TABLE II

OPTICAL DATA[a]

Dye no.		Diluent	0[c]	5	10	20	30	40	50	60	70	80	90	95	97.5	100
			Volume of pyridine[e]													
II[b,c]	$\lambda_{max.}$, Å.	H_2O	4440		4570	4690	4750	4820	4870	4950	5070	5270	5500			6050
	$\epsilon_{max.} \times 10^{-4}$		2.7		3.1	3.14	3.25	3.3	3.4	3.6	3.7	3.87	3.96			7.65
IV[c]	$\lambda_{max.}$, Å.	H_2O	4460		4660	4770	4820	4890	4990	5020	5110	5300	5530	5640		5750
	$\epsilon_{max.} \times 10^{-4}$		2.7		3.8	4.05	4.05	4.20	4.40	4.46	4.68	5.4	6.46	8.5		10.5
V[d]	$\lambda_{max.}$, Å.	H_2O	4900	5060	5150	5280	5340	5380	5460	5500	5560	5620	5660	5660	5660	5650
	$\epsilon_{max.} \times 10^{-4}$		3.9	4.8	5.25	5.7	6.0	6.45	6.85	7.05	7.7	9.8	12.7	12.8	12.1	9.7
V[f]	$\lambda_{max.}$, Å.	H_2O	4900	5100	5200	5300	5370	5400	5470	5520	5570	5620	5660	5660		5610
	$\epsilon_{max.} \times 10^{-4}$		3.90	5.45	5.75	6.3	6.7	6.7	7.15	7.5	8.8	9.7	11.8	10.0		8.1
VII[g]	$\lambda_{max.}$, Å.	H_2O	5060	5220	5320	5420	5480	5520	5560	5600	5640	5670	5680	5700	5680	5660
	$\epsilon_{max.} \times 10^{-4}$		4.1	6.1	6.6	7.5	8.3	8.7	9.5	10.6	12.6	13.65	13.6	12.3	11.2	9.8
VIII	$\lambda_{max.}$, Å.	H_2O		5380	5460	5540	5580	5610	5630	5660	5680	5700	5700	5700	5690	5640
	$\epsilon_{max.} \times 10^{-4}$			7.4	8.3	9.5	10.4	11.1	11.5	12.3	13.4	13.4	12.8	11.0	9.6	8.5
IX[h]	$\lambda_{max.}$, Å.	H_2O	5200	5300	5370	5420	5440	5460	5480	5500	5510	5510	5510			5440
	$\epsilon_{max.} \times 10^{-4}$		5.0	6.0	7.0	8.0	8.9	9.6	10.4	10.3	10.0	7.9	6.1			5.7
X[i]	$\lambda_{max.}$, Å.	H_2O		5450	5480	5520	5530	5540	5540	5560	5540	5540	5520	5480		5400
	$\epsilon_{max.} \times 10^{-4}$			5.8	6.0	6.1	6.0	5.8	5.7	4.8	4.5	3.8	3.6	3.4		2.9
XI[k]	$\lambda_{max.}$, Å.	H_2O		5600	5700	5800		5870		5940	5980	6050	6150	6200	6250	6300
	$\epsilon_{max.} \times 10^{-4}$			3.82	4.16	4.49		4.97		5.22	5.36	5.46	5.32	5.29	4.97	4.56
XI[l]	$\lambda_{max.}$, Å.	MeOH	5860			5940		5980		6080		6150	6200			6300
	$\epsilon_{max.} \times 10^{-4}$		5.23			5.33		5.41		5.46		5.48	5.46			4.56
XII[m]	$\lambda_{max.}$, Å.	H_2O		5600	5670	5740	5750	5770	5780	5800	5830	5860	5880	5900	5910	5900
	$\epsilon_{max.} \times 10^{-4}$			3.3	4.8	5.6	5.7	5.8	6.1	6.3	6.5	6.6	6.4	5.7	5.1	4.3

