

condition can be shown approximately equivalent to

$$(\bar{R}_{\text{C}_2\text{H}_6}/\bar{R}_{\text{CH}_4})^2 \gg 4 \quad (13)$$

a condition which is amply met by the present experiments. However, the absorption of mercury dimethyl has been shown to increase when a medium pressure mercury arc was used as light source. Although no quantitative measurements were made, it is not improbable that this increase should vary in an exponential manner and give rise to a somewhat higher activation energy than the true one. The agreement between the two methods must therefore be regarded as somewhat fortuitous and the value of  $E_s = 9000 + \frac{1}{2} E_1$  cal. will be considered the correct one. This gives for  $E_s$  the value

$$E_s = 8400 + \frac{1}{2} E_1 \text{ cal.} \quad (14)$$

This value is considerably higher than the one obtained by Smith and Taylor.<sup>3</sup> This discrepancy may be due to the fact that these authors used concentrations of butane so large that methane formation exceeded ethane formation. Under these conditions the  $\text{CH}_3$  steady-state concentration must have decreased by a factor of 2 or 3 over the temperature interval in question. If the lowest two temperatures given are used to calculate  $E_s$ , a value of 6400 cal. is obtained, in contrast to the over-all value of 5500 cal. Here the rate of ethane formation decreased by a factor of 2.25 as the temperature increased from 369 to 404°K. Since concentrations of mercury dimethyl high enough to be completely absorbing were used, these data probably were free from the compensating error of increased light absorption. These arguments probably apply to other cases where the activation energy of hydrogen abstraction was calculated on the basis of increase in methane formation as a function of temperature.

The question arises whether the present work deals with the abstraction of primary or secondary hydrogens. It has been pointed out by Hinshel-

wood<sup>6</sup> that compound reactions yielding the same measurable product should give rise to bent curves in the plots of  $\ln$  rate *vs.*  $1/T$ . It can be shown that the asymptotes to the high and low temperature branches of the curve (corresponding to the high and low activation energy steps) intersect at a temperature given by

$$(E_2 - E_1)/R \ln a_2/a_1 = T_{\text{intersection}} \quad (15)$$

where  $a_1$  and  $a_2$  are the pre-exponential factors corresponding to the activation energies  $E_1$  and  $E_2$ . A real intersection can occur only when  $a_2 > a_1$ , for  $E_2 > E_1$ .

If the difference in pre-exponential factors for primary and secondary hydrogen abstraction in butane is small,  $T_{\text{intersection}}$  will be quite high, even if  $E_{\text{prim.}} - E_{\text{sec.}}$  is small. If the pre-exponential factors may be assumed proportional to the number of primary and secondary hydrogens, this temperature will be 600°K, if  $E_{\text{prim.}} - E_{\text{sec.}}$  is only 500 cal., which is unlikely. Any *linear* portion of the  $\ln$  rate *vs.*  $1/T$  curve below  $T_{\text{intersection}}$  must be ascribed to the low activation energy reaction. It is therefore likely that the present work deals with the abstraction of secondary hydrogens.

### Summary

1. The reaction of methyl radicals produced from mercury dimethyl with butane has been studied.

2. The activation energy difference between the reactions of methyl radicals with mercury dimethyl and butane (to give methane in each case) is 640 cal. leading to an activation energy of about  $8400 + \frac{1}{2} E_1$  cal. for the reaction of  $\text{CH}_3$  radicals with butane.

3. The reaction with butane may involve mostly secondary hydrogens.

(6) C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," The Clarendon Press, Oxford, 1933, p. 67.

ROCHESTER, NEW YORK

RECEIVED AUGUST 1, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ROCHESTER]

## The Fluorescence of Cyanine and Related Dyes in the Monomeric State<sup>1</sup>

By L. J. E. HOFER,<sup>2</sup> ROBERT J. GRABENSTETTER<sup>3</sup> AND EDWIN O. WIIG\*<sup>4</sup>

A great deal of work has been done on the correlation of the position of the principal absorption maxima of cyanine and related dyes in the monomeric state and the structure of these

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(1) This article is based on portions of theses by L. J. E. Hofer and R. J. Grabenstetter submitted to the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) Now at Proctor and Gamble Co., Ivorydale, Ohio.

dyes.<sup>4-9</sup> No data for the corresponding fluorescence maxima have been published except some

(4) L. G. S. Brooker, "Nuclear and Theoretical Organic Chemistry," Vol. III, Frontiers in Chemistry, Interscience Publishers, Inc., New York, N. Y., 1945.

(5) L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, Jr., and G. van Zandt, *Chem. Rev.*, **41**, 325 (1947).

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

(7) Beilensen, N. I. Fisher and F. M. Hamer, *ibid.*, **A163**, 138 (1937).

(8) Herzfeld and Sklar, *Rev. Modern Phys.*, **14**, 294 (1942).

