinedione
R13	Diethoxymethyl acetate
R14	β-Ethoxyacrolein acetal

Details of the preparation of the compounds marked with an asterisk follow.

1-Methyl-4-phenylmercaptopyridinium *p*-Toluenesulfonate (QS1).—4-Phenylmercaptopyridine (1.9 g., 1 mol.) and methyl *p*-toluenesulfonate (1.9 g., 1 mol.) were heated together for 90 minutes at 100°. The viscous mass was washed with ether and used without further purification.

2-(2-Anilinovinyl)-1-ethyl-3,3-dimethylpseudoindolium Iodide (QS7).—1-Ethyl-2,3,3-trimethylpseudoindolium iodide (9.45 g., 1 mol.) and diphenylformamidine (7.0 g., 1.2 mols.) were heated together for 12 minutes at 150–160°. The product was cooled and a small amount of acetone added. The solid was filtered off, washed with acetone and dried; yield 8.6 g. (64%). Recrystallization from 95% ethyl alcohol gave 34% of yellow crystals, m.p. 214–215° dec.

Anal. Calcd. for $C_{20}H_{23}IN_2$: I, 30.35. Found: I, 30.10.

2-(2-Acetanilidovinyl)-3-ethylbenzoselenazolium Iodide (QS8).—3-Ethyl-2-methylbenzoselenazolium iodide (17.6 g.. 1 mol.) and diphenylformamidine (9.8 g., 1 mol.) were refluxed in acetic anhydride (75 ml.) for 10 minutes. The reaction mixture was cooled, filtered and washed with acetone; yield 17.2 g. (69%), m.p. 216–221°. The product was used without further purification.

2-(2-Anilinovinyl)-1-ethylnaphtho[1,2]thiazolium Iodide (QS9).—1-Ethyl-2-methylnaphtho[1,2]thiazolium iodide (12 g., 1 mol.) and diphenylformamidine (13.2 g., 2 mols.) were heated together for 10 minutes at 150°. The product was powdered and washed with acetone; yield 14.3 g. (93%). Recrystallization from methyl alcohol (180 ml./g.) gives golden yellow prisms, m.p. 257–258°.

Anal. Calcd. for $C_{21}H_{19}IN_2S$: I, 27.70. Found: I, 27.45.

3-(2-Anilinovinyl)-4-ethylbenzo[f]quinolinium Iodide (QS13).—4-Ethyl-3-methylbenzo[f]quinolinium iodide (10 g., 1 mol.) and diphenylformamidine (5.6 g., 1 mol.) were heated together 10 minutes at 180°. The product was pulverized and washed with acetone; yield 13 g. (100%). Recrystallization from methyl alcohol (85 ml./g.) gave orange-brown needles, m.p. 277–279°.

Anal. Calcd. for $C_{23}H_{21}IN_2$: I, 28.07. Found: I, 28.06.

3-Ethyl-2-methylhexahydrobenzothiazolium *p*-Toluenesulfonate (QS17).—2-Methylhexahydrobenzothiazole (1.55 g., 1 mol.) and ethyl *p*-toluenesulfonate (2 g., 1 mol.) were heated together for 3 hours at 120°. The mass was washed with ether and used directly.

2-(4-Methoxy-1,3-butadienyl)-3,3-dimethyl-1-phenylpseudoindolium Perchlorate (QS24).—2,3,3-Trimethyl-1-phenylpseudoindolium perchlorate (6.6 g., 1 mol.) and 1,1,3-trimethoxypropene (5.3 g., 2 mols.) were heated for 15 minutes at 100°. The product was precipitated by addition of ether, stirred with methyl alcohol and filtered; yield 4.65 g. (58%) of brownish crystals. The product was used without further purification.

2-(4-Acetanilido-1,3-butadienyl)-1-ethyl-3,3-dimethylpseudoindolium Iodide (QS25).—1-Ethyl-2,3,3-trimethylpseudoindolium iodide (18.9 g., 1 mol.) and β-anilinoacrolein anil hydrochloride (15.6 g., 1 mol.) were refluxed in acetic anhydride (120 ml.) for 15 minutes. After precipitation with ether, stirring with acetone and filtration, the brownish crystals weighed 21.3 g. (71%). The product was used without further treatment.

