

[CONTRIBUTION NO. 103 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

## Copolymerization. XVI.<sup>1</sup> The Copolymerization of 2-Chlorobutadiene, 2,3-Dichlorobutadiene and 1,1-Diphenylethylenes with Olefins

BY KENNETH W. DOAK AND DENNIS L. DINEEN

By the use of monomer reactivity ratios<sup>2</sup> for the copolymerization of ethylenic monomers with different substituents, Mayo, Lewis and Walling<sup>3</sup> have established an average reactivity series of monomers, and a donor-acceptor series in which monomers are placed in the order of increasing ability to accept electrons (or decreasing ability to donate electrons). Butadiene was placed in these series, and was similar to styrene in its reactivity and ability to donate electrons. No substituted butadienes were studied. It becomes of interest to determine the effects of substituents upon the position of butadiene in both series. Therefore, 2-chlorobutadiene-1,3 and 2,3-dichlorobutadiene-1,3 have been copolymerized with representative ethylenic monomers, and the monomer reactivity ratios have been determined. Two systems have been studied previously (*cf.* Table II). In addition, three 1,1-diphenylethylenes were copolymerized with two olefins.

### Experimental

**Monomers.**—The 2-chlorobutadiene was available commercially as a 50% solution. It was carefully fractionated (b.p. 59° (760);  $n_D^{20}$  1.4580) and stored in a refrigerator. Just before being used, it was distilled under high vacuum in order to remove any polymer, which usually began to form within a few hours. The 2,3-dichlorobutadiene (b.p. 39–40° (80);  $n_D^{20}$  1.4900) was a sample prepared by F. O. Guenther, and stored in Dry Ice until used. 1,1-Diphenylethylene (b.p. 121–124 (7),  $n_D^{20}$  1.6086) and 1,1-di-*p*-chlorophenyl-ethylene (m.p. 85.5–87°; 28.29% Cl) were prepared<sup>4</sup> by procedures previously described. 1,1-Di-*p*-anisyl-ethylene (m.p. 139–141°) was obtained from Northwestern University. The other monomers were commercial samples which had been redistilled.

**Procedure.**—The procedure was essentially that of Mayo and Lewis.<sup>2</sup> The reaction mixtures contained 0.08 mole per cent. benzoyl peroxide. The tubes were degassed twice and sealed at a pressure of about  $10^{-3}$  mm. The reaction temperature was  $60.0 \pm 0.1^\circ$ . The copolymers of acrylonitrile and the diphenylethylenes were purified by dissolving in acetone, precipitating (three times) as finely divided powders from hexane, and dried at 60° at 1 mm. The other copolymers were purified by dissolving in benzene, precipitating with hexane (three times), and dried by the frozen benzene technique of Lewis and Mayo.<sup>3</sup> The products from acrylonitrile (85%) and 2-chlorobutadiene were soluble in benzene containing 10–15% acetone. Most of the copolymers of 2-chlorobutadiene sintered, forming a relatively thin layer of soft polymer on the walls of the flasks used. Drying was completed at 65° and 1 mm. for 16 hours.

The copolymers of 2-chlorobutadiene decomposed rapidly when exposed to oxygen and light. In some cases, the amount of chlorine would drop several per cent. in 2 or 3 days. Consistent analytical results could be obtained only when the polymer samples, immediately after drying, were stored under nitrogen in the freezing compartment of the refrigerator until just before they were analyzed.

The experiments with the diphenylethylenes were carried out using a large excess of the second monomer, because the

high melting points of the substituted diphenylethylenes limited their solubility in the second monomer. This procedure permits the determination of only one reactivity ratio, that for the acrylonitrile or methyl acrylate radical, determined by the intersection with the  $r_1$  axis. No significant error is thus introduced, since the calculated lines are so nearly parallel to the  $r_2$  axis. A more nearly equiva-