(9) H. Kuhn, *J. Chem. Phys.*, **16**, 840 (1948).

qualitative visual data by Fisher and Hamer.<sup>6</sup> In the present paper an experimental technique is described for studying the monomeric fluorescence (as contrasted to polymeric fluorescence),<sup>10</sup> a survey of the fluorescence of a necessarily limited number of cyanine and related dyes is presented, and the effect of solvents of widely varying dielectric constants on certain of the dyes is demonstrated.

### Experimental

**Materials.**—The glycerol was J. T. Baker C. P. double distilled which was further purified by two vacuum distillations at 155–160° and 9 mm. pressure. Only the middle half of each distillation was taken.

The acetone was Commercial Solvents, Inc., C. P. grade. It was purified by one distillation from over potassium permanganate. Then it was redistilled twice. Only the middle half of the distillate was taken in the last two distillations.

The methyl alcohol was J. T. Baker C. P. which was further purified by three distillations in a fractionating column. The middle 80% of each distillation was utilized.

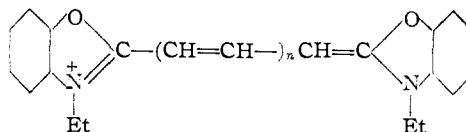
The cyclohexane was Eastman Kodak Co. White Label grade. It was fractionated before use; the first and last 20% of distillate were discarded.

The pyridine was a commercial product. It was dried over sodium hydroxide and fractionated. Only the middle fraction was retained. The pyridine for the following experiments was a water solution 50% by volume.

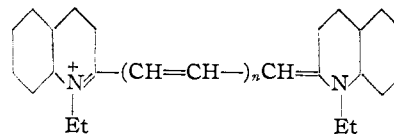
Eastman Kodak Co. Spectroscopic Plates, emulsion type I, of high speed and medium contrast were used. The sensitizings employed were G, 4600–5800 Å; F, 4600–6800 Å; N, 6800–8600 Å; and P, 8200–9300 Å. The plates were developed for eight minutes at 18° in Eastman D19.

**Apparatus and Procedure.**—About 25 ml. of each dye solution was prepared in an individual cell consisting of 15 cm. of 22-mm. Pyrex glass tubing closed at one end and provided with a neck of 10-mm. tubing at the other. Most of the samples were then frozen in solid carbon dioxide, evacuated, and sealed off at the neck on the cell but this process seemed to have no special advantages. The fluorescence was excited by a beam from a 500-watt tungsten filament projection bulb focussed with two quartz lenses 5.5 cm. in diameter and of 12 cm. focal length. The beam struck the cell at right angles to the cell axis and came to a focus within the cell. The collimator of a Large Bausch and Lomb Constant Deviation Spectrograph with camera attachment was lined up at right angles to the beam of the exciting radiation. The cell was held in the proper position on the optical bench by means of a cell holder and a fairly elaborate set of shields was necessary to prevent reflected light from passing into the spectrometer. However, the apparatus could be operated for twelve hours with a non-fluorescent liquid-like methyl alcohol in a cell in the cell holder with no detectable effect on a plate in the spectrograph. The spectrograph was calibrated with wave length drum set at 6700 Å. with photographs of the spectra of mercury, iron and barium. A mercury arc was placed on the optical bench on the side of the fluorescence from the projection lamp. Light from the mercury arc could be scattered from an iron oxide sol in the fluorescence cell directly into the collimator. By this means every plate was calibrated with a comparison spectrum. The fluorescence bands were rarely broader than 500 Å. and the positions of the maxima on the spectrographic plates were easily determined visually.

**Dyes.**—The following homologous series of dyes were studied: I, 2,2'-diethyloxycarbocyanine iodide (b) and 2,2'-diethyloxatricarbocyanine iodide (d),  $n = 1^*, 3^*$  (' $n$ ' values corresponding to fluorescent dyes are distinguished by an asterisk).

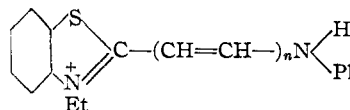


II, 1,1'-diethyl-2,2'-cyanine iodide (a) to 1,1'-diethyl-2,2'-tricarbo-cyanine iodide (d),  $n = 0, 1^*, 2^*, 3^*$ .



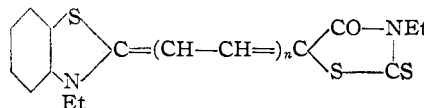
III, 2,2'-diethylthiacyanine iodide (a) to 2,2'-diethylthiatricarbocyanine iodide (d), structural formula analogous to (S. f. a. t.) I,  $n = 0, 1^*, 2^*, 3^*$ .

IV, 2-anilinobenzothiazole ethiodide (a) to 2-(6-anilino-1,3,5-hexatrienyl)-benzothiazole ethiodide (d),  $n = 0, 1^*, 2^*, 3^*$ .



