

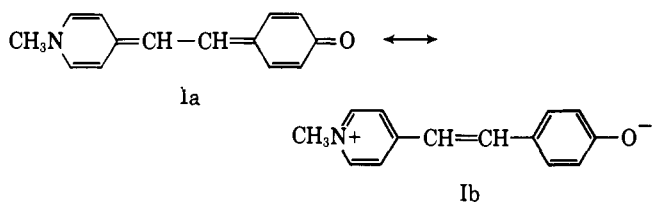
# Color and Constitution. XIII.<sup>1</sup> Merocyanines as Solvent Property Indicators<sup>2</sup>

Leslie G. S. Brooker, Arnold C. Craig, Donald W. Heseltine, Philip W. Jenkins, and Lewis L. Lincoln

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. Received December 5, 1964

The suggestion made in 1951 that certain highly polar merocyanine dyes be used as solvent property indicators is reaffirmed and its usefulness extended. However, merocyanines of this kind, which show blue shifts, are of limited usefulness in solvents of low polarity because of insolubility, a disadvantage shared by indicators suggested more recently by Kosower and by Dimroth. Certain weakly polar merocyanines, which show red shifts, are readily soluble in solvents of low polarity such as hydrocarbons, and prove to be sensitive indicators for this type of solvent. It is suggested that the transition energies in kcal./mole of dyes IV and VII, which are blue- and red-shifting, respectively, be designated  $\chi_B$  and  $\chi_R$ , respectively, and used as criteria of gross solvent property. The solvent sequence given by  $\chi_R$  values differs significantly from that given by values of  $\chi_B$ . These differences are discussed. Whereas  $\chi_B$  values correlate excellently with data of Kosower, Dimroth, and Winstein,  $\chi_R$  values do not. On the other hand, the latter correlate well with recent data of Pincock and of Ingold.

The absorptions of dyes of the merocyanine class are characteristically solvent sensitive to a greater or less degree,<sup>3</sup> one especially striking effect being the large "blue" shifts shown by merocyanines of intrinsically high polarity and with long conjugated chains. Certain of these latter dyes, for example, I, are so solvent sensitive that they were suggested as "solvent polarity indicators."<sup>4</sup>



Kosower has commented that as solvent polarity indicators the merocyanines "suffer from two disadvantages."<sup>5</sup> He stated that "these dye molecules possess large  $\pi$ -electron systems which are subject to specific interaction with solvent molecules, especially in the low-polarity region. Secondly, the maxima change less in position with solvent change than the 1-alkylpyridinium complexes." Kosower concluded

(1) Part XII: L. G. S. Brooker and G. H. Keyes, *J. Am. Chem. Soc.*, **73**, 5356 (1951).

(2) Presented at the Symposium on Solvation Phenomena, Calgary Section, Chemical Institute of Canada, Calgary, Alberta, Aug. 29, 1963.

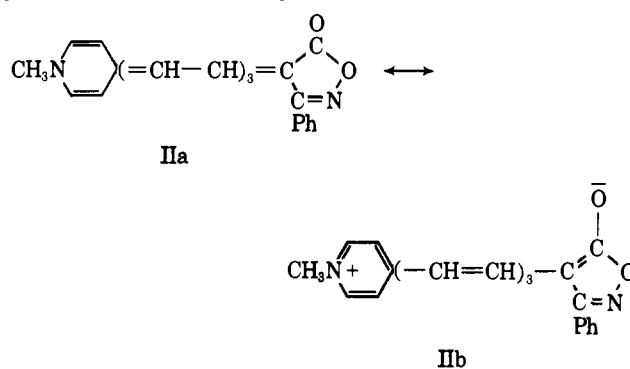
(3) Part X: L. G. S. Brooker, *et al.*, *J. Am. Chem. Soc.*, **73**, 5332 (1951).

(4) Part XI: L. G. S. Brooker, G. H. Keyes, and D. W. Heseltine, *ibid.*, **73**, 5350 (1951).