TABLE I

Millimoles				Time, hr.	Polymer analysis
[M <sub>1</sub> ]	[M <sub>1</sub> ] <sub>0</sub>	[M <sub>2</sub> ] <sub>0</sub>	[M <sub>2</sub> ]		
2-Chlorobutadiene (M <sub>1</sub> )–Styrene (M <sub>2</sub> )					
58.04	48.25	40.51	39.62	5.8	36.19 Cl
28.41	16.54	172.73	164.73	9	22.39
2-Chlorobutadiene (M <sub>1</sub> )–Methyl methacrylate (M <sub>2</sub> )					
57.32	40.06	44.69	42.38	7	34.81 Cl
28.96	18.10	170.25	161.25	9	20.67
2-Chlorobutadiene (M <sub>1</sub> )–Diethyl fumarate (M <sub>2</sub> )					
57.04	44.95	38.42	37.16	5	33.29 Cl
28.83	20.37	168.39	163.55	7	19.18
2-Chlorobutadiene (M <sub>1</sub> )–1,1-Diphenylethylene (M <sub>2</sub> )					
47.30	27.42	51.05	45.29	55	68.73 C
78.14	48.08	19.84	17.37	48	59.86
2-Chlorobutadiene (M <sub>1</sub> )–Methyl acrylate (M <sub>2</sub> )					
48.77	35.70	50.06	48.63	15	36.21 Cl
29.26	13.98	169.35	159.44	24	24.57
2-Chlorobutadiene (M <sub>1</sub> )–Acrylonitrile (M <sub>2</sub> )					
39.48	27.64	59.93	56.83	9	3.58 N
30.32	13.11	169.41	155.41	15	26.92 Cl
69.36	51.97	30.51	29.02	7	1.29 N
2,3-Dichlorobutadiene (M <sub>1</sub> )–Styrene (M <sub>2</sub> )					
29.44	17.73	170.74	164.21	5	39.22 Cl
49.74	36.66	49.53	48.18	3	53.07
2,3-Dichlorobutadiene (M <sub>1</sub> )–1,1-Diphenylethylene (M <sub>2</sub> )					
61.58	22.85	86.86	74.97	17	39.78 Cl
61.67	26.53	40.49	33.95	17	45.31
2,3-Dichlorobutadiene (M <sub>1</sub> )–Methyl methacrylate (M <sub>2</sub> )					
29.76	19.59	169.53	163.44	7	38.76 Cl
49.72	37.28	49.71	48.44	4	53.25
Acrylonitrile (M <sub>1</sub> )–1,1-Di- <i>p</i> -anisyl-ethylene (M <sub>2</sub> )					
251.62	244.61	4.99	1.72	120	8.48 N
Methyl acrylate (M <sub>1</sub> )–1,1-Di- <i>p</i> -anisyl-ethylene (M <sub>2</sub> )					
250.44	243.95	4.99	3.19	124	66.34 C
Acrylonitrile (M <sub>1</sub> )–1,1-Di- <i>p</i> -chlorophenyl-ethylene (M <sub>2</sub> )					
193.13	187.38	4.97	2.51	116	8.78 N
Methyl acrylate (M <sub>1</sub> )–1,1-Di- <i>p</i> -chlorophenyl-ethylene (M <sub>2</sub> )					
192.50	187.12	5.00	3.87	145	10.77 Cl
Acrylonitrile (M <sub>1</sub> )–1,1-Diphenylethylene (M <sub>2</sub> )					
96.08	92.82	5.11	3.15	139	8.66 N
Methyl acrylate (M <sub>1</sub> )–1,1-Diphenylethylene (M <sub>2</sub> )					
92.38	89.92	5.12	4.26	168	71.6 C

(1) For the preceding paper in this series, see Doak, *THIS JOURNAL*, **72**, 4681 (1950).

(2) Mayo and Lewis, *ibid.*, **66**, 1594 (1944).

(3) Mayo, Lewis and Walling, *ibid.*, **70**, 1529 (1948).

(4) "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., p. 226.

(5) Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 184 (1945).

lent ratio of monomers, as was shown for 1,1-diphenylethylene, gives copolymers so close to 1:1 that the monomer reactivity ratio becomes indistinguishable from zero.