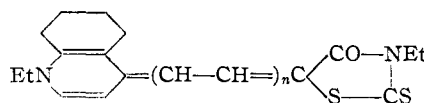
V, 2-(N-methylanilino)-benzothiazole iodide (a) to 2-[6-(N-methylanilino)-1,3,5-hexatrienyl]-benzothiazole ethiodide (d), S. f. a. t. IV,  $n = 0, 1^*, 2^*, 3^*$ .

VI, 3-ethyl-5-(3-ethyl-2(3)-benzothiazolylidene)-rhodanine (a) to 3-ethyl-5-[(3-ethyl-2(3)-benzothiazolylidene)-hexadienylidene]-rhodanine (d),  $n = 0, 1^*, 2^*, 3^*$ .



VII, 3-ethyl-5-(3-ethyl-2(3)-benzoxazolylidene)-rhodanine (a) to 3-ethyl-5-[(3-ethyl-2(3)-benzoxazolylidene)-butenylidene]-rhodanine (c), S. f. a. t. VI,  $n = 0, 1^*, 2^*$ .

VIII, 3-ethyl-5-(1-ethyl-4(1)-quinolylidene)-rhodanine (a) to 3-ethyl-5-[(1-ethyl-4(1)-quinolylidene)-ethylidene]-rhodanine (b),  $n = 0^*, 1^*$ .



### Results

In Table I the fluorescence data on the various homologous series of dyes are summarized and compared with the absorption data. The solutions used are very dilute (of the order of  $10^{-5}$  mole/liter). No aqueous solutions were used. All studies were made at room temperature. Polymerization sets in at concentrations  $\sim 10^{-3}$  mole/liter in aqueous solutions.<sup>10</sup> The fluorescence spectra of dyes I to V were determined with the dye dissolved in glycerol. This strengthened the fluorescence considerably. Dyes VI to VIII were dissolved in acetone and methyl alcohol because these dyes did not dissolve readily in glycerol. Preliminary experiments showed that the fluorescence maxima were essentially the same in methyl alcohol, acetone and ether. Columns 4 and 5 of Table I can therefore be directly compared.

(10) Hutten and Pringsheim, *J. Chem. Phys.* 13, 121 (1945).

TABLE I

COMPARISON OF THE FLUORESCENCE MAXIMA WITH THE ABSORPTION MAXIMA OF SOME CYANINE AND RELATED DYES IN THE MONOMERIC STATE

Dye	Concn., moles/l. × 10 <sup>4</sup>	Expt. <sup>c</sup>	Color of fluores.	Fluores. maximum,	Abs. max. Å. (in CH <sub>3</sub> OH)	Δ, Å.
Ia	...	.....	.....	...	3720	...
Ib	0.5	1	Greenish-yellow	5120 <sup>a</sup>	4850	270
Ic	...	.....	.....	...	5800	...
Id	0.1	2	Red	6950 <sup>a</sup>	6840	110
IIa	0.5	300	None	... <sup>a</sup>	5220	...
IIf	0.4	0.25	Red	6410 <sup>a</sup>	6050	360
IIc	1.9	15	Invisible	7600 <sup>a</sup>	7080	520
IIId	2.1	15	Invisible	8670 <sup>a</sup>	8080	590
IIIa	0.5	90	None	... <sup>a</sup>	4220	...
IIIb	0.5	0.012	Orange	5860 <sup>a</sup>	5570	290
IIIc	0.9	0.15	Red, faint	6910 <sup>a</sup>	6500	410
IIId	1.6	0.20	Invisible	8050 <sup>a</sup>	7620	430
IVa	0.5	30	.....	... <sup>a,b</sup>	2985	...
IVb	0.8	75	Robins egg blue	No distinct max. <sup>a</sup>	4140	...
IVc	0.4	0.025	Yellow	5730 <sup>a</sup>	5160	570
IVd	0.4	0.012	Red	6660 <sup>a</sup>	6125	535
Va	6.3	60	.....	... <sup>a,b</sup>	2930	...
Vb	0.7	60	Blue	No distinct max. <sup>a</sup>	4000	...
Vc	1.5	0.1	Yellow-green	5470 <sup>a</sup>	4965	505
Vd	0.9	0.02	Red	6520 <sup>a</sup>	5975	545
VIa	1.4	80	None	... <sup>d</sup>	4260	...
VIb	1.3	1.0	Yellow	5800 <sup>d</sup>	5240	560
VIc	0.6	0.6	Red	6430 <sup>d</sup>	6050	380
VIId	1.2	1.0	Invisible	7740 <sup>d</sup>	6340	400
VIIa	1.1	800	None	... <sup>d</sup>	...	...
VIIb	2.7	30	Yellow	5810 <sup>d</sup>	4900	910
VIIc	0.6	2.5	Red	6410 <sup>d</sup>	5790	620
VIIIa	...	.....	.....	5766 <sup>a</sup>	5150	616
VIIIb	...	.....	.....	6575 <sup>a</sup>	6170	405
VIIIc	...	.....	.....	...	7160	...
VIIIId	...	.....	.....	...	8200	...