(5) E. M. Kosower, *ibid.*, **80**, 3253 (1958).

"that [merocyanines] cannot provide the same information as the pyridinium iodide complexes."

The blue shift reported for the merocyanine II<sup>3</sup> was compared by Kosower with that shown by his solvent polarity indicator of choice, 1-ethyl-4-carbomethoxy-pyridinium iodide. The absorption maximum of II moves from 487.5 in water to 710  $m\mu$  in pyridine,<sup>3</sup> and we now find that it continues its shift to 740  $m\mu$  in 2,6-lutidine. The shift to the latter value from the position in water corresponds to a difference in transi-



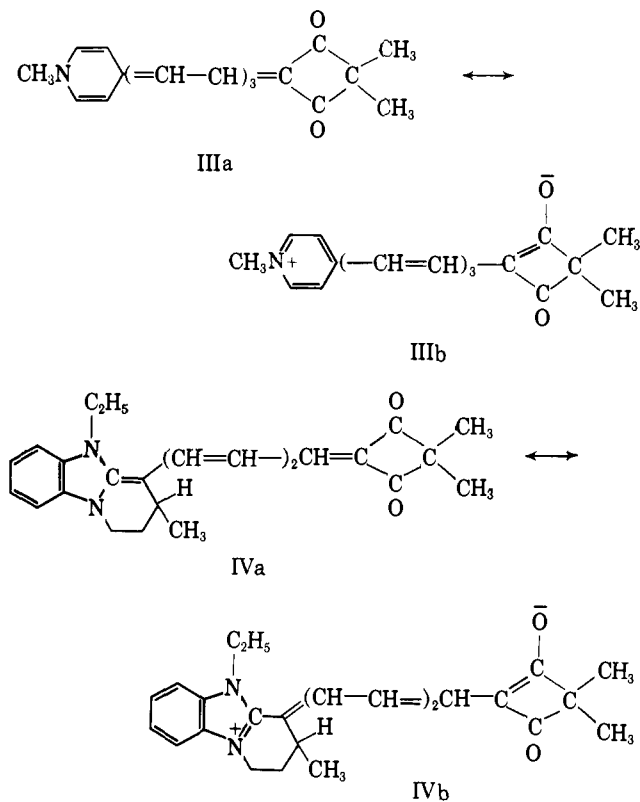
tion energies ( $\Delta E_T$ ) of 19.8 kcal./mole.

We have now prepared two more merocyanines of intrinsically high polarity (III and IV) using as one starting material the highly reactive 2,2-dimethyl-1,3-cyclobutanedione.<sup>6</sup> As estimated by the deviation procedure (details given in Experimental section), the acidity of the cyclobutanedione nucleus in IIIa is higher even than that of the phenylisoxazolone nucleus in IIa; hence it is not surprising that III is even more solvent sensitive than II.<sup>3,4</sup> With  $\lambda$  458  $m\mu$  in water, the shift to 723  $m\mu$  in 2,6-lutidine is 265  $m\mu$ , and 274  $m\mu$  to 732  $m\mu$  in toluene. The larger of these shifts corresponds to a  $\Delta E_T$  value of 23.3 kcal./mole.

The benzimidazole nucleus present in IVa is even more highly basic, judging by its deviation (see Experimental section), than the 4-pyridine nucleus in I, II, and III, so that IV is of an even higher intrinsic polarity than III. With  $\lambda$  415  $m\mu$  in water and  $\lambda$  685  $m\mu$  in toluene, the blue shift shown by this dye between these two solvents is 270  $m\mu$ , which in this region of the spectrum corresponds to a  $\Delta E_T$  value of 27.2 kcal./mole.<sup>7</sup>

(6) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **27**, 3743 (1962), whom we wish to thank for generous gifts of material.