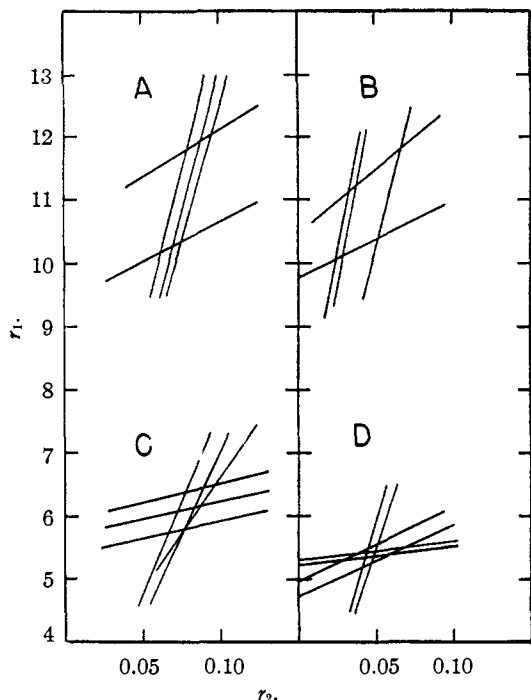


Fig. 1.—Monomer reactivity ratios of radicals: A, 2-chlorobutadiene ( $r_1$ )—methyl acrylate ( $r_2$ ); B, 2,3-dichlorobutadiene ( $r_1$ )—styrene ( $r_2$ ); C, 2-chlorobutadiene ( $r_1$ )—methyl methacrylate ( $r_2$ ); D, 2-chlorobutadiene ( $r_1$ )—acrylonitrile ( $r_2$ ).

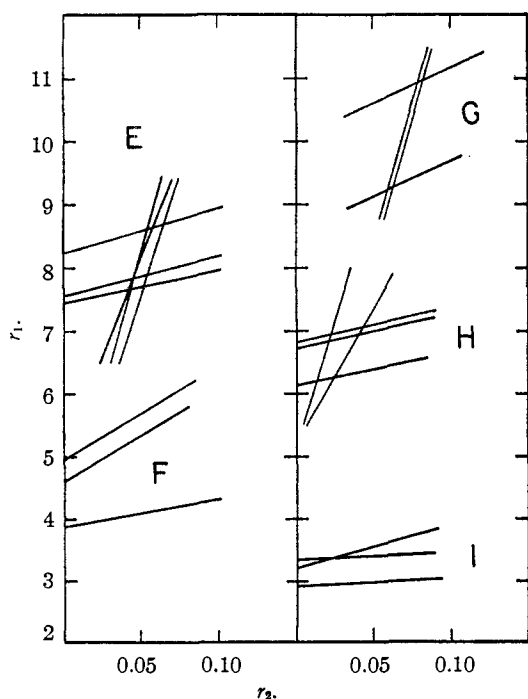


Fig. 2.—Monomer reactivity ratios of radicals: E, 2-chlorobutadiene ( $r_1$ )—styrene ( $r_2$ ); F, 2,3-dichlorobutadiene ( $r_1$ )—1,1-diphenylethylene ( $r_2$ ); G, 2,3-dichlorobutadiene ( $r_1$ )—methyl methacrylate ( $r_2$ ); H, 2-chlorobutadiene ( $r_1$ )—diethyl fumarate ( $r_2$ ); I, 2-chlorobutadiene ( $r_1$ )—1,1-diphenylethylene ( $r_2$ ).