<sup>a</sup> Glycerol. <sup>b</sup> It is doubtful if enough activating radiation reached this dye in order to excite its fluorescence or that the fluorescence even if excited could have penetrated the glass optics of the spectrograph. <sup>c</sup> Slit opening (mm.) × exposure time (minutes). <sup>d</sup> Acetone. <sup>e</sup> Methyl alcohol.

Two features of these results at once become apparent from Table I. 1. The wave length of the fluorescence band maximum is always of longer wave length than that of the absorption band. This is to be expected from Stokes law. The difference in wave length between the absorption band maximum and the fluorescence band maximum, Δ, is roughly constant for vinylenes homologous series of symmetrical dyes and varies from 110 to 910 Å. for the dyes here studied. The relationship between fluorescence maxima and absorption maxima is graphically illustrated in Fig. 1 for the homologous series 1,1'-diethyl-2,2'-cyanine iodide to 1,1'-diethyl-2,2'-tricarbo-cyanine iodide. 2. The first members of the vinylenes homologous series do not fluoresce with the exception of dye VIIIa. (Dyes IVa and Va probably cannot reveal their fluorescence bands by the method of examination here employed.) Even the second members of the series do not always fluoresce characteristically as in the case of dyes IVb and Vb. It was impossible to excite fluorescence even when using

exposures 7000 times as great as for the dyes of the rest of the series as the example of Series III shows. In general the registration of the fluorescence band on the photographic plate for all the remaining dyes of a given series required roughly the same exposure. The non-fluorescence of dye IIa in dilute solutions is well established since this dye has been studied extensively.<sup>10</sup>

It is well known that the absorption bands of the merocyanines (VI, VII, VIII) are especially sensitive to solvent effects.<sup>4</sup> In order to study corresponding effects in fluorescence, solutions of dyes were made up in cyclohexane (ε, dielectric constant, = 2.012), methyl alcohol (ε = 31.2), and pyridine-water, 50-50 (dielectric constant unknown but believed to be very high). The results are summarized in Table II. In Fig. 2 the data for dye VI are graphically presented.

The following conclusions may be drawn: 1. The fluorescence maxima are progressively shifted to longer wave lengths as the dielectric constant of the solvent increases. A similar phenomenon is observed for the absorption spectra of these

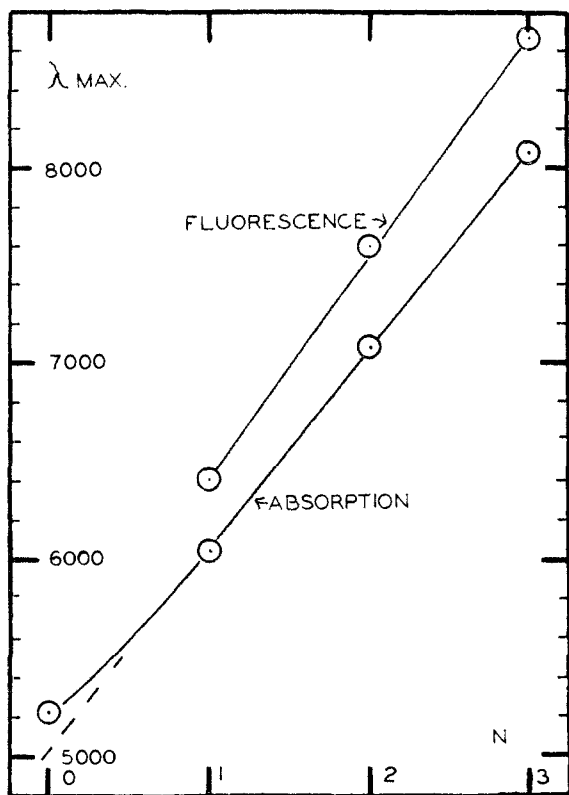


Fig. 1.—Fluorescence and absorption maxima of a typical series of dyes, 1,1'-diethyl-2,2'-cyanine iodide to 1,1'-diethyl-2,2'-tricarbo-cyanine iodide.

dyes. However, the solvent has much less influence on the shift of the fluorescence maxima than on the shift of the absorption maxima.

TABLE II

FLUORESCENCE AND ABSORPTION MAXIMA OF MERO-CYANINES IN DIFFERENT SOLVENTS

Dyes	Ångströms				Pyridine-water	
	Cyclohexane Abs.	Fluo.	Methyl alcohol Abs.	Fluo.	Abs.	Fluo.
VIa	4210	None	4260	None	4320	None
VIb	4920	5480	5240	5596	5395	5627
VIc	5370	6330	6050	6440	6330	6510
VIId	5700	7440	6340	7653	7100	7833
VIIIa	4992	5740	5150	5766	°	5810
VIIIb	5480	6420	6170	6575	°	6633
VIIIc	5845	..	7160	..	°	..
VIId	6065	..	8200	..	°	..

