457. *Effect of Alkyl Substitution on Absorption Spectra.*

By H. C. Barany and M. Pianka.

The hypsochromic shifts observed in the absorption spectra of azines containing alkyl substituents on the carbon atoms of the azomethine groups, and in those of the thia- and selena-carbocyanines with an alkyl substituent on the *meso*-carbon atom, as well as the bathochromic shifts in the absorption spectra of 2 : 4-dinitrophenylhydrazones of aliphatic aldehydes, may be due to the hyperconjugative effect of the alkyl group. The effect of alkyl groups on the absorption maxima of the above-mentioned 2 : 4-dinitrophenylhydrazones and thia- and selena-carbocyanines is found to be comparable with the effect of alkyl groups in the *p*-position on the hydrolysis of diphenylmethyl chloride.

Azines substituted with an alkyl group in the azomethine chain, and thia- and selena-carbocyanines with an alkyl substituent on the *meso*-carbon atom, exhibit hypsochromic shifts with respect to their parent compounds. These shifts cannot be due to the steric effect, since in both the azines and the cyanines the bulkier ethyl group causes a smaller hypsochromic shift than the methyl group (Tables 1 and 2; absorption spectra of some carbocyanines in methanol are given in Fig. 1). Moreover, for thia- and selena-carbocyanines it was shown that there is no shift of absorption if the ethyl group is replaced by *n*-propyl, *n*-butyl, or amyl groups (Brooker and White, *J. Amer. Chem. Soc.*, 1935, **57**, 547).

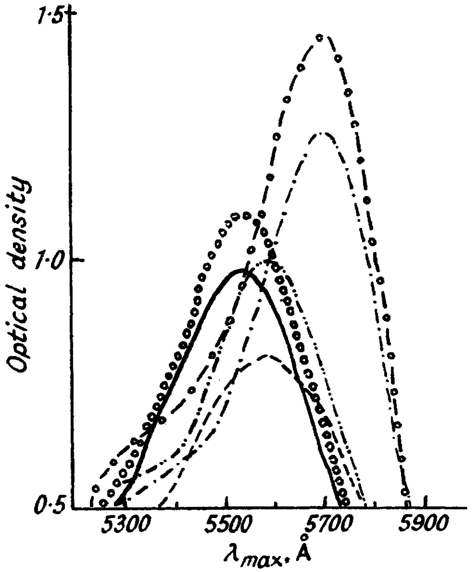


Fig. 1. *Absorption spectra of carbocyanines (in methanol).*

— · — · — 3 : 3′-Diethylselenacarbocyanine iodide.
———— 3 : 3′-Diethyl-9-methylselenacarbocyanine iodide.
— — — — 3 : 3′ : 9-Triethylselenacarbocyanine iodide.
—o—o— 3 : 3′-Diethyl-5 : 6 : 5′ : 6′-tetramethylthiacarbocyanine iodide.
ooooooo 3 : 3′-Diethyl-5 : 6 : 5′ : 6′ : 9-pentamethylthiacarbocyanine iodide.
— ·· — ·· — 3 : 3′ : 9-Triethyl-5 : 6 : 5′ : 6′-tetramethylthiacarbocyanine iodide.

The replacement of an ethylenic by an azomethine group in azines and carbocyanines causes a hypsochromic shift in their absorption maxima. In azines this shift corresponds to an increase in the excitation energy by about 3 kcal./mole (Barany, Braude, and Pianka, *J.*, 1949, 1898), which may be due to impedance of the flow of π-electronic energy along the conjugated system by the high electronic density on the nitrogen atoms of the azomethine groups. Thus replacement of CH: by N: brings about resistance to complete conjugation. In azines, alkyl substituents attached to the carbon atoms of the azomethine groups may exert a hyperconjugative effect (Pianka, Thesis, London, 1950, pp. 85—89; Szmant and Planinsek, *J. Amer. Chem. Soc.*, 1950, **72**, 4983), thereby increasing the electron density on the nitrogen atoms. This may yet further impede the π-electron flow along the conjugated system, thus causing still greater hypsochromic shifts (Table 1; only principal absorption bands are given).

TABLE 1.

	$\lambda_{max.}$, Å	ε	$\Delta\lambda_{max.}$, Å *	$\Delta\lambda_{max.}$, Å †
1 : 4-Diphenylbutadiene	3280	41,000 [1]	—	
Benzylideneazine	3000	28,000 [2]	−280	—
Methyl phenyl ketazine	2670	24,500 [2]		−330
Ethyl phenyl ketazine	2700	20,500 [3]		−300
1 : 8-Diphenyloctatetraene	3750	90,000 [1]	—	
Cinnamylideneazine	3500	65,000 [2]	−250	—
Methyl styryl ketazine	3220	45,100		−280
1-Naphthylmethyleneazine	3540	30,000 [3]		—
Methyl 1-naphthyl ketazine	2930	18,000 [3]		−610
2-Naphthylmethyleneazine	3300	69,000 [2]		—
Methyl 2-naphthyl ketazine	2620	48,000 [3]		−680

* Effect of replacing CH·CH by N·N. † Effect of alkyl substitution.