(7) This may be compared with the figure of 30.6 kcal./mole indicative of the solvent sensitivity of 1-ethyl-4-carbomethoxypyridinium iodide obtained from Kosower's data.<sup>5</sup> The solvent-sensitive optical transition of Kosower's iodide is overlaid in water and highly aqueous solutions by another absorption band. The value of 30.6 for  $\Delta E_T$  is the difference between the transition energy of 64.0 kcal./mole measured in pyridine and a value for water of 94.6 kcal./mole which was obtained by extrapolation. The transition energies ( $Z$  values) showing the greatest difference which Kosower measured directly for his standard iodide are 63.2 for chloroform and 86.4 for 70% ethanol, this difference being 23.2 kcal./mole.



Whether or not II, III, and IV have "specific interactions" with solvents, the fact remains that the  $E_T$  values for one of these dyes in 2,6-lutidine and water and mixtures of the two show a linear relationship

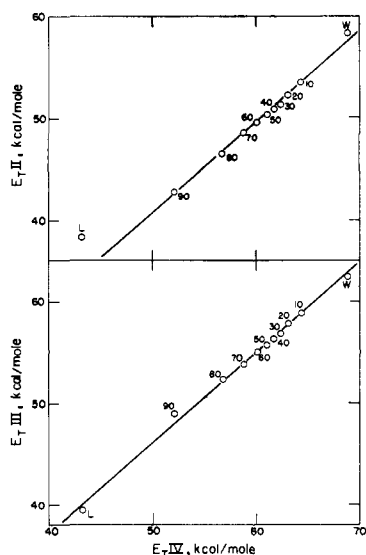


Figure 1. Transition energies of IV ( $E_T$  (IV)) for 2,6-lutidine (L) and water (W) and mixtures of the two plotted against corresponding  $E_T$  values for II and III. The numbers against points indicate volumes per cent lutidine in the aqueous solutions.  $N$  vol. % A in a mixture of A and B is defined throughout this paper as  $N$  volumes of A and  $(100 - N)$  volumes of B, both at 25° before mixing.

when plotted against corresponding values for either of the other dyes (Figure 1). Moreover, a linear relationship exists between transition energies of IV for a number of pure solvents and the  $Z$  values for these given by Kosower<sup>5</sup> (Figure 2). The high correlation

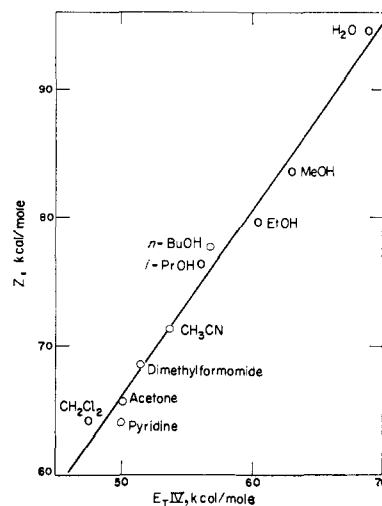


Figure 2. Transition energies of IV ( $E_T$  (IV)) in ten solvents plotted against  $Z$  values of Kosower<sup>5</sup> in the same solvents.

coefficient obtained by the method of least squares indicates the essential equivalence of the  $E_T$  and  $Z$  values. A summary of this and other linear regressions is given in Table I.

It is clear from the curves for the lutidine-water series dealt with in Figure 1 that a small change in solvent composition produces the greatest effect on the absorption in the neighborhood of the pure solvents. The further nature of the solvent composition-absorption relationship for IV is shown in Figure 3. The steep slope at each end of the curve reflects high sensitivity to a small change in solvent composition, in agreement with examples reported previously.<sup>3</sup>

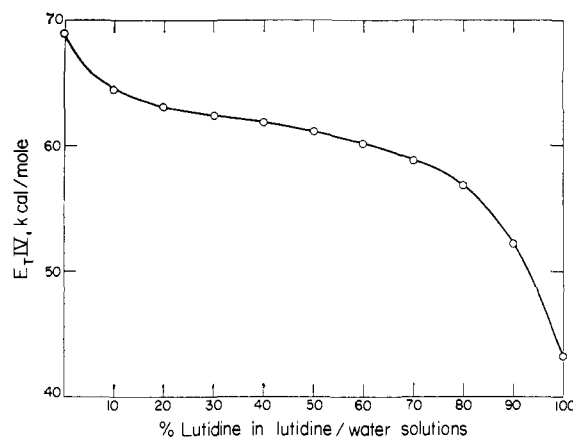


Figure 3. Transition energies of IV ( $E_T$  (IV)) in lutidine-water mixtures plotted against solvent composition.