° Data not available.

2. When the wave length of the fluorescence maxima is plotted against the length of the polymethine chain in dye Series VI the resulting curve is concave upward, *i. e.*, the series diverges in Brooker's nomenclature. In sharp contrast the corresponding absorption maxima form a curve which is concave downward *i. e.*, the series converges. In the case of the absorption maxima, increase in dielectric constant of the solvent

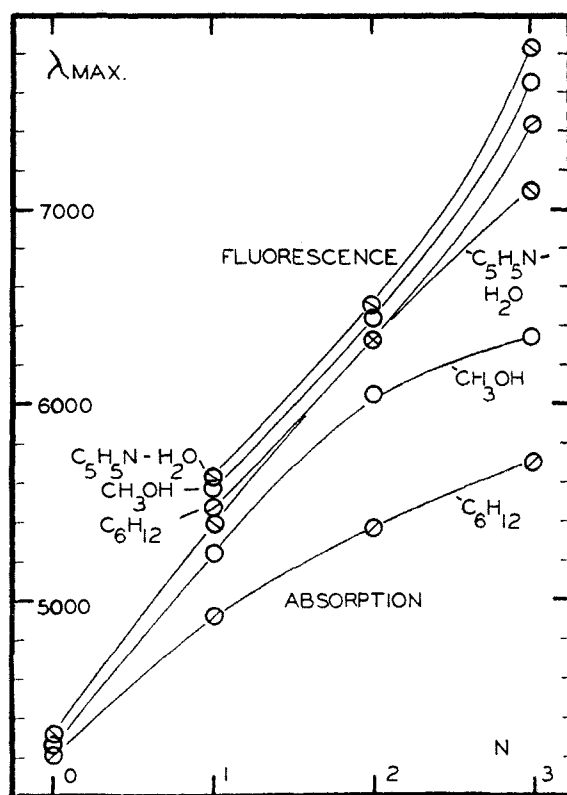


Fig. 2.—Fluorescence and absorption maxima of the series of dyes, 3-ethyl-5-(3-ethyl-2(3)-benzothiazolydene)-rhodanine to 3-ethyl-5-[(3-ethyl-2(3)-benzothiazolydene)-hexadienyldene]-rhodanine.

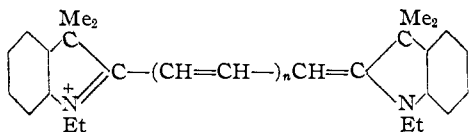
decreases the convergence of the series so that in pyridine-water the curve is nearly a straight line.

3. The change in dielectric constant of the solvent will not cause a non-fluorescent dye to fluoresce or vice versa.

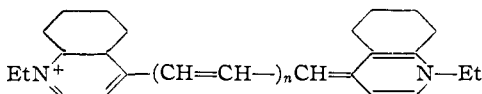
### Discussion

In any complete discussion of the fluorescence of cyanine dyes in the monomeric state the data of Fisher and Hamer must be considered since they include extreme cases which constitute a rigorous test for any theory. The dyes which these authors studied (other than dyes of series I, II, and III) were: IX, 2,2'-diethyl-3,4,3',4'-dibenzoxacyanine iodide (a) to 2,2'-diethyl-3,4,3',4'-dibenzoxadicyanine iodide (c), S. f. a. t. I,  $n = 0^*$ ,  $1^*$ ,  $2^*$ ; X, 2,2'-diethyl-5,6,5',6'-dibenzoxacyanine iodide (a) to 2,2'-diethyl-5,6,5',6'-dibenzoxadicyanine iodide (c), S. f. a. t. I,  $n = 0^*$ ,  $1^*$ ,  $2^*$ ; XI, 2,2'-diethyl-3,4,3',4'-dibenzthiacyanine iodide (a) to 2,2'-diethyl-3,4,3',4'-dibenzthiatricyanine iodide (d), S. f. a. t. III,  $n = 0$ ,  $1^*$ ,  $2^*$ ,  $3^{**}$ ; XII, 2,2'-diethyl-5,6,5',6'-dibenzthiacyanine iodide (a) to 2,2'-diethyl-5,6,5',6'-dibenzthiatricyanine iodide (d), S. f. a. t. III,  $n = 0$ ,  $1^*$ ,  $2^*$ ,  $3^{**}$ ; XIII, 2,2'-diethylselenacyanine iodide (a) to 2,2'-diethylselenatricyanine iodide (d), S. f. a. t. III,  $n = 0$ ,  $1^*$ ,  $2^*$ ,  $3^{**}$ ; XIV,

3,3,3',3'-tetramethyl-1,1'-diethylindomonocarbocyanine (b) to 3,3,3',3'-tetramethyl-1,1'-diethylindotricarbocyanine iodide (d),  $n = 0, 1^*, 2^*, 3^{**}$ .