[a] Data for I are already given.[1] [b] Additional data for II in pyridine–water solutions not given in the body of the table follow, the percentage volume of pyridine is given followed by $\lambda_{max.}$ in Å. and $\epsilon_{max.} \times 10^{-4}$: 92, 5560, 4.06; 94, 5640, 4.15; 96, 5730, 4.55; 98, 5840, 5.5; 99, 5940, 6.31. [c] Plus a trace of piperidine. [d] Additional data for V follow, the figures being given as in *b:* 92.5, 5660, 12.9. [e] The second row of data against V are for α-picoline–water solutions. [f] Values in this horizontal row are for α-picoline–water solutions. Additional data are as follows, the figures being given as in footnote *b:* 85, 5640, 11.0; 92.5, 5660, 11.4. [g] Additional values follow, the figures being given as in footnote *b;* 1, 5120, 4.8; 2, 5140, 5.4; 86, 5680, 14.1; 87.5, 5700, 13.8. [h] Additional values follow, the figures being given as in *b:* 1, 5240, 5.35; 3, 5280, 5.5; 7.5, 5360, 6.4. [i] Additional values follow, the figures being given as in *b:* 1, 5400, 4.9. [k] Additional value of $\lambda_{max.}$ for 2 volumes % of pyridine is 5540 Å. [l] Absorptions in this row were run plus a trace of triethylamine. [m] Additional values follow, the figures being given as in *b:* 7, 5650, 4.1; 15, 5700, 5.2.

given in Table I, followed by the yield after constant melting point had been attained by several recrystallizations from the solvent indicated.

Optical data are given in Table II.

ROCHESTER 4, NEW YORK RECEIVED APRIL 11, 1951

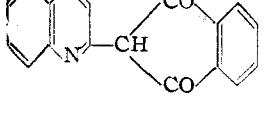
[COMMUNICATION NO. 1399 FROM THE KODAK RESEARCH LABORATORIES]

Color and Constitution. XII.[1] Absorption of the Phthalones

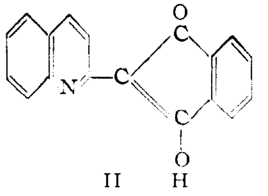
BY L. G. S. BROOKER AND G. H. KEYES

The shift of $\lambda_{max.}$ to shorter wave lengths shown by N-methylpyrophthalone (VI) in passing from chloroform as a solvent to water, which was observed by Kuhn and Bär [*Ann.*, **516**, 155 (1935)], is characteristic of strongly polar merocyanines, to which category VI belongs. The higher vinylog of VI shows a larger shift in the same direction. The corresponding quinoline dyes also show these shifts, as do pyrophthalone and quinophthalone themselves.

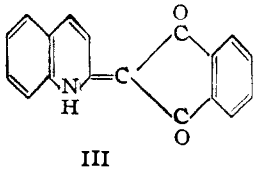
Many years ago formula I was suggested by Eibner[2] for the yellow dye, quinophthalone, but this



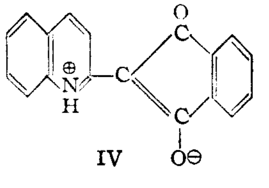
I



II



III



IV

was rejected by Kuhn and Bär because it showed no conjugation between the two ring systems.[3] Both II and III show such conjugation, however, and of these III was selected by Kuhn and Bär because methylation (under rigidly prescribed conditions) gave an N-methyl derivative (V) (the structure of which was established by oxidation to 1-methyl-2-quinolone) and because of the close correspondence between the absorption curves of quinophthalone and V.

Dye V is a merocyanine[4] which is easily prepared by the condensation of 2-phenylmercaptoquinoline metho-*p*-toluenesulfonate with 1,3-indandione. Use of 2-iodopyridine methiodide similarly furnished the N-methyl "pyrophthalone" (VI), which Kuhn and Bär had also obtained by their special methylation procedure.[3]

Kuhn and Bär commented on the considerable water-solubility of VI and also on the fact that it

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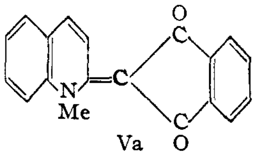
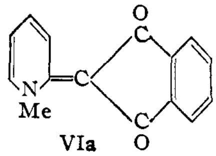
[1] Part XI, THIS JOURNAL, **73**, 5350 (1951).