[1] Hausser, Kuhn, and Smakula, *Z. physikal. Chem.*, 1935, *B*, **29**, 384. [2] Barany, Braude, and Pianka, *loc. cit.* [3] Blout, Eager, and Gofstein, *J. Amer. Chem. Soc.*, 1946, **68**, 1986.

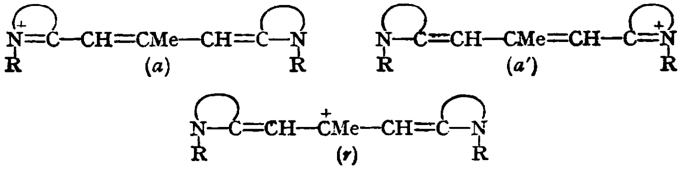
TABLE 2.

No. and name of dye (iodides)	$\lambda_{max.}$, Å	$\lambda_{max.}$, Å, 9-Me substituted dye	$\lambda_{max.}$, Å, 9-Et substituted dye	$\Delta\lambda'_{max.}$, Å, 9H to 9Me	$\Delta\lambda''_{max.}$, Å, 9H to 9Et	$\dfrac{\Delta\lambda''_{max.}}{\Delta\lambda'_{max.}}$
(C1) 3 : 3′-Diethylthiacarbocyanine	5575 [1]	5430 [1]	5475 [1]	−145	−100	0·69
(C2) 3 : 3′-Diethyl-6 : 6′-dimethylthiacarbocyanine	5620	5475	5525	−145	− 95	0·66
(C3) 3 : 3′-Diethyl-5 : 6 : 5′ : 6′-tetramethylthiacarbocyanine	5700	5530	5580	−170	−120	0·70
(C4) 3 : 3′-Diethyl-6 : 7 : 6′ : 7′-dibenzothiacarbocyanine	5940 [2]	5700 [2]	5740 [2]	−240	−200	0·83
(C5) 3 : 3′-Diethyl-4 : 5 : 4′ : 5′-dibenzothiacarbocyanine	5950 [1]	5750 [1]	5785 [1]	−200	−165	0·83
(C6) 3 : 3′-Diethyl-4 : 5 : 4′ : 5′-tetraphenylthiazolocarbocyanine	5890	5600	5670	−290	−220	0·76
(C7) 3 : 3′-Diethylselenacarbocyanine	5675 [1, 3]	5525 [1]	5575 [2]	−150	−100	0·67
(C8) 3 : 3′-Diethyl-5 : 5′-dimethoxyselenacarbocyanine	5890	5670		−220		
C9) 3 : 3′-Diethyl-6-methyl-4′ : 5′-benzothiacarbocyanine	5800	5510	5635	−290	−165	0·57
(C10) 3 : 3′-Diethyl-5-methoxyselena-4′ : 5′-benzothiacarbocyanine	5920	5675	5720	−245	−200	0·82

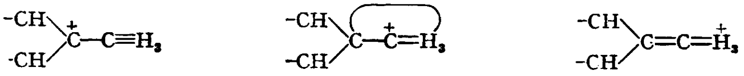
[1] Brooker and White, *loc. cit.* [2] *Idem, ibid.*, p. 2480. [3] Clark *J.*, 1933, 216.

Moffitt (*Proc. Phys. Soc.*, 1950, **63**, *A*, 700) considered the following structures as the most important contributors to the total resonance of the formamidinium ion: (*a*) $\overset{+}{N}R_2{:}CH{\cdot}NR_2$; (*a*′) $NR_2{\cdot}CH{:}\overset{+}{N}R_2$; (*r*) $NR_2{\cdot}\overset{+}{C}H{\cdot}NR_2$. Of these, *a* and *a*′ may be combined to give combinations a^+, a^- of both symmetries; *r* is essentially of the completely symmetric + species. The ground state of the formamidinium ion and its higher vinylogues is completely symmetric. The first excited state is, however, anti-symmetric with respect to a reflection in the plane of symmetry (*i.e.*, perpendicular to the molecular plane). Structures which are essentially symmetric can therefore only contribute to the ground state. Hence structure *r* contributes to the stabilisation of the ground state only.

