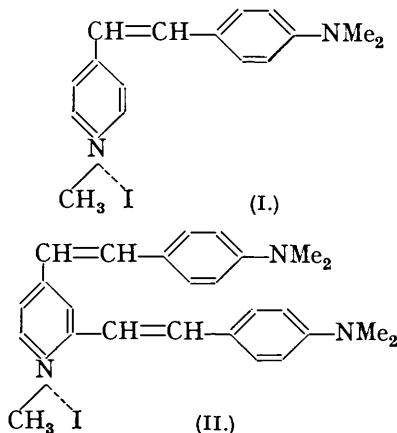
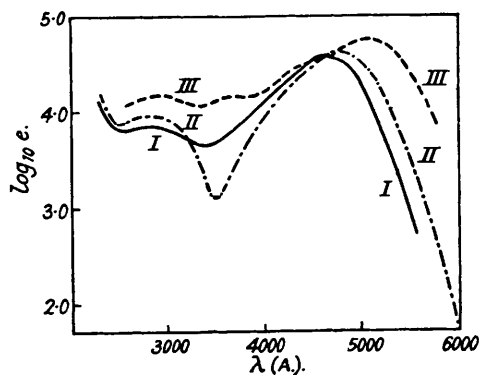


275. *The Absorption Spectra of 4-(p-Dimethylaminostyryl)pyridine Methiodide and 2 : 4-Di-(p-dimethylaminostyryl)pyridine Methiodide.*

By G. R. CLEMO and G. A. SWAN.

p-Dimethylaminobenzaldehyde has been condensed with the methiodides of 4-methyl- and 2 : 4-dimethyl-pyridine, and the absorption spectra of the products have been plotted.

THE condensation between *p*-dimethylaminobenzaldehyde and 2-methylpyridine methiodide was investigated by Mills and Pope (J., 1922, **121**, 946), who observed that the product, 2-(*p*-dimethylaminostyryl)pyridine methiodide, had a powerful sensitising action for green light on the photographic plate; they also plotted the absorption spectrum in the visible region. As 4-methylpyridine is now available here (this vol., p. 478), its methiodide has been condensed with *p*-dimethylaminobenzaldehyde to give 4-(*p*-dimethylaminostyryl)pyridine methiodide (I); the methiodide of 2 : 4-dimethylpyridine has been similarly condensed to give 2 : 4-bis-(*p*-dimethylaminostyryl)pyridine methiodide (II).



The absorption spectra of the three condensation products have been plotted (see figure). Each shows a strongly absorbing band at the blue end of the visible range; and the following values were obtained for maximum absorption (e = molecular extinction coefficient) :

	λ .	$\log_{10} e$.	Graph.
2-(<i>p</i> -Dimethylaminostyryl)pyridine methiodide	4600	4.57	I
4-(<i>p</i> -Dimethylaminostyryl)pyridine methiodide	4800	4.62	II
2 : 4-Bis-(<i>p</i> -dimethylaminostyryl)pyridine methiodide.....	5100	4.75	III

Mills and Odams (J., 1924, 125, 1913) plotted the absorption spectra of a number of carbocyanines, and gave the following values for maximum absorption for two bands in the visible region :

	λ_1 .	λ_2 .
2 : 2'-Carbocyanine	6070	5625
2 : 4'-Carbocyanine	6570	6065
4 : 4'-Carbocyanine	7115	6550

Hence, in the carbocyanines, the increase in length of the conjugated system by one —CH=CH— group causes an increase of roughly 500 Å. in the wave-length for maximum absorption, but with 2- and 4-(*p*-dimethylaminostyryl)pyridine methiodides, the increase is only about 200 Å.

EXPERIMENTAL.

4-(*p*-Dimethylaminostyryl)pyridine Methiodide.—4-Methylpyridine (0.23 g.) and *p*-dimethylaminobenzaldehyde (0.15 g.) in methyl alcohol (5 c.c.) with piperidine (3 drops) were refluxed for 5 hours. On cooling, crystals separated; these were filtered off, washed with, and recrystallised from, methyl alcohol, giving dark red needles with blue metallic reflex (0.15 g.; m. p. 255°) (Found: C, 52.1; H, 4.9; N, 8.0; I, 34.5. $C_{16}H_{18}N_2I$ requires C, 52.4; H, 5.2; N, 7.7; I, 34.7%). The absorption spectra were measured in the visible region with a Hilger-Nutting Spectrophotometer, and in the ultra-violet with a Hilger Medium Quartz Spectrograph, the solution (in ethyl alcohol) being approximately 5.5×10^{-5} M between 2300 and 4400 Å., 1.5×10^{-5} M between 4400 and 5400 Å., and 15×10^{-5} M between 5400 and 6000 Å.

2 : 4-Bis-(*p*-dimethylaminostyryl)pyridine Methiodide.—2 : 4-Dimethylpyridine (0.24 g.) and *p*-dimethylaminobenzaldehyde (0.5 g.) in methyl alcohol (5 c.c.) with piperidine (3 drops) were refluxed for 21 hours. The mixture was filtered hot, and the resulting crystalline solid was recrystallised from methyl alcohol, giving red needles with greenish reflex (0.5 g.; m. p. 318°, softening at 308°) (Found: C, 59.8; H, 5.6; N, 8.2. $C_{26}H_{30}N_2I$ requires C, 61.1; H, 5.9; N, 8.2%). For the absorption-spectra measurements, the solution (in ethyl alcohol) was approximately 10^{-4} M between 2500 and 4200 Å., and 15×10^{-6} M between 4200 and 5800 Å.

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UNIVERSITY OF DURHAM, KING'S COLLEGE,
NEWCASTLE-UPON-TYNE.

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