XV, 1,1'-diethyl-5,6,5',6'-dibenz-2,2'-cyanine iodide (a) to 1,1'-diethyl-5,6,5',6'-dibenz-2,2'-tricarbo-cyanine iodide (d), S. f. a. t. II,  $n = 0, 1^{**}, 2^{**}, 3^{**}$ ; XVI, 1,1'-diethyl-4,4'-cyanine iodide (a) to 1,1'-diethyl-4,4'-tricarbo-cyanine iodide (d),  $n = 0, 1^{**}, 2^{**}, 3^{**}$



In addition Fisher and Hamer observed Ia and Ic to be fluorescent.

A careful examination of Fisher and Hamer's data shows that every non-fluorescent dye is either (1) an initial member of a homologous series or (2) a dye whose fluorescence band probably is beyond 6800 Å. and hence the fluorescence can be detected either with great difficulty or not at all with the naked eye. Strangely enough dyes Ia, IXa and Xa are fluorescent though initial members of a homologous series; any theory explaining the non-fluorescence of some of the initial members of homologous series must explain the fluorescence of these dyes. The position of the fluorescence maximum for a non-fluorescent dye can be estimated by means of the known absorption maximum and a reasonable value for the Stokes law shift. It can also be estimated from the position of the fluorescence maxima of other members of the homologous series as estimated from the fluorescence color. All such estimates (not detailed here) confirmed the non-observability of the fluorescence of the dyes belonging to group (2) noted above. These dyes must be considered fluorescent and the "n" values of such dyes are indicated by a double asterisk in the list of Fisher and Hamer's dyes here shown.

These results, both of Fisher and Hamer and the present authors, seem to indicate that some steric factor very similar to the Brunings-Corwin<sup>11</sup> effect is the cause of the non-fluorescence of these initial members of the vinylenes homologous series. Whatever the nature of this steric effect, much less crowding is necessary to produce it than is necessary for the Brunings-Corwin effect. In order to study more quantitatively this steric effect accurate scale sketches (Fig. 3-9) of some of the most informative dye molecules are necessary. For this purpose the bond radii, bond angles and interference radii shown in Table III may be used. These data are based largely on those of Pauling.<sup>12</sup>

(11) Brunings and Corwin, *THIS JOURNAL*, **64**, 593 (1942).

(12) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

However, in order to avoid confusion in the sketches the interference radii were taken arbitrarily as 10% less than those of Pauling. Furthermore, a distinction is drawn between the interference radii of the methyl group and that of the ethyl group. This is justified by the experimental observation<sup>5</sup> that the ethyl group produces a more pronounced Brunings-Corwin effect than the methyl group in a similar position. As Brooker, *et al.*,<sup>5</sup> have shown, the most probable structure is generally the least crowded and, accordingly, in every case the least crowded structure is here shown.

TABLE III

DIMENSIONS USED IN SKETCHING THE DYE MOLECULES

Bond radii, Å.	Bond angles Single Bond, Double Bond, 125°	Interference radii —(Pauling radii × 0.9) Å.		
H	—0.30	C-S-C 105°	H	1.08
C aliph.	0.77	C-O-C 105°	N	1.35
C ethylenic	0.67	C-N-C 120°	O	1.26
C aromatic	0.70		S	1.67
O ket.	0.55		Se	1.80
N amino	0.70		CH <sub>3</sub>	1.80
S	1.04		C <sub>2</sub> H <sub>5</sub>	2.20

An inspection of the sketches shows that the degree of crowding closely correlates with the fluorescence or non-fluorescence of the dyes. Fluorescent dyes IIb and IIIb are considerably less crowded than the corresponding non-fluorescent dyes IIa and IIIa. Obviously fluorescent dyes IIc, IIId, IIc, and IIId, are even less crowded than IIb and IIIb, respectively, and are, accordingly, fluorescent. Dyes of Series XV have structures similar to Series II and dyes of Series XI, XII, and XIII have structures similar to Series III. Accordingly, dyes XVa, XIa, XIIa, and XIIIa should be non-fluorescent and the rest of the dyes should be fluorescent—this is in accordance with the experimental observation. Non-fluorescent dye VIIa is more crowded than fluorescent dye VIIb. In order to save space, a sketch of the closely related fluorescent VIIb is used for comparison; this dye is even more crowded than VIIb by virtue of the replacement of a sulfur for the oxygen in one of the heterocyclic nuclei. Obviously non-fluorescent dye VIa is more crowded than fluorescent dye VIIb, so there is no need for a sketch of it. Series IV and V are somewhat unusual in that they have only one heterocyclic nucleus instead of two. Dye IVb (not shown) seems to be a borderline case as is also Vb (not shown) since neither of these dyes has a typical fairly narrow fluorescence band but instead they have a very broad general fluorescence which is difficult to photograph spectrographically. Both of these dyes are more crowded than IVc and Vc.