The hypsochromic effect of *meso*-alkyl substituents in thia- and selena-carbocyanines (as shown in Table 2) can therefore be explained. In the absence of any hyperconjugative effect, the energetic relation of the three most important contributors to the resonance of the system, *viz.*,


(*a*) (*a′*) (*r*)

is, of course, the same as if the substitution had not been effected. However, by the co-operation of the hyperconjugative effect the positive charge may migrate out of the main conjugation path. (This movement of the positive charge in cationic systems is critical, other effects being of only secondary importance; therefore, basically the same considerations will apply to carbocyanines with two different heterocyclic nuclei.) The charge can move only through the medium of structure *r* as follows:



(In the case of higher alkyl substituents, second- instead of first-order hyperconjugation is operative. This is reflected in a less pronounced hypsochromic shift.) Since these structures are completely symmetric, they have the effect of stabilising structure *r*, which can thus participate more fully in the resonance which stabilises the ground state with respect to the excited state. The nearer *r* and *a*,*a′* approach each other in energy, the greater the stabilisation. Accordingly, the transition from the ground state to the first excited state is hypsochromically affected.

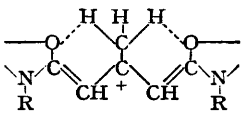
The oxacarbocyanines differ from the thia- and selena-carbocyanines in that they show bathochromic shifts when substituted in the *meso*-position by alkyl groups, which exert a weighting effect of 30—60 Å per methylene group (Table 3) (Pianka and Barany, *J.*, 1948, 309).

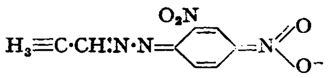
TABLE 3.

	No. and name of dye (iodides)	$\lambda_{max.}$, Å	$\lambda_{max.}$, Å, 9-Me substituted dye	$\Delta\lambda_{max.}$, Å, 9H to 9Me
(C11)	3 : 3′-Diethyloxacarbocyanine	4825 [*]	4885 [*]	+60
(C12)	3 : 3′-Diethyl-5 : 5′-diphenyloxacarbocyanine	4940	5000	+60
(C13)	3 : 3′-Diethyl-5 : 6 : 5′ : 6′-tetramethyloxacarbocyanine	4955	5010	+55

[*] Brooker and White, *loc. cit.*, p. 551.

Koch (*J.*, 1951, 514) postulated hydrogen bonding between the carbonyl and the methyl group in *O*-methyltropolone to account for its having essentially the same C=O frequency (1615 cm.$^{-1}$) as in tropolone (1620 cm.$^{-1}$). Similar hydrogen bonding may occur in oxacarbocyanines, leading to the formation of six-membered rings involving the hydrogen atoms of the alkyl groups and the oxygen atoms of the heterocycle as in (I). (Short, *J.*, 1952, 4587, found that hydrogen bonding occurs not only with semipolar, but also with covalent, oxygen atoms, as with those of dioxan.) This hydrogen bonding would exclude the movement of the positive charge out from the main conjugation path in the manner and by the mechanism suggested for structure *r*. There would be therefore no contribution from type *r* to the ground state, and consequently no stabilisation of the ground state with respect to the excited state.

(I)



(II)

In oxathia- and oxaselena-carbocyanines there is the possibility of hydrogen bonding between the oxygen atom of the oxazole and the *meso*-alkyl group which would weaken the latter's hyperconjugative effect. This may be responsible for the less pronounced hypsochromic shift (Table 4) than in thia- and selena-carbocyanines. The effect of terminal alkyl groups is visible in Table 5, showing the absorption maxima of 2 : 4-dinitrophenylhydrazones of a homologous series of aliphatic aldehydes (results of Braude and Jones, *J.*, 1945, 499; only principal bands are quoted).

TABLE 4.

	No. and name of dye (iodides)	$\lambda_{max.}$, Å	$\lambda_{max.}$, Å, 9-Me substituted dye	$\Delta\lambda_{max.}$, Å, 9H to 9Me
(C14)	3 : 3′-Diethyl-5′ : 6′-dimethyl-5-phenyloxathiacarbocyanine	5300	5260 *	−40
(C15)	3 : 3′-Diethyl-5′-methoxy-5-phenyloxaselenacarbocyanine	5405	5340	−65

* Isolated as perchlorate.

FIG. 2. *Curves obtained on plotting the absorption maxima of 2 : 4-dinitrophenylhydrazones of aliphatic aldehydes (Table 5) (————) and the kinetic constants at 0° of the hydrolysis of the diphenylmethyl derivatives (Table 6) (– – – – – –) against the ascending homologous series.*

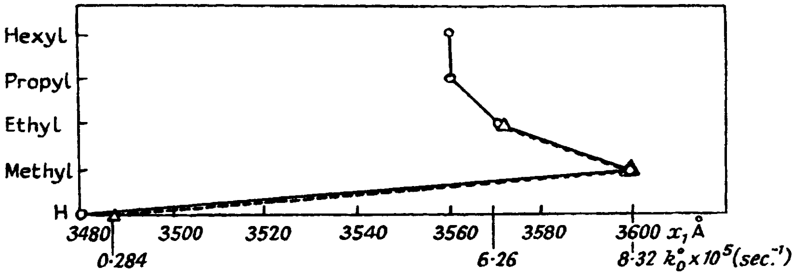


TABLE 5.