Kosower's pyridinium iodide indicator, an ionized compound, has the disadvantage of almost complete insolubility in nonpolar solvents such as the hydrocarbons, a shortcoming shared by many of the solvent-sensitive pyridinium betaines, discussed by Dimroth and collaborators,<sup>8</sup> and to a somewhat less extent by highly polar merocyanines of the type II, III, and IV.

On the other hand, weakly polar merocyanines, though soluble in solvents of low polarity, have not so

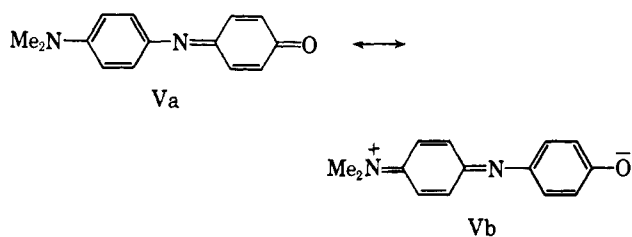
(8) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann.*, **661**, 1 (1963).

Table I. Summary of Linear Regressions

Regression	Solvent parameter	$n^a$	$\rho^b$	$r^c$	$s^d$	$sp^e$	$Y_0^f$
<i>E<sub>T</sub></i> (IV) ( $\chi_B$ ) vs.							
1	<i>E<sub>T</sub></i> (II)	35 <sup>o</sup>	0.885	0.971	1.27	0.038	-3.23
2	<i>E<sub>T</sub></i> (III)	20 <sup>h</sup>	0.905	0.989	0.971	0.032	0.25
3	<i>Z</i> <sup>i</sup>	10 <sup>j</sup>	1.45	0.989	1.51	0.075	-6.34
4	log <i>k</i> <sup>k</sup>	7 <sup>l</sup>	0.179	0.982	0.273	0.015	-13.8
5	<i>E<sub>T</sub></i> (30) <sup>m</sup>	12 <sup>n</sup>	1.03	0.991	1.14	0.043	-8.86
6	-∫ <i>H<sub>p</sub></i> -NO <sub>2</sub> <sup>o</sup>	6 <sup>p</sup>	-0.0108	0.232	0.277	0.023	10.9
<i>E<sub>T</sub></i> (VII) ( $\chi_R$ ) vs.							
7	<i>E<sub>T</sub></i> (VI)	20 <sup>q</sup>	0.766	0.999	0.151	0.0083	16.8
8	<i>E<sub>T</sub></i> (VI)	32 <sup>r</sup>	0.782	0.997	0.230	0.0107	16.1
9	<i>E<sub>T</sub></i> (VI)	88 <sup>s</sup>	0.779	0.986	0.417	0.0139	16.1
10	<i>E<sub>T</sub></i> (IV)	38 <sup>t</sup>	-1.44	0.620	4.41	0.304	118.4
11	<i>Z</i> <sup>i</sup>	17 <sup>u</sup>	-1.94	0.524	7.03	0.814	159.8
12	-∫ <i>H<sub>p</sub></i> -NO <sub>2</sub> <sup>o</sup>	19 <sup>v</sup>	-0.189	0.812	0.320	0.033	18.7
13	log <i>k</i> <sub>2</sub> <sup>w</sup>	16 <sup>x</sup>	-0.236	0.958	0.159	0.0191	12.4
14	log [ <i>k</i> <sub>3</sub> / <i>k</i> <sub>5</sub> <sup>1/2</sup> ] <sup>y</sup>	10 <sup>z</sup>	-0.053	0.993	0.017	0.0022	0.86