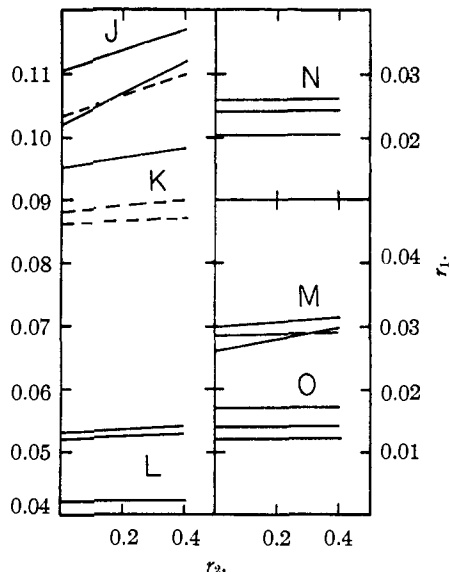


Fig. 3.—Monomer reactivity ratios of radicals: J, (—) methyl acrylate ( $r_1$ )—1,1-diphenylethylene ( $r_2$ ); K, (---) methyl acrylate ( $r_1$ )—1,1-di-(*p*-chlorophenyl)-ethylene ( $r_2$ ); L, methyl acrylate ( $r_1$ )—1,1-di-(*p*-anisyl)-ethylene ( $r_2$ ); M, acrylonitrile ( $r_1$ )—1,1-diphenylethylene ( $r_2$ ); N, acrylonitrile ( $r_1$ )—1,1-di-(*p*-chlorophenyl)-ethylene ( $r_2$ ); O, acrylonitrile ( $r_1$ )—1,1-di-(*p*-anisyl)-ethylene ( $r_2$ ).

Typical experiments appear in Table I; the results of additional experiments are shown graphically in Figs. 1–3.

Results and Discussion

The monomer reactivity ratios for the systems studied are recorded in Table II, together with some values taken from the literature. The monomers  $M_2$  are arranged in the

TABLE II  
MONOMER REACTIVITY RATIOS<sup>d</sup>

$r_1$	$r_2$	$M_1$	$M_2$	$r_1 r_2$	$r_1 r_2$
2-Chlorobutadiene ( $M_1$ )					
3.2	≈0.2	1,1-Diphenylethylene	0.0	≈0.05	<0.16
3.41	.07	Butadiene <sup>c</sup>	.059	.014	.20
8.11	.34	Styrene	.053	.005	.43
7.0	2.0	Styrene <sup>b</sup>	.05	.02	.35
6.12	.20	Methyl methacrylate	.080	.007	.49
11.1	1.5	Methyl acrylate	.078	.010	.87
5.35	.20	Acrylonitrile	.045	.004	.24
6.07	.53	Acrylonitrile <sup>c</sup>	.005	.011	.030
6.65	.37	Diethyl fumarate	.027	.009	.18
2,3-Dichlorobutadiene ( $M_1$ )					
4.5	0.5	1,1-Diphenylethylene	(0)		
10.8	1.5	Styrene	.041	.012	.44
10.3	2.0	Methyl methacrylate	.073	.015	.75
Methyl acrylate ( $M_1$ )					
0.102	0.006	1,1-Diphenylethylene	(0)		
.092	.006	1,1-Di-[ <i>p</i> -chlorophenyl]-ethylene	(0)		
.049	.005	1,1-Di-[ <i>p</i> -anisyl]-ethylene	(0)		
Acrylonitrile ( $M_1$ )					
0.028	0.003	1,1-Diphenylethylene	(0)		
.024	.003	1,1-Di-[ <i>p</i> -chlorophenyl]-ethylene	(0)		
.014	.003	1,1-Di-[ <i>p</i> -anisyl]-ethylene	(0)		

<sup>a</sup> Values recorded as (0) when  $r_1$  was calculated by inter-section of experimental lines with  $r_1$  axis. <sup>b</sup> Reference 6. <sup>c</sup> Hennery-Logan and Nichols; cf. Mayo and Walling, *Chem. Revs.*, 46, 191 (1950). <sup>d</sup> The experimental errors reported represent deviations in experiments; in some cases the absolute error possibly is larger.

TABLE III  
 RELATIVE REACTIVITIES OF MONOMERS WITH DIFFERENT RADICALS

Monomer	Radical →	Butadiene	Styrene	Methyl methacrylate	2,3-Dichlorobutadiene	2-Chlorobutadiene	Methyl acrylate	Acrylonitrile
Styrene		0.72	1.00	2.17 <sup>c</sup>	0.093	0.123	5.6 <sup>a</sup>	> 13 <sup>c</sup>
Methyl methacrylate		1.33 <sup>b</sup>	1.92 <sup>c</sup>	1.00	.098	.160		
Butadiene		1.00	1.28 <sup>b</sup>	4.0 <sup>b</sup>		.29 <sup>d</sup>		
2-Chlorobutadiene		17 <sup>d</sup>	19	12.5		1.00	13	22
2,3-Dichlorobutadiene			24	13.7	1.00			
1,1-Diphenylethylene					0.22	0.31	9.8	36
1,1-Di-[ <i>p</i> -chlorophenyl]-ethylene							11.4	42
1,1-Di-[ <i>p</i> -anisyl]-ethylene							20.4	71