[R = 2 : 4-$(NO_2)_2C_6H_3$·]

	$\lambda_{max.}$, Å	$+\Delta\lambda_{max.}$, Å		$\lambda_{max.}$, Å	$+\Delta\lambda_{max.}$, Å
H·CH:N·NHR	3480	—	Pr·CH:N·NHR	3560	80
Me·CH:N·NHR ...	3600	120	Hexyl·CH:N·NHR...	3560	80
Et·CH:N·NHR	3570	90			

In so far as there is a bathochromic shift of 120 Å from the first to the second member of the series, and of only 80 Å between successive higher homologues, there cannot be a weighting effect, since this causes a bathochromic shift of 30—60 Å per CH_2 group (Pianka and Barany, *loc. cit.*). These shifts can be attributed to the hyperconjugative effect which is most pronounced in the acetaldehyde derivative through production of forms such as (II) by first-order hyperconjugation. A similar ratio (0·75 ± 0·09) is found among thia- and selena-carbocyanines between the hypsochromic shifts of dyes substituted in the *meso*-position with an ethyl and those substituted with a methyl group (last col. of Table 2; the ratio does not hold, however, for dye No. 9). This ratio of 0·75 also obtains for the kinetic constants governing the hydrolysis of alkyl-substituted diphenylmethyl chlorides (Table 6 and Fig. 2).

TABLE 6.[a, b]

p-R·C_6H_4·CHPhCl	$k_{25} \times 10^3$ (sec.⁻¹)	$+\Delta k$	$k_0 \times 10^5$ (sec.⁻¹)	$+\Delta k$	$E_{act.}$ (kcal.)	ΔE
R = H	0·072	—	0·284	—	20·9	—
R = Me	1·559	1·487	8·32	8·036	18·9	−2·0
R = Et	1·260	1·188	6·26	5·976	19·4	−1·5

[a] Hughes, Ingold, and Taher *J.*, 1940, 949. [b] Arnold, Murai, and Dodson, *J. Amer. Chem. Soc.*, 1950, **72**, 4193.

EXPERIMENTAL

Key to Symbols used in Tables, etc.—Bases according to the following references: (B 1) 2 : 6-Dimethylbenzothiazole (Jacobson, *Ber.*, 1889, **22**, 907), (B 2) * 2 : 5 : 6-trimethylbenzothiazole, (B 3) 2-methyl-4 : 5-diphenylthiazole (Hubacher, *Annalen*, 1890, **259**, 244), (B 4)* 5-methoxy-2-methylbenzoselenazole, (B 5)* 2-methyl-5-phenylbenzoxazole, (B 6) 2 : 5 : 6-trimethylbenzoxazole (Diepolder, *Ber.*, 1911, **44**, 2499), (B 7) 2-methyl-β-naphthathiazole (Hamer, *J.*, 1929, 2589).

Quaternary agents. (QA 1) Diethyl sulphate, (QA 2) ethyl iodide, (QA 3) ethyl toluene-*p*-sulphonate.

Orthoesters and anilides. (R 1) Ethyl orthoformate, (R 2) ethyl orthoacetate, (R 3) ethyl orthopropionate, (R 4) ethyl *N*-phenylthiolacetimidate, (R 5) ethyl *N*-phenylthiolpropionimidate, (R 6) trianilinomethane.