2-(6-Acetanilido-1,3,5-hexatrienyl)-1-ethyl-3,3-dimethylpseudoindolium Iodide (QS31).—1-Ethyl-2,3,3-trimethylpseudoindolium iodide (3.1 g., 1 mol.) and glutaconaldehydedianilide hydrochloride (2.75 g., 1 mol.) were refluxed together in acetic anhydride (20 ml.) for 3 minutes. After precipitation with ether, stirring with acetone and filtration, the brownish crystals weighed 3 g. (59%). The product was used without further treatment.

5-Anilinomethylene-3-ethylrhodanine.—3-Ethylrhodanine (32 g., 1 mol.) and diphenylformamidine (3.9 g., 1 mol.) in kerosene (150 ml.) were heated 1 hour at 120°. Filtration and washing with methyl alcohol gave 41 g. (77%) of yellow needles. After recrystallization from acetic acid (15 ml./g.), the product had m.p. 184–186°.

Anal. Calcd. for $C_{12}H_{12}N_2OS_2$: N, 10.60. Found: N, 10.55.

5-Acetanilidomethylene-3-ethylrhodanine (R1).—5-Anilinomethylene-3-ethylrhodanine (7.8 g., 1 mol.) was heated for 10 minutes at 100° in acetic anhydride (60 ml.) with triethylamine (3 g., 1 mol.). After cooling and filtration, the product weighed 8.0 g. (89%). Pale yellow needles separated from methyl alcohol; these melted at 85–87°, resolidified and melted again at 128–130°.

Anal. Calcd. for $C_{14}H_{14}N_2O_2S_2$: N, 9.15. Found: N, 8.86.

5-(3-Acetanilidoallylidene)-1,3-diethylbarbituric Acid (R4).—1,3-Diethylbarbituric acid (9.2 g., 1 mol.), β-anilinoacrolein anil hydrochloride (13 g., 1 mol.) and sodium acetate (4.1 g., 1 mol.) in acetic anhydride (25 ml.) were refluxed for 3 minutes. After cooling, filtering, washing with water and with methyl alcohol, the brownish-yellow product (12.2 g., 69%) had m.p. 194–196°. It was used without further purification.

4-(3-Acetanilidoallylidene)-3-phenyl-5(4H)-isoxazolone (R5).—3-Phenyl-5(4H)-isoxazolone (8 g., 1 mol.), β-anilinoacrolein anil hydrochloride (12.9 g., 1 mol.) and sodium acetate (8.2 g., 2 mols.) in acetic anhydride (30 ml.) were refluxed for 3 minutes. After cooling, filtering, washing with water and with methyl alcohol, the brownish product (7.5 g., 90%) had m.p. 160–165°. It was used without further purification.

4-(6-Acetanilido-2,4-pentadienylidene)-3-phenyl-5(4H)-isoxazolone (R6).—3-Phenyl-5(4H)-isoxazolone (8 g., 1 mol.), glutaconaldehyde dianilide hydrochloride (14.2 g., 1 mol.) and sodium acetate (4.1 g., 1 mol.) in acetic anhydride (30 ml.) were refluxed for 3 minutes. After cooling, filtering, washing with water and with methyl alcohol, the brownish product (9 g., 50%) had m.p. 198–200°. It was used without further purification.

4-Acetanilidomethylene-3-phenyl-5(4H)-isoxazolone (R7).—4-Anilinomethylene-3-phenyl-5(4H)-isoxazolone (44.5 g., 1 mol.) in acetic anhydride (60 ml.) and triethylamine (8.5 g., 1 mol.) were heated to the boiling point and cooled. After filtering and washing with methyl alcohol, the yield was 31.6 g. (64%). Recrystallization from methyl alcohol gave nearly colorless crystals, m.p. 142–144°. The product was used without further purification.

5-Anilinomethylene-3-ethyl-2-thio-2,4-oxazolidenedione.—3-Ethyl-2-thio-2,4-oxazolidenedione (52.2 g., 1 mol.) and diphenylformamidine (70.2 g., 1 mol.) in kerosene (270 ml.) were heated for 1 hour at 120–125°. Filtration and washing with methyl alcohol gave 41.2 g. (48%) of yellow crystals. After recrystallization from methyl alcohol, the product had m.p. 237–239° without decomposition. The product was used without further purification.