<sup>a</sup> Ref. 8. <sup>b</sup> Lewis, Walling, Cummings, Briggs and Wenisch, *THIS JOURNAL*, **70** 1527 (1948). <sup>c</sup> Ref. 11. <sup>d</sup> Footnote *c*, Table II.

order in which they appear in the polarity series of Mayo, Lewis and Walling<sup>3</sup> (Table I). For 2-chlorobutadiene, the products of the ratios, which are used as a qualitative measure of the alternating tendency, increase to methyl acrylate, with which the alternating tendency is negligible, then decrease, indicating that 2-chlorobutadiene fits into the polarity series close to methyl acrylate, and alternates best with monomers at either end of the series. These results check the conclusion of Alfrey, Goldberg and Hohenstein<sup>6</sup> that 2-chlorobutadiene is a better electron acceptor than butadiene, presumably because of the ability of the chlorine atom to attract electrons.

2,3-Dichlorobutadiene alternates with styrene and methyl methacrylate to about the same extent (within experimental error) as does 2-chlorobutadiene, indicating that the effect of the second chlorine upon the electron accepting tendency of the diene system is negligible. This result is somewhat surprising, since it has been shown that the dichloroethylenes are better electron acceptors than vinyl chloride.<sup>7</sup>

Although 2-chlorobutadiene appears to fit into the polarity series adjacent to methyl acrylate, it should be pointed out that the alternating tendency with styrene is less than that of methyl acrylate with styrene. (The ratio products are 0.42 and 0.14,<sup>8</sup> respectively.) This apparent discrepancy may be caused by a low polar interaction between the

2-chlorobutadiene radical,  $R-\overset{\text{Cl}}{\text{C}}=\text{CH}-\dot{\text{C}}\text{H}_2$ , and styrene. There may be a higher interaction between the styrene radical and 2-chlorobutadiene, if the reaction of 2-chlorobutadiene is principally at the chlorovinyl group.

The relative reactivities of eight monomers with different radicals have been estimated from the reciprocals of reactivity ratios, and are shown in Table III.

2-Chlorobutadiene is 15–17 times as reactive as butadiene toward the styrene and butadiene radicals, both of which are good donors, and show an alternating tendency with 2-chlorobutadiene. 2-Chlorobutadiene, however, is only 3.1–3.4 times as reactive as butadiene toward the methyl methacrylate and 2-chlorobutadiene radicals, which are fair acceptors, and show an alternating tendency with butadiene. Similarly, 2,3-dichlorobutadiene is 19 times as reactive as butadiene toward the styrene radical, but only 3.4 times as reactive toward the methyl methacrylate radical. These facts are an indication that 2-chlorobutadiene and 2,3-dichlorobutadiene are comparable to methyl methacrylate in their donor-acceptor properties.

2,3-Dichlorobutadiene is only 1.3 times as reactive as 2-chlorobutadiene toward the styrene radical and 1.1 times as reactive toward the methyl methacrylate radical. If one assumes that 2-chlorobutadiene is attacked principally at the chlorovinyl group, and that 2,3-dichlorobutadiene is equally reactive at both vinyl groups, it follows that the chlorovinyl group in 2-chlorobutadiene is more reactive than the same group in 2,3-dichlorobutadiene, a result which is somewhat surprising.<sup>9</sup>

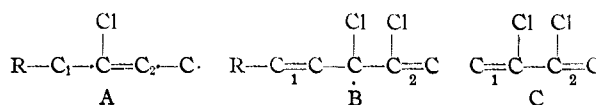
(6) Alfrey, Goldberg and Hohenstein, *THIS JOURNAL*, **68**, 2464 (1946).

(7) Doak, *ibid.*, **70**, 1525 (1948).

(8) Lewis, Walling, Cummings, Briggs and Mayo, *ibid.*, **70**, 1519 (1948).

(9) It should be pointed out that these relative reactivities are determined from the reciprocals of fairly small reactivity ratios. The above conclusions are valid only if the absolute error is no greater than the deviation in experiments, an assumption of doubtful application.