Quaternary salts. (QS 1) 3-Ethyl-2 : 6-dimethylbenzothiazolium ethyl sulphate, (QS 2) 3-ethyl-2 : 6-dimethylbenzothiazolium iodide, (QS 3) 3-ethyl-2 : 5 : 6-trimethylbenzothiazolium iodide, (QS 4) 3-ethyl-2-methyl-4 : 5-diphenylthiazolium ethyl sulphate; (QS 5) 3-ethyl-5-methoxy-2-methylbenzoselenazolium iodide, (QS 6) 2-(2-acetanilidovinyl)-3-ethyl-6-methylbenzothiazolium iodide, (QS 7) 2-2′-anilinopropenyl-3-ethyl-6-methylbenzothiazolium iodide, (QS 8) 2-(2-anilinobut-1-enyl)-3-ethyl-6-methylbenzothiazolium iodide, (QS 9) 2-2′-acetanilidovinyl-3-ethyl-5-methoxybenzoselenazolium iodide, (QS 10) 2-2′-anilinopropenyl-3-ethyl-5-methoxybenzoselenazolium iodide, (QS 11) 2-(2-anilinobut-1-enyl)-3-ethyl-5-methoxybenzoselenazolium iodide, (QS 12) 3-ethyl-2-methyl-5-phenylbenzoxazolium toluene-*p*-sulphonate, (QS 13) 3-ethyl-2-methyl-5-phenylbenzoxazolium ethyl sulphate, (QS 14) 3-ethyl-2 : 5 : 6-trimethylbenzoxazolium toluene-*p*-sulphonate, (QS 15) 3-ethyl-2 : 5 : 6-trimethylbenzoxazolium ethyl sulphate, (QS 16) 2-2′-acetanilidovinyl-3-ethyl-5-phenylbenzoxazolium ethyl sulphate, (QS 17) 2-2′-anilinopropenyl-3-ethyl-5-phenylbenzoxazolium ethyl sulphate, (QS 18) 3-ethyl-2-methyl-β-naphthathiazolium toluene-*p*-sulphonate.

3 : 4-*Dimethylphenylthiourea.*—Hydrochloric acid (32%; 52 c.c.) was added during 30—40 min. to 3 : 4-xylidine (64 g.) at 90°. Chlorobenzene (150 c.c.) was added and then, at 60°, dry ammonium thiocyanate (40 g.), after which the mixture was stirred during 5 hr. at 90° and set aside overnight at 10°; the yellow solid which separated was filtered off and washed well with water. Buff needles of the *thiourea*, obtained from ethanol, had m. p. 188° (Found: C, 60·0; H, 6·6; N, 15·4. $C_9H_{12}N_2S$ requires C, 59·9; H, 6·6; N, 15·5%).

2-*Amino*-5 : 6-*dimethylbenzothiazole.*—3 : 4-Dimethylphenylthiourea (33 g.) was suspended in chlorobenzene (150 c.c.; dried by distilling off 10% under reduced pressure). To the well-stirred mixture initially cooled to 5° (ice-bath), sulphuryl chloride (16 c.c.) and a few drops of bromine were added slowly from a dropping-funnel, the mixture being kept at 15—20°; it was then stirred at room temperature for 12 hr. Water (30 c.c.) was added, and the chlorobenzene removed by steam-distillation. The clear solution was filtered from a little solid matter, and cooled, and the base was precipitated by an excess of 15% aqueous sodium hydroxide. After two recrystallisations from methanol (charcoal), the *thiazole* was obtained as a light yellow powder, m. p. 185° (Found: C, 64·1; H, 6·0; N, 16·5. $C_9H_{10}N_2S$ requires C, 64·2; H, 5·9; N, 16·6%).

2-*Acetamido*-4 : 5-*dimethylphenyl Thiolacetate.*—2-Amino-5 : 6-dimethylbenzothiazole (5·4 c.c.), potassium hydroxide (5·8 g.), and water (18 c.c.) were heated in an autoclave for 6 hr. at 210°. The resulting clear brown solution was diluted with water (35 c.c.) and cooled to 0—5°, and a mixture of glacial acetic acid (32 c.c.) and acetic anhydride (32 c.c.) added, the temperature being kept at 5°. The white *thiolacetate* which separated was stirred for 1 hr., filtered off, washed with water, and dried in a vacuum-desiccator; it formed colourless crystals, m. p. 225°, from alcohol (Found: C, 60·7; H, 6·2; N, 5·8. $C_{12}H_{15}O_2NS$ requires C, 60·7; H, 6·3; N, 5·9%).

2 : 5 : 6-*Trimethylbenzothiazole* (B 2).—The foregoing thiolacetate (47·5 g.) was added during 30 min. to a boiling mixture of glacial acetic acid (30 c.c.) and acetic anhydride (45 c.c.), which was then refluxed for 9 hr. during which zinc dust (3 g.) was added in small portions. The cold solution was poured on crushed ice (250 g.), made alkaline with 3N-sodium hydroxide, and extracted with carbon tetrachloride (3 × 100 c.c.). After drying (Na_2SO_4), the solvent was removed, and the *base* distilled at 143°/5 mm., m. p. 83° (from benzene) (Found: C, 67·6; H, 6·3; N, 7·8. $C_{10}H_{11}NS$ requires C, 67·7; H, 6·2; N, 7·9%).