Even when comparing dyes of different series it is possible to predict roughly whether or not a dye is fluorescent. Non-fluorescent dye XVIa has roughly the same degree of crowding as non-

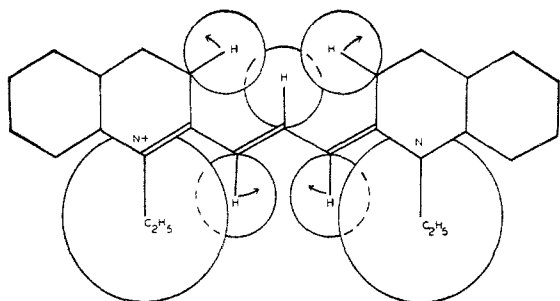


Fig. 3.—Dye IIb, 1,1'-diethyl-2,2'-monocarbocyanine iodide.

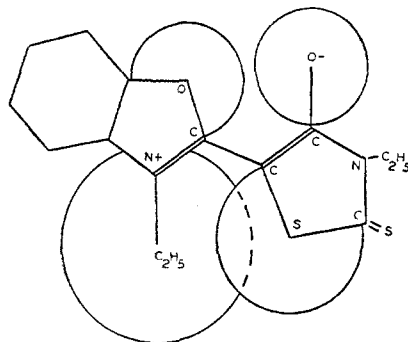


Fig. 7.—Dye VIIa, 3-ethyl-5-(3-ethyl-2(3)-benzoxazolyli-dene)-rhodanine.

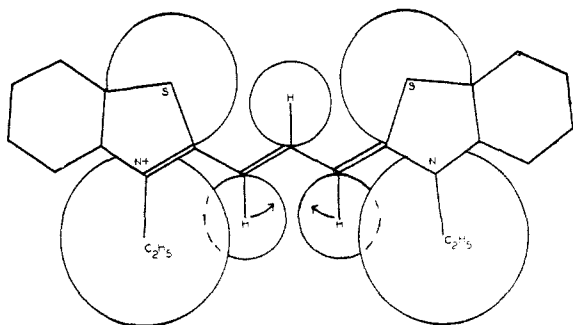


Fig. 4.—Dye IIIb, 1,1'-diethylthiamonocarbocyanine iodide.

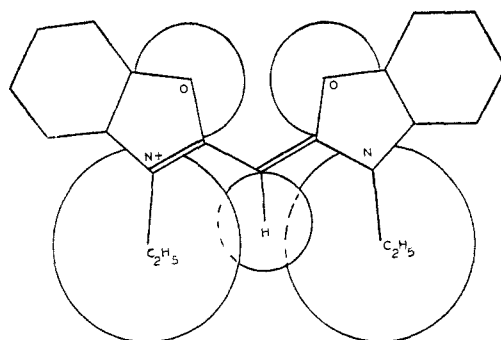


Fig. 8.—Dye Ia, 2,2'-diethyloxacyanine iodide.

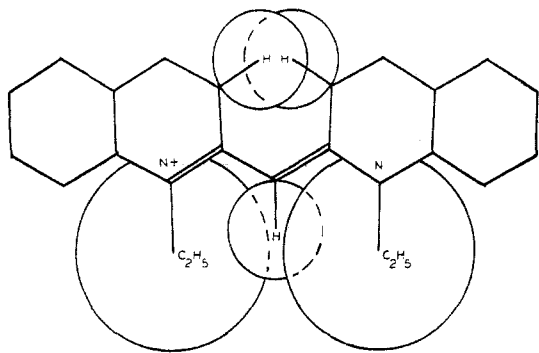


Fig. 5.—Dye IIa, 1,1'-diethyl-2,2'-cyanine iodide.

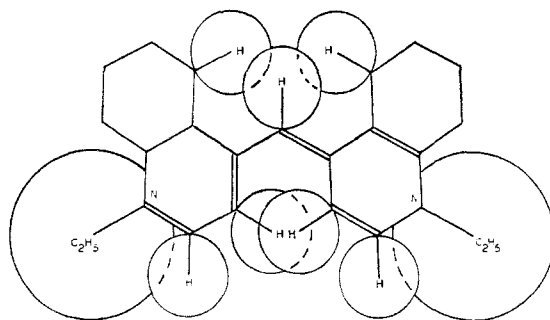


Fig. 9.—Dye XVIa, 1,1'-diethyl-4,4'-cyanine iodide.