Presumably, a chlorovinyl group in 2-chlorobutadiene is activated by resonance, in the transition state, with the chlorine atom and with the other vinyl group. The principal forms involving the vinyl groups are the allylic isomers A and B.



However, if a second chlorine atom is substituted, as in C, resonance, in the ground state, between the chlorine atom and bond 2 will increase the stability of the diene system, possibly increasing the energy required to form the allylic radical. Thus, it appears possible for the second chlorine atom to deactivate slightly a chlorovinyl group. Such resonance effects conceivably can affect the donor-acceptor properties of a chlorovinyl group, particularly if the driving force in alternation is partly caused by resonance in the transition state.<sup>10</sup>

1,1-Diphenylethylene is 2.4–2.7 times as reactive as styrene toward the 2-chlorobutadiene and 2,3-dichlorobutadiene radicals. Since diphenylethylene is a better donor than styrene, it thus appears that the acceptor properties of the two diene radicals are similar, a conclusion reached from a comparison of the ratio products in Table II.

The difference in reactivity of styrene and 1,1-diphenylethylene is less than might be expected. The effect of the second substituent is less than for vinyl chloride and vinylidene chloride.<sup>7</sup> The two phenyl groups, although on the same carbon, may offer increased steric hindrance to the approach of the attacking radical. Since the activating effect of a phenyl group presumably is caused principally by resonance in the transition state, with a planar configuration preferred, it is also possible that the two phenyl groups mutually offer some steric hindrance to such resonance.

Systems containing 1,1-diphenylethylenes appear to have low rates of copolymerization compared with systems containing styrene, and generally give poor yields (*cf.* Table I).<sup>8,11</sup>

This inhibitory action may result from the formation of radicals ending in 1,1-diphenylethylene units which are less reactive than radicals ending in styrene units, because of additional resonance stabilization. Such radicals may not readily propagate the kinetic chain,<sup>1</sup> although kinetic measurements have not been made. If this be correct, then steric hindrance to resonance must not be very great.

1,1-Di-[*p*-chlorophenyl]-ethylene appears to be slightly more reactive (10–20%) than 1,1-diphenylethylene toward both the acrylonitrile and methyl acrylate radicals, while 1,1-di-[*p*-anisyl]-ethylene is about twice as reactive. This effect of *p*-chloro and *p*-methoxy groups upon the reactivity of 1,1-diphenylethylene is thus similar to that observed by Walling, Briggs, Wolfstirn and Mayo<sup>10</sup> for the copolymerization of substituted styrenes with methyl methacrylate.

## Summary

Monomer reactivity ratios have been determined for 2-chlorobutadiene with six olefins, and for 2,3-dichlorobutadiene with three olefins. These two

(10) Walling, Briggs, Wolfstirn and Mayo, *THIS JOURNAL*, **70**, 1537 (1948).

(11) Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945).

dienes have similar donor-acceptor properties being close to methyl methacrylate and methyl acrylate in the donor-acceptor series.

2-Chlorobutadiene is 3-16 times as reactive as butadiene, depending on the reference radical. 2,3-Dichlorobutadiene is 1.1-1.3 times as reactive as 2-chlorobutadiene. The chlorovinyl group in 2-chlorobutadiene appears to be more reactive than those in 2,3-dichlorobutadiene.

1,1-Diphenylethylene is only 2.0-2.5 times as reactive as styrene. The second phenyl group presumably offers some steric hindrance, either to resonance in the transition state, or to approach of the attacking radical. Substitution of chlorines in the para-positions increases the reactivity 10-20%; para-methoxy groups double the reactivity toward methyl acrylate or acrylonitrile radicals.

PASSAIC, N. J.