2 : 2′-*Diamino*-4 : 4′-*dimethoxydiphenyl Diselenide.*—2-Nitro-*p*-anisidine (25 g.) was heated

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* The preparation of the bases thus marked and of the required intermediates is described in detail.

in concentrated hydrochloric acid (25 c.c.) till dissolved (15 min.) and cooled to 0°; crushed ice (75 g.) was added, and then sodium nitrite (13·4 g.) at 5°. The diazotized solution was made alkaline to Congo-red with sodium acetate. An aqueous solution of potassium selenocyanate (152 c.c.) [prepared by dissolving selenium (129 g.) in a solution of potassium cyanide (112 g.) in water (63 c.c.) at 100° and dilution with water (89 c.c.)] was added during 2 hr., at $<10°$. The brown precipitate which separated was filtered off and washed with water. This was probably 4-methoxy-2-nitrophenyl selenocyanate, but could not be obtained pure as it decomposed on drying. It was reduced by dissolving it in an aqueous solution of sodium hydroxide (11 g.), adding sodium dithionite (hydrosulphite) (15 g.) in water (60 c.c.) at 65°, and stirring the mixture at 90° for 30 min. When air was bubbled through the cold mixture, the yellow *diselenide* separated. When filtered off, washed well with water, and dried in a desiccator, this formed yellow crystals, m. p. 170° (from ethanol) (Found: N, 6·8. $C_{14}H_{16}O_2N_2Se_2$ requires N, 6·9%).

5-*Methoxy*-2-*methylbenzoselenazole* (B 4).—The above diselenide (25 g.) was dissolved in acetic anhydride (140 c.c.) at 70°. The solution was stirred, heated under reflux to boiling, and zinc dust (22 g.) added during 10 hr. with stirring; the mixture was refluxed for a further 15 hr., then cooled, and zinc acetate was filtered off and washed with hot glacial acetic acid (40 c.c.). The filtrate and washings were freed from solvent under reduced pressure (18 mm.), and the residue was extracted with methylene chloride (3 × 50 c.c.). The crude base, which distilled at 150°/10 mm., was dissolved in hydrochloric acid (30%), the solution treated with charcoal and filtered, and the base reprecipitated with dilute ammonia and extracted with methylene chloride. The extract was dried (Na_2SO_4), and the pure *base* distilled as a yellow oil, b. p. 190°/3 mm., m. p. 54° (from methylene chloride) (Found: N, 6·1. C_9H_9ONSe requires N, 6·2%).

2-*Methyl*-5-*phenylbenzoxazole* (B 5).—Acetic anhydride (60 c.c.) and 3-amino-4-hydroxydiphenyl (20 g.) (Raiford and Colbert, *J. Amer. Chem. Soc.*, 1925, **47**, 1457) were refluxed for 2 hr., and then distilled under reduced pressure. The *base* distilled as a pale yellow oil at 158°/2—3 mm., m. p. 60—61° (from ethanol) (Found: N, 6·9. $C_{14}H_{11}ON$ requires N, 6·9%).

Details of preparation of quaternary compounds.

	Reactants				Bath-temp.	Reaction time, hr.	M. p.	Formula	Found (%):		Reqd. (%):	
									N	I	N	I
QS 1 *	B 1	3·3 g.	QA 1	3·5 c.c.	120°	0·3	—	—	—	—	—	—
QS 2[1]	B 1	3·7 g.	QA 2	2·1 c.c.	100 †	48	157—158°	—	—	—	—	—
QS 3	B 2	21 g.	QA 2	12 c.c.	100	18	235	$C_{12}H_{16}NSI$	4·1	37·8	4·2	38·0
QS 4 *	B 3	5 g.	QA 1	2·7 c.c.	160	0·3	—	—	—	—	—	—
QS 5	B 4	22·6 g.	QA 2	9·3 g.	100	48	204 ‡	$C_{11}H_{14}ONSeI$	3·6	33·0	3·7	33·3
QS 12 *	B 5	4·25 g.	QA 3	4 g.	130	0·5	—	—	—	—	—	—
QS 13 *	B 5	6 g.	QA 1	3·3 g.	140—150	0·3	—	—	—	—	—	—
QS 14 *	B 6	10·5 g.	QA 3	10·5 g.	140	4	—	—	—	—	—	—
QS 15 *	B 6	5·6 g.	QA 1	3·3 c.c.	160	0·3	—	—	—	—	—	—
QS 18 *	B 7	33·5 g.	QA 3	33·5 g.	180	5	—	—	—	—	—	—

* Quaternary salts marked with an asterisk were not isolated, but the whole yield was used, after cooling, for the subsequent condensation to dyes, except that QS 18 was triturated with ether–acetone, and the solid used for subsequent condensations. QS 2, QS 3, and QS 5 were purified by grinding them with excess of acetone, filtering, and washing with acetone and then ether, and then recrystallising them from ethanol. All three compounds are crystalline.

† In closed tube. ‡ With decomp.

[1] Jacobson, *Ber.*, 1889, **22**, 907.