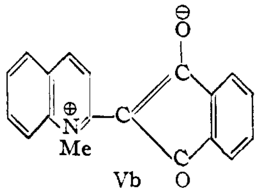
[2] A. Eibner and H. Merkel, *Ber.*, **35**, 2297 (1902); **37**, 3006 (1904); A. Eibner and K. Hofmann, *ibid.*, **37**, 3011 (1904); A. Eibner, *Chem. Ztg.*, **28**, 1206 (1904).

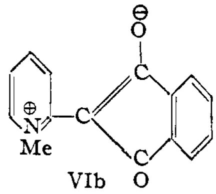
[3] R. Kuhn and F. Bär, *Ann.*, **516**, 155 (1935).

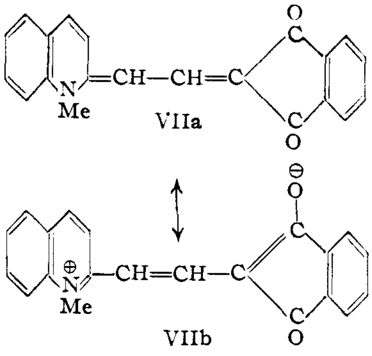
[4] THIS JOURNAL, **73**, 5350 (1951).

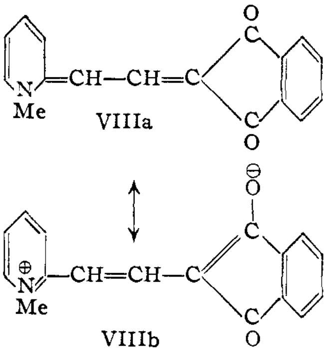

Va


VIa


Vb


VIb


VIIa VIIb


VIIIa VIIIb

had the unusual property of absorbing in chloroform at longer wave lengths than in water. This they attributed to a favoring of the polar "form" (VIb) in water, but they apparently had a tautomeric equilibrium in mind (although tautomerism between VIa and VIb is not possible, since one structure is derived from the other not by the movement of an atom but only of an electron) and they made no distinction between the displacement of the absorption band of VI with change of solvent, and shifts observed with 4-phenylazo-1-naphthol, which they proved in the immediately preceding paper was due to a true tautomeric change.[5]

Even if VI is treated as a resonance hybrid VIa ←→ VIb, favoring structure VIb in an energetic sense, *i.e.*, lowering its energy relative to VIa, would not necessarily account for a shift of $\lambda_{\max.}$ to shorter wave lengths in a more polar solvent. In fact, for the many un-ionized dyes that receive relatively small contributions from polar structures, increasing the stability of the latter by going to a more highly polar solvent will usually shift the absorption toward longer wave lengths.[6] Only when the polar structure is of exceptionally high stability will the absorption move in the opposite direction.[6]

That this latter condition actually holds for VI follows from the fact that the 2-pyridine and 1,3-indandione rings combined in the dye are of high basicity and high acidity, respectively[6]; VI thus belongs to that special category of merocyanines which are strongly polar and which show, as a characteristic feature, marked shifts of $\lambda_{\max.}$ to shorter wave lengths with increasing polarity of the solvent.[1,6] The solubility in water is also thus accounted for.

The absorption shifts of strongly polar merocyanines have been found to be more pronounced the longer the conjugated chain of the dye.[6] The higher vinylogs of V and VI (VII and VIII, respectively) were therefore prepared. Of these, VII was obtained by the condensation of 1,3-indandione with 2-(β-acetanilidovinyl)-quinoline metho-*p*-toluenesulfonate using triethylamine as condensing agent, but this method was not successful for VIII, and this dye was obtained by the condensation of α-picoline methiodide with 1,3-indandione and diethoxymethyl acetate in the presence of excess of piperidine.