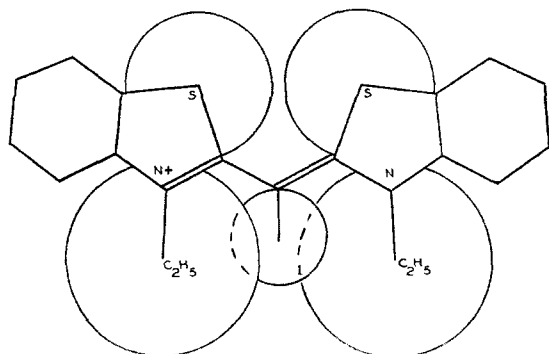


Fig. 6.—Dye IIIa, 1,1'-diethylthiacyanine iodide.

fluorescent dye IIa. Non-fluorescent dye IIa is definitely more crowded than fluorescent dye Ia by virtue of the substitution of a sulfur atom for an oxygen atom in both heterocyclic nuclei. Furthermore, Ia is less crowded than the non-fluorescent IIa, VIa, VIIa, XIa, XIIa, XIIIa, XVa and XVIa. Dye VIIIa, although an initial member of a homologous series, fluoresces, but examination of its absorption bands shows it to be atypical with two bands and examination of the scale sketch (not shown) shows that it is on the border between a fluorescent and non-fluorescent state.

The steric effect can be represented by a plot of potential energy against the angle between the plane of the two heterocyclic nuclei. For most

of the dyes here discussed this curve will have maxima at 0 and 180°, *i. e.*, the steric hindrance is a maximum when the dye has either of the two possible positions where the heterocyclic nuclei are co-planar. The resonance energy curve is similar except that it exhibits minima at 0 and 180°. The details of both these curves may vary considerably. These curves are represented schematically in Fig. 10. To some extent the two curves cancel each other and produce a resultant curve whose trough is much shallower than that in the resonance energy curve. This means that the constraints maintaining the molecule in a planar form are small when the steric effect is strong compared with the case where it is not. The resultant curve becomes equivalent to the resonance energy curve when the steric effect becomes negligible.

A tentative mechanism may be advanced to account for this steric quenching. Pauling has pointed out that conjugated, resonating systems of double bonds tend to be planar if steric relationships permit. When steric hindrance is sufficiently great so that the dye is forced out of the normal planar configuration, the resonance energy is decreased and the absorption band is shifted to the red. This is the Brunings-Corwin effect.<sup>11</sup>

One of the possible motions which a cyanine or cyanine-like molecule can execute is a twisting motion of the two heterocyclic ends of the molecule with respect to each other. By virtue of the small constraints this motion is more readily excited in the molecule exhibiting steric hindrance than when there is little steric hindrance. Thus the electronic energy of the excited dye molecule is easily converted to vibrational energy and eventually dissipated as heat or infrared radiation. This is simply another aspect of Lewis and Calvin's "Loose Bolt Theory"<sup>13</sup> which has been used to account for the loss of fine structure in the absorption spectra when chromophoric groups are loaded down with heavy saturated substituents.

It would be highly desirable to extend this study to a much larger group of dyes, especially those exhibiting the Brunings-Corwin effect.

(13) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

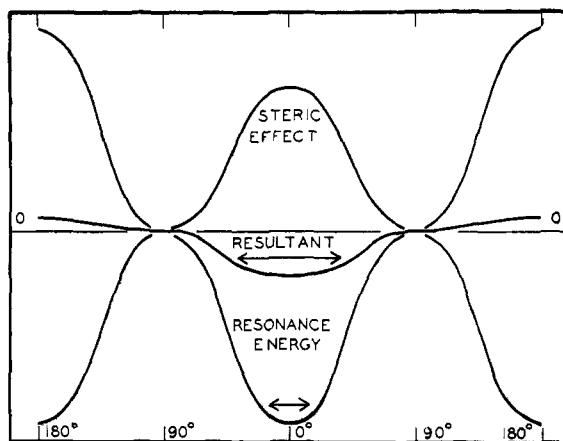


Fig. 10.—Schematic diagram of the interrelationship between the resonance energy and the steric effect which leads to internal quenching of fluorescence.

**Acknowledgments.**—The authors are highly indebted to Drs. L. G. S. Brooker and C. E. K. Mees of the Eastman Kodak Company for supplying the dyes and for invaluable suggestions. One of the authors (L. J. E. H.) wishes to express his gratitude to the Sherman Clarke Fund of the University of Rochester for the grant of a fellowship held during a part of this investigation.

#### Summary

1. The fluorescence of very dilute solutions of various cyanines and related dyes has been photographed.
2. Various solvents with a wide range of dielectric constant have been shown to have a smaller effect on the fluorescence spectrum than on the absorption spectrum of the dyes.
3. There is a strong tendency for the first members of vinylene homologous series of dyes to be non-fluorescent.
4. This tendency has been related to a steric effect and to the Lewis-Calvin Loose Bolt Hypothesis.

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RECEIVED JUNE 27, 1949