Details of Dye Syntheses.—With the exception of C 14M which was isolated as the perchlorate, all dyes were isolated as the iodides. Those for which quaternary salts other than iodides were used, were converted into the iodides by pouring the cooled reaction mixtures into excess of 10% aqueous potassium iodide with vigorous stirring. The crude dyes were then allowed to solidify, filtered off, washed with acetone, and twice recrystallised from methanol. For all dye condensations dry pure pyridine was used. The condensations were carried out in boiling-tubes provided with a long air-condenser and immersed in an oil-bath kept between 120° and 140°.

Table 2*a* gives details of syntheses of the dyes listed in Table 2; the last letter in the number of dye signifies that the *meso*-substituent (on $C_{(9)}$) is a hydrogen atom (H), or a methyl (M) or ethyl group (E).

Table 3*a* corresponds to Table 3 and Table 4*a* to Table 4. The convention as regards H, M, and E operates also here.

Methyl Styryl Ketazine.—This, m. p. 166° (from benzene), was prepared from benzylideneacetone and hydrazine sulphate as described by Knoepfer (*Monatsh.*, 1909, **30**, 38).

Details of syntheses of anilinovinyl compounds.

	Reactants				Solvents (c.c.) *	Bath-temp.	Reaction time, min.	M. p.	Formula	N, %:	
										Found	Reqd.
QS 6	QS 2	10·7 g.	R 6	10·7 g.	An (3·6), Ac (3·6)	100°	180	249—250°	$C_{20}H_{21}ON_2SI$	6·2	6·0
QS 7	QS 2	10·6 g.	R 4	6·4 c.c.	---	170	30	230	$C_{19}H_{21}N_2SI$	6·6	6·4
QS 8	QS 2	10·6 g.	R 5	6·9 c.c.	---	170	30	190	$C_{20}H_{23}N_2SI$	6·2	6·2
QS 9	QS 5	7·6 g.	R 6	6·4 g.	An (2·3), Ac (2·3)	100	180	238—239	$C_{20}H_{21}O_2N_2SeI$	5·2	5·3
QS 10	QS 5	12·7 g.	R 4	6·4 c.c.	---	170	30	216	$C_{19}H_{21}ON_2SeI$	5·3	5·6
QS 11	QS 5	12·7 g.	R 5	6·9 c.c.	---	170	30	194	$C_{20}H_{23}ON_2SeI$	5·2	5·5
QS 16	QS 13 from 6 g. of B 5		R 6	9·1 g.	An (3), Ac (3)	100	180	187	$C_{27}H_{28}O_6N_2S$	5·4	5·5
QS 17	QS 13 from 6 g. of B 5		R 4	5·9 c.c.	---	180	180	190	$C_{26}H_{28}O_5N_2S$	5·6	5·8

* An = Acetic anhydride; Ac = glacial acetic acid; --- no solvent.

Purification : After cooling, the anilinovinyl compounds were repeatedly triturated with methanol–ether (1 : 1). The solids which separated were filtered off, washed with ether till the washings were colourless, and recrystallised twice from methanol.

Appearance : QS 6, rust-red plates; QS 7, violet crystals; QS 8, glittering, maroon needles; QS 9, olive-green crystals; QS 10, bluish-grey crystals; QS 11, green powder; QS 16 orange-yellow powder; QS 17 yellow powder.

TABLE 2*a*.