<sup>a</sup> Number of points. <sup>b</sup> Slope of the regression line. <sup>c</sup> Correlation coefficient. <sup>d</sup> Standard deviation of experimental measurements from the regression line. <sup>e</sup> Standard deviation of the slope of the regression line. <sup>f</sup> The intercept of the regression line with the ordinate ( $\chi_B$  or  $\chi_R = 0$ ). <sup>g</sup> The solvents used were those shown in Figure 1 plus pyridine-water mixtures (90, 80, 70, 60, 50, 30, 20, and 10%), dioxane-water mixtures (90, 80, 70, 60, 50, 30, and 10%), MeOH, EtOH, *n*-BuOH, *t*-PrOH, CH<sub>3</sub>CN, DMF, acetone, pyridine, and CH<sub>2</sub>Cl<sub>2</sub>. <sup>h</sup> The solvents used were those shown in Figure 1 plus MeOH, EtOH, *n*-BuOH, *t*-PrOH, CH<sub>3</sub>CN, DMF, acetone, pyridine, and toluene. <sup>i</sup> Kosower's *Z* value; see ref. 5. <sup>j</sup> For solvents, see Figure 2. <sup>k</sup> Logarithm of the rate constant of the ionization of *p*-methoxyneophyl *p*-toluenesulfonate; see ref. 12. <sup>l</sup> The solvents used were H<sub>2</sub>O, MeOH, EtOH, CH<sub>3</sub>CN, DMF, pyridine, and acetone. <sup>m</sup> Energy of transition of the pentaphenyl betaine 30 of ref. 8. <sup>n</sup> Solvents: H<sub>2</sub>O, MeOH, EtOH, *n*-BuOH, *i*-PrOH, CH<sub>3</sub>CN, DMF, acetone, pyridine, and CH<sub>2</sub>Cl<sub>2</sub>, 2,6-lutidine, and toluene. <sup>o</sup> The shielding parameter of *p*-fluoronitrobenzene in p.p.m. relative to fluorobenzene; see ref. 15. <sup>p</sup> Solvents: MeOH, acetone, pyridine, DMF, CH<sub>3</sub>CN, and CH<sub>2</sub>Cl<sub>2</sub>. <sup>q</sup> For solvents, see Figure 4. <sup>r</sup> For solvents, see Figure 5. <sup>s</sup> For 54 single solvents and 34 binary mixtures. <sup>t</sup> For solvents, see Figure 6. <sup>u</sup> Solvents: dioxane-water mixtures (90, 80, and 70%), MeOH, EtOH, *n*-BuOH, *n*-PrOH, *i*-PrOH, ethylene glycol, acetone, DMF, CH<sub>3</sub>CN, pyridine, DMSO, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and isooctane. <sup>v</sup> Solvents: cyclohexane, benzene, CCl<sub>4</sub>, *p*-dioxane, Et<sub>2</sub>O, THF, ethyl acetate, chlorobenzene, MeOH, acetone, pyridine, DMF, benzonitrile, nitrobenzene, CH<sub>3</sub>CN, CH<sub>3</sub>NO<sub>2</sub>, DMSO, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub>. <sup>w</sup> Logarithm of the rate constant of the base-catalyzed decomposition of *t*-butyl peroxyformate; see ref. 13. <sup>x</sup> For solvents, see Figure 7. <sup>y</sup> The logarithm of the solvent-sensitive rate-constant ratio of the autoxidation of styrene; see ref. 14. <sup>z</sup> Solvents: CCl<sub>4</sub>, *p*-xylene, toluene, benzene, chlorobenzene, bromobenzene, *i*-PrOH, EtOH, and nitrobenzene; the  $\chi_R$  value for *n*-heptane was used with the rate-constant ratio in *n*-decane.