5-Acetanilidomethylene-3-ethyl-2-thio-2,4-oxazolidenedione (R12).—5-Anilinomethylene-3-ethyl-2-thio-2,4-oxazolidenedione (41.2 g., 1 mol.) was heated for 10 minutes at 100° in acetic anhydride (150 ml.) with triethylamine (17.5 g., 1 mol.). After cooling and filtering, the yield was 42 g. (84%) of nearly colorless crystals. After recrystallization from methyl alcohol, the product had m.p. 158–160° without decomposition.

Anal. Calcd. for $C_{14}H_{14}N_2O_3S$: N, 9.66. Found: N, 9.43.

Details of the preparation of new dyes are given in Table I. These include merocyanines (designated by M; the numbers are continued from those in the previous paper[6]), *p*-dimethylaminobenzylidene derivatives (B), *p*-dimethylaminostyryl dyes (S), oxonols (O), symmetrical cyanines (C) and one unsymmetrical cyanine (U). The names of the dyes are given in Tables II, III, IV and V. In the syntheses, the reactants were heated together in the specified medium for the period indicated. Triethylamine (in 5% excess) was used as the condensing agent except where otherwise stated. Dyes of categories M, B and S and some of category C separated either spontaneously or on cooling. Oxonols were isolated by one of two methods; addition of a large volume of ether to the reaction mixture precipitated either the triethylamine or the pyridine salt of the dye, which was then purified as such, or acidification with hydrochloric acid precipitated the free oxonol. If a cyanine did not separate from its reaction mixture it was precipitated as a more sparingly soluble salt. The yield of washed dye is given, followed by the yield after two recrystallizations from the solvent indicated.

Absorption data for structurally unsymmetrical dyes in methyl alcohol are given in Table II and for symmetrical dyes in Table III. Data for absorptions in solvents other than methyl alcohol are given in Table IV and data required for Fig. 9 in Table V.

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[Communication No. 1398 from the Kodak Research Laboratories]

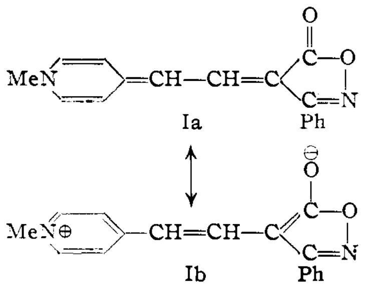
Color and Constitution. XI.[1] Anhydronium Bases of *p*-Hydroxystyryl Dyes as Solvent Polarity Indicators

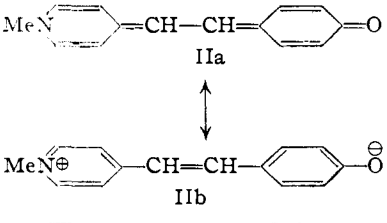
By L. G. S. Brooker, G. H. Keyes and D. W. Heseltine

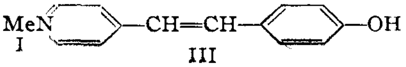
Two exceedingly polar merocyanines, for which the dipolar structures dominate even in pure pyridine solution, show such large shifts of $\lambda_{max.}$ to shorter wave lengths on increasing the polarity of the solvent (by adding water), that they could be used for the colorimetric determination of water in pyridine, or *vice versa*. For each of a number of somewhat less polar merocyanines, a characteristic change of direction in the absorption maximum–solvent composition curve (of pyridine-water mixtures) occurs at a point where the extreme resonance structures are thought to be energetically equivalent. On one side of this point the uncharged structure dominates, whereas the dipolar structure dominates on the other.

From a consideration of strongly polar nonionic dyes such as I[1] it could be predicted that the merocyanine II would also be strongly polar, for each of its rings acquires very considerable additional stabilization in the dipolar structure, IIb, relative to IIa; in IIa the rings are both *p*-quinonoidal, whereas in IIb they are benzenoidal. The polar atoms of II are also relatively exposed, consequently II might be expected to exhibit a particularly pronounced inversion of the normal behavior of un-ionized dyes toward change in the polarity of the solvent, and show a marked shift of $\lambda_{max.}$ to *shorter* wave lengths with increasing polarity of the solvent.

These expectations have been fully realized. The compound II was obtained as reddish crystals by the action of ammonia on 4-*p*-hydroxystyrylpyridine methiodide (III), obtained by the condensation of *p*-hydroxybenzaldehyde with γ-picoline methiodide.[2] So obtained, II is a dye which


Ia
Ib


IIa
IIb


I
III

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[1] Part X, This Journal, 73, 5332 (1951).

[2] A. P. Phillips, *J. Org. Chem.*, 14, 302 (1949).