No. of dye	Reactants *				Pyridine (c.c.)	Reaction time, min.	M. p.	Formula	N, %:	
									Found	Reqd.
C 2H [1]	QS 1	N.I.	R 1	2 c.c.	5	60	275—276°	$C_{23}H_{25}N_2S_2I$	5·47	5·38
C 2M [1, 2]	QS 2	2 g.	R 2	4·6 c.c.	15	45	274	$C_{24}H_{27}N_2S_2I$	5·30	5·21
C 2E [2]	QS 1	N.I.	R 5	2 c.c.	5	150	245—247	$C_{25}H_{29}N_2S_2I$	5·15	5·11
C 3H	QS 3	2·3 g.	R 1	0·76 g.	20	60	265—267	$C_{25}H_{29}N_2S_2I$	4·87	5·11
C 3M	QS 3	2·3 g.	R 2	0·9 g.	20	60	275—276	$C_{26}H_{31}N_2S_2I$	4·86	4·98
C 3E	QS 3	3·3 g.	R 5	1·5 c.c.	5	90	254—255	$C_{27}H_{33}N_2S_2I$	5·09	4·86
C 6H [3]	QS 4	N.I.	R 1	2·3 c.c.	15	90	247—250	$C_{37}H_{33}N_2S_2I$	4·02	4·02
C 6M	QS 4	N.I.	R 2	2·3 c.c.	15	90	253	$C_{38}H_{35}N_2S_2I$	4·05	3·94
C 6E	QS 4	N.I.	R 3	2·3 c.c.	15	90	261	$C_{39}H_{37}N_2S_2I$	3·75	3·87
C 8H	QS 5	3·9 g.	R 1	1·8 c.c.	20	60	267—268	$C_{23}H_{25}O_2N_2Se_2I$	4·49	4·33
C 8M	QS 5	3·9 g.	R 2	1·8 c.c.	20	60	248—249	$C_{24}H_{27}O_2N_2Se_2I$	4·37	4·24
C 9H	QS 6	1·6 g.	QS 18	2·2 g.	15	90	216	$C_{26}H_{25}N_2S_2I$	5·03	5·04
C 9M	QS 7	1·7 g.	QS 18	2·2 g.	15	16 hr.	252—254	$C_{27}H_{27}N_2S_2I$	5·08	4·91
C 9E	QS 8	1·7 g.	QS 18	2·2 g.	15	16 hr.	225	$C_{28}H_{29}N_2S_2I$	4·55	4·79
C 10H	QS 9	4·0 g.	QS 18	4·4 g.	15	60	237—238	$C_{26}H_{25}ON_2SSeI$	4·35	4·52
C 10M	QS 10	2·1 g.	QS 18	2·2 g.	15	60	227—228†	$C_{27}H_{27}ON_2SSeI$	4·30	4·42
C 10E	QS 11	2 g.	QS 18	2 g.	10	150	210—213†	$C_{28}H_{29}ON_2SSeI$	4·40	4·31

* N.I. denotes that the quaternary salt was not isolated, but used *in situ*. The quantities are shown in the Table giving details of preparation of quaternary compounds (p. 2222).

† With decomp.

[1] Kiprianov, Suitnik, and Suich, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 42. [2] U.S.P. 2,378,783/1945. [3] U.S.P. 2,079,376/1939.

Appearance of dyes : C 2H, greenish-black needles; C 2M, mauve crystals; C 2E, greenish-black crystals; C 3H, glittering black needles; C 3M, mauve crystals; C 3E, ink-blue crystals; C 6H, dark purple plates; C 6M, dark green crystals; C 6E, dark violet powder; C 8H, dark green needles; C 8M, dark violet plates with a reddish reflex; C 9H, dark blue crystals; C 9M, purple crystals; C 9E, dark crystals with a violet reflex; C 10H, dark violet crystals with a bluish reflex; C 10M, dark purple plates; C 10E, violet crystals with olive-green reflex.

TABLE 3*a*.

No. of dye	Reactants				Pyridine (c.c.)	Reaction time, min.	M. p.	Formula	N, %:	
									Found	Reqd.
C 12H	QS 12	N.I.*	R 1	12 c.c.	12	30	240°	$C_{33}H_{29}O_2N_2I$	4·69	4·58
C 12M	QS 13	N.I.	R 4	3·1 c.c.	10	150	273—274	$C_{34}H_{31}O_2N_2I$	4·23	4·47
C 13H	QS 14	N.I.	R 1	6·8 c.c.	32	240	280—281	$C_{25}H_{29}O_2N_2I$	5·50	5·43
C 13M	QS 15	N.I.	R 4	3·1 c.c.	10	150	253—256	$C_{26}H_{31}O_2N_2I$	5·16	5·28

* See footnote * in Table 2A.

Appearance of dyes : C 12H, scarlet needles; C 12M, red powder; C 13H, glittering red long needles; C 13M, red powder.

TABLE 4*a*.

No. of dye	Reactants, g.				Medium * (and c.c.)	Reaction time, min.	M. p.	Formula	N, %: Found	Reqd.
C 14H	QS 16	3·4	QS 3	3·3	Py (20), An (2)	60	270°	$C_{29}H_{29}ON_2SI$	4·53	4·83
C 14M	QS 17	6	QS 3	6	Py (18)	180	250—253	$C_{30}H_{31}O_5N_2SCl$	4·81	4·94
C 15H	QS 16	1·2	QS 5	0·95	Py (3·5), An (3·5)	20	262	$C_{28}H_{27}ON_2SeI$	4·28	4·57
C 15M	QS 17	3·5	QS 5	3·8	Py (20), An (25)	60	247	$C_{29}H_{29}ON_2SeI$	4·33	4·31

* Py = pyridine; An = acetic anhydride.

Appearance of dyes : C 14H, glittering dark green needles; C 14M (precipitated as perchlorate by stirring and forming the crude dye with excess of 10% aqueous potassium perchlorate), plum-red crystals; C 15H, glittering, dark blue needles; C 15M, dark maroon crystals.

Light-absorption Measurements.—Absorptions of the carbocyanines were determined in methanol solution, that of methyl styryl ketazine in ethanol.

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