far shown large shifts, with the single exception of phenol blue (V). This is a dye in which a feebly basic residue is linked to one that is strongly acidic, and shows a red shift from 552 in cyclohexane to 668 m $\mu$  in water.<sup>9</sup>

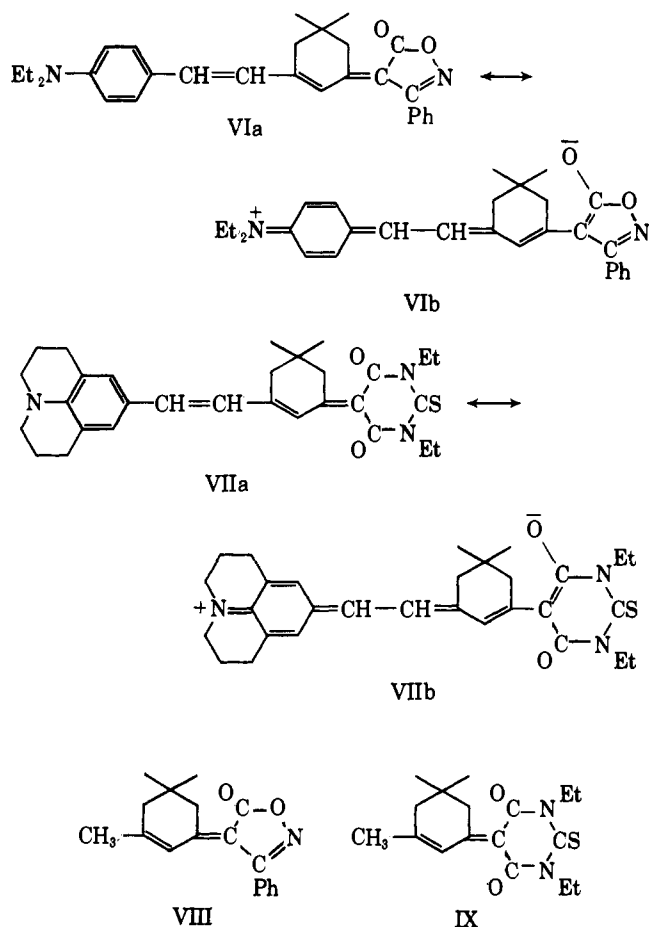


It was accordingly considered of interest to examine the behavior of the intrinsically weakly polar dyes VI and VII, in each of which a weakly basic residue is conjugated with one that is highly acidic. These dyes, furthermore, have unusually long conjugated chains for compounds of this sort. They were obtained by the condensation of the appropriate aldehyde with VIII and IX, which, in turn, were prepared by the condensation of isophorone with 3-phenyl-2-isoxazolin-5-one and 1,3-diethyl-2-thiobarbituric acid, respectively.<sup>10</sup>

The new dyes VI and VII are indeed soluble in non-polar hydrocarbon-like solvents (though correspondingly insoluble in highly aqueous solvents) and give unprecedentedly large red shifts.

(9) L. G. S. Brooker and R. H. Sprague, *J. Am. Chem. Soc.*, **63**, 3214 (1941).

(10) L. G. S. Brooker and D. W. Heseltine, U. S. Patent 2,856,404 (1958).



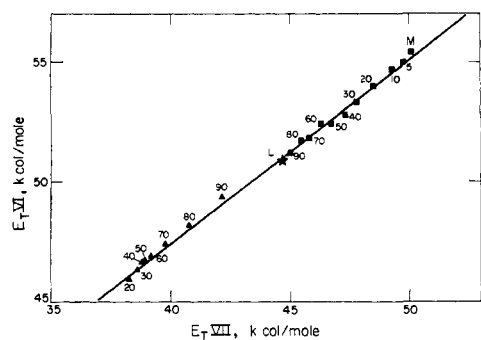


Figure 4. Transition energies ( $E_T$ ) of VII plotted against corresponding values of VI for 2,6-lutidine (L) and methylcyclohexane (M) and mixtures of the two. The numbers shown against points  $\square$  between L and M indicate volume per cent lutidine in methylcyclohexane. Points  $\Delta$  apply to lutidine-water mixtures; the numbers indicate volume per cent lutidine in water.