Absorption maximum–solvent composition curves for the four dyes (for solutions in pyridine and water, and mixtures of the two) are given in Fig. 1. Several conclusions can be drawn from these curves. They show that the absorption maximum of V is shifted toward shorter wave lengths with increasing polarity of the solvent in much the same way as that of VI. For VI, the shift in $\lambda_{\max.}$ from pyridine to water is 340 Å., while for the higher vinylog VIII the shift is 620 Å. In the quinoline series, however, there is no such increase in shift in going from V to VII. For VIII, too, the shape of the curve is that already observed for strongly polar dyes (*cf.* curves in Fig. 1 of preceding paper[1]). The isoenergetic point[1] would therefore appear to be at an extrapolation of this curve in an upward direction. The curve for VII, on the other hand, appears to show an incipient "hook,"[1] and although the curve is flat at the apex, it is probable that the apex corresponds to the isoenergetic point.

Finally, absorption maximum–solvent composition curves were determined for quinophthalone (III) and for pyrophthalone (Fig. 1,P). While $\lambda_{\max.}$ values for these dyes are also shifted toward shorter wave lengths with increasing polarity of the solvent, the shifts are considerably less than for the N-methyl compounds. Why this is so remains uncertain for the present; it may be connected with a possible decrease in basicity of the heterocyclic rings in the dyes with > NH relative to those with > NMe.

Acknowledgment.—We desire to thank Mr. Don F. Ketchum and his department for the microanalyses and Mr. Edward L. Long for the absorptions.

Experimental

All melting points are corrected.

2-[1-Methyl-2(1H)-quinolylidene)-1,3-indandione (V).—1,3-Indandione (1.45 g., 1 mol.), 1-methyl-2-phenylmercaptoquinolinium *p*-toluenesulfonate (4.2 g., 1 mol.), ethyl alcohol (100 ml.) and triethylamine (2 g., 1 mol.) were refluxed for 15 minutes. The yield of washed dye was 76% before, and 58% after, two recrystallizations from methyl

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(5) R. Kuhn and F. Bär, *Ann.*, **516**, 143 (1935).

(6) Part X, THIS JOURNAL, **73**, 5332 (1951).

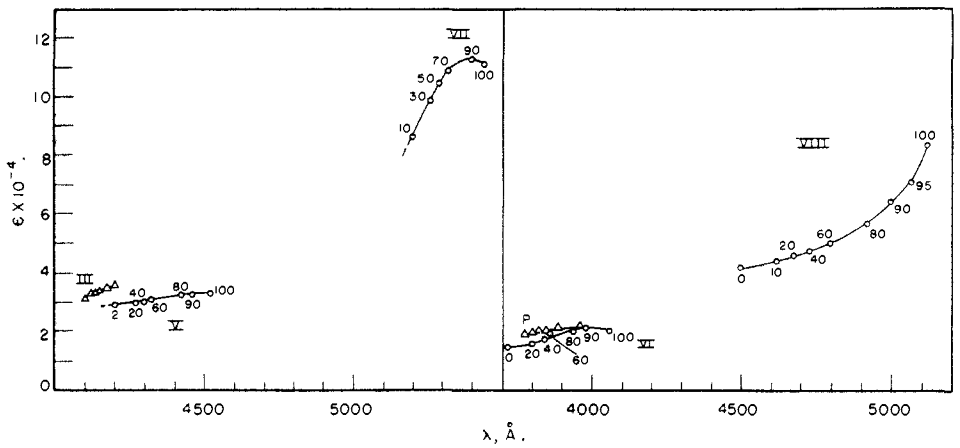

Fig. 1.—Absorption maxima ($\lambda_{max.}$ and $\epsilon_{max.}$) plotted for solutions in pyridine and water, and mixtures of the two. The numbers against the points indicate volumes of pyridine per 100 volumes of solvent. For the curve for III, the six points correspond to 10, 20, 40, 60, 80 and 100 volumes of pyridine per cent., reading from left to right, while for the curve for pyrophthalone (P) the corresponding numbers are 2, 20, 40, 60, 80 and 100.