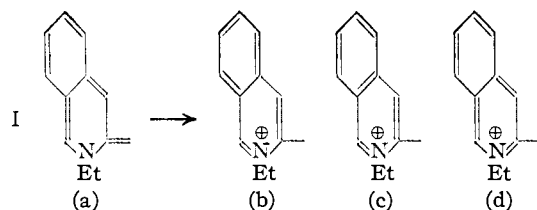
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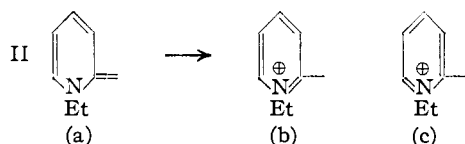
## Color and Constitution. IX.<sup>1</sup> Absorption of Cyanines Derived from 3-Methylisoquinoline; a Rule Relating Basicity and Absorption in Symmetrical Cyanines

BY L. G. S. BROOKER, F. L. WHITE AND R. H. SPRAGUE

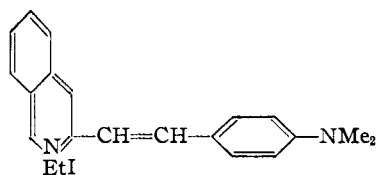
The absorption spectra of the cyanines derived from 3-methylisoquinoline<sup>2</sup> show several features of special interest. The basicity of the ring would be expected to be very high, for although it is possible to write only one structure of the Kekulé type (Ia) for the uncharged form of the ring, three may be written for the positively charged form (Ib, c and



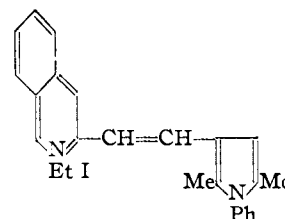
d). The gain in resonance stabilization on acquiring a positive charge is therefore very great indeed, greater even than for 2-linked pyridine, where the uncharged form of the ring may be written in one way (IIa) and the positively charged form in two (IIb and c).



Such high basicity of the 3-linked isoquinoline ring (more precisely the high "N<sup>IV</sup> minus N<sup>III</sup> stabilization")<sup>3</sup> would be expected to result in an exceptionally high "deviation" in  $\lambda_{\max}$  for both the styryl dye III and for the unsymmetrical 3-isoquinino-3'-pyrrolocarbocyanine IV. These predictions actually hold. With  $\lambda_{\max}$  4250 Å. in nitro-

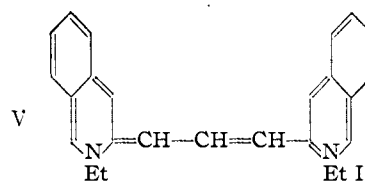


III  
 $\lambda_{\max}$  4220 Å.,  $\epsilon_{\max}$   $3.1 \times 10^4$  in MeOH  
 $\lambda_{\max}$  4250 Å.,  $\epsilon_{\max}$   $3.2 \times 10^4$  in MeNO<sub>2</sub>



IV  
 $\lambda_{\max}$  3890 Å.,  $\epsilon_{\max}$   $2.6 \times 10^4$  in MeOH

methane, III shows a deviation of 1455 Å., while IV shows one of 1005 Å. as calculated in the usual way.<sup>3</sup> These values are higher than any deviations previously reported in the two series of dyes to which III and IV belong.<sup>3</sup> Until now the highest deviations were shown by the 1,3-diethylbenzimidazole nucleus and were 1405 and 920 Å. for the



V  
 $\lambda_{\max}$  5300 Å.,  $\epsilon_{\max}$   $1.3 \times 10^4$  in MeOH  
 $\lambda_{\max}$  5310 Å.,  $\epsilon_{\max}$   $1.2 \times 10^4$  in MeNO<sub>2</sub>

dyes corresponding to III and IV, respectively.<sup>3</sup> The 2-ethyl-3-isoquinoline nucleus is thus the most strongly basic ring so far encountered in work on the cyanine dyes.

The "proportional deviations" of dyes III and IV, 103.5 and 109 units, respectively, are indicated in Fig. 1 together with those of a selection of the more basic nuclei of the group previously studied.<sup>3</sup>

Another feature of considerable interest is the fact that the 3-isoquinocarbocyanine V absorbs at markedly shorter wave lengths than the isomeric dye VI (pinacyanol) and even than the 2,2'-pyridocarbocyanine VII. In fact, V provides the first recorded example of a carbocyanine derived from a simpler carbocyanine (VII) by the addition of ben-

(1) Presented in part before the Organic Section of the American Chemical Society, April 11, 1946, at Atlantic City, New Jersey. Part VII, see THIS JOURNAL, 67, 1889 (1945).

(2) *Ibid.*, 73, 1094 (1951).

(3) Part VII, *ibid.*, 67, 1881 (1945).