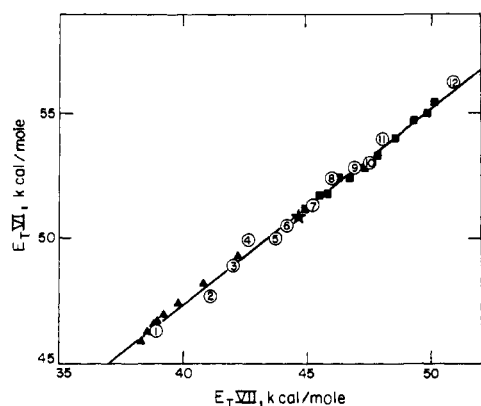


Figure 5. Transition energies  $E_T$  (VII) vs.  $E_T$  (VI). The points shown in Figure 4 are reproduced here, together with those for the following 12 solvents: (1) propargyl alcohol, (2) aniline, (3) dimethyl sulfoxide, (4)  $\gamma$ -butyrolactone, (5) dimethylformamide, (6) chloroform, (7) chlorobenzene, (8) ethyl N,N-dibutylcarbamate, (9) benzene, (10) mesitylene, (11) *p*-cymene, and (12) isooctane.

The absorption maximum of VI in isooctane lies at 508 and moves to 632  $m\mu$  in highly aqueous lutidine (10 vol. % lutidine in water),  $\Delta E_T$  being 11.3 kcal./mole, whereas VII, with  $\lambda_{max}$  562  $m\mu$  in isooctane, shifts 185 to 747  $m\mu$  in highly aqueous lutidine (20 vol. % lutidine in water), with a  $\Delta E_T$  of 12.6 kcal./mole. This latter red shift is believed to be the largest so far recorded for any dye for these solvents.

The transition energies for VI in 2,6-lutidine and methylcyclohexane and mixtures of the two are plotted in Figure 4 against the corresponding figures for VII, and the plot was extended by using aqueous lutidine solutions, though readily measurable absorptions could not be obtained when the solvent contained more water than is present in 20 vol. % of lutidine in water. Considered as a single group, these 20 points show excellent linearity; the correlation coefficient is 0.999.

The points shown in Figure 4 are given again in Figure 5, where to them are added points for the 12 pure solvents listed. The rectilinearity of all of these is self-evident; the correlation coefficient is 0.997, and the line in Figure 5 is almost, although not exactly, coincident with that in Figure 4.

Certain un-ionized dyes which show red shifts have recently been described.<sup>11</sup> These dyes, of which X and

(11) (a) M. A. Mostoslavskii and V. A. Izmail'skii, *Dokl. Akad. Nauk*

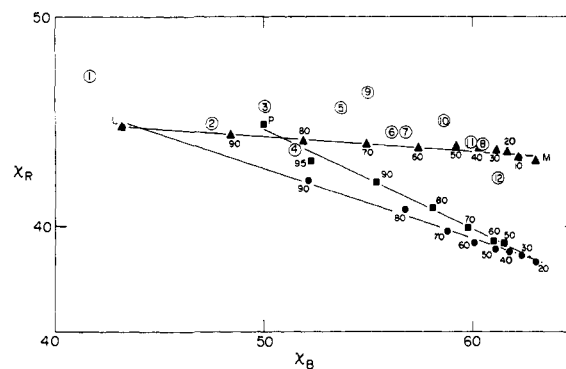
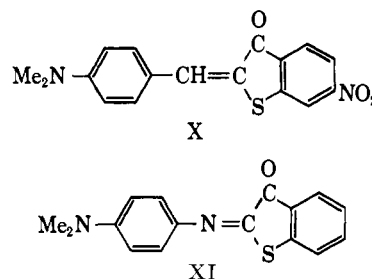