TABLE I

OPTICAL DATA

% pyridine in water by volume	Dye: III		V		VI		VII		VIII		Pyrophthalone	
	$\lambda_{max.}$, Å.	$\epsilon_{max.} \times 10^{-4}$	$\lambda_{max.}$, Å.	$\epsilon_{max.} \times 10^{-4}$	$\lambda_{max.}$, Å.	$\epsilon_{max.} \times 10^{-4}$	$\lambda_{max.}$, Å.	$\epsilon_{max.} \times 10^{-4}$	$\lambda_{max.}$, Å,	$\epsilon_{max.} \times 10^{-4}$	$\lambda_{max.}$, Å,	$\epsilon_{max.} \times 10^{-4}$
0					3720	1.5			4500	4.15		
2			4200	2.9							3750	1.96
10							5200	8.7	4620	4.4		
20	4120	3.3	4270	2.96	3800	1.6			4680	4.6	3800	2.0
30							5260	9.8				
40	4130	3.3	4300	3.0	3840	1.72			4730	4.75	3820	2.04
50							5290	10.5				
60	4140	3.36	4320	3.07	3860	1.94			4800	5.0	3840	2.04
70							5320	10.8				
80	4170	3.46	4420	3.22	3940	2.06			4920	5.64	3880	2.1
90			4460	3.24	3980	2.16	5400	11.3	5000	6.4		
95									5070	7.1		
100	4200	3.54	4520	3.27	4060	2.06	5440	11.1	5120	8.35	3960	2.16

alcohol. The deep yellow needles had m.p. 248–250° dec. Kuhn and Bär give m.p. 249.5°.

Anal. Calcd. for $C_{19}H_{13}NO_2$: C, 79.39; H, 4.56. Found: C, 78.7; H, 4.6.

2-[1-Methyl-2(1H)-pyridylidene]-1,3-indandione (VI).—2-Iodo-1-methylpyridinium iodide (7 g., 1 mol.), 1,3-indandione (2.9 g., 1 mol.), ethyl alcohol (30 ml.) and triethylamine (4 g., 2 mols.) were refluxed for 15 minutes. Most of the alcohol was removed under slightly reduced pressure and the residue was dissolved in 35 ml. of water. The dye was extracted from this solution with chloroform (200 ml.) and the extract was dried by azeotropic distillation, reducing it to about 25 ml. The dye was then precipitated by adding petroleum ether (200 ml.). The yield of crude dye was 51% before, and 9% after, two recrystallizations from ethyl alcohol. The yellow crystals had m.p. 163–165° dec. Kuhn and Bär give m.p. 165°.

Anal. Calcd. for $C_{14}H_{11}NO_2$: C, 75.93; H, 4.68. Found: C, 75.8; H, 4.4.

2-[(1-Methyl-2(1H)-quinolylidene)-ethylidene]-1,3-indandione (VII).—1,3-Indandione (1.45 g., 1 mol.), 2-(2-acetanilidovinyl)-1-methylquinolinium *p*-toluenesulfonate (4.75 g., 1 mol.), triethylamine (1 g., 1 mol.) and ethyl alcohol (50 ml.) were refluxed for 15 minutes. The yield of washed dye was 96% before, and 14% after, two recrystallizations from methyl alcohol. The reddish-brown crystals had m.p. 315–317° dec.

Anal. Calcd. for $C_{21}H_{15}NO_2$: C, 80.50; H, 4.83. Found: C, 80.3; H, 4.5.

2-[(1-Methyl-2(1H)-pyridylidene)-ethylidene]-1,3-indandione (VIII).—1-Methyl-2-picolinium iodide (2.35 g., 1 mol.), 1,3-indandione (1.45 g., 1 mol.), diethoxymethyl acetate (3.2 g., 1 mol. + 100% excess) and piperidine (10 ml.) were heated at 130–140° for 30 minutes. The yield of crude but washed dye was 80% before, and 17% after, two recrystallizations from benzene. The reddish-bronze crystals had m.p. 248–250° dec.

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.52; H, 4.95. Found: C, 77.0; H, 5.0.

The optical data are given in Table I.

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RECEIVED APRIL 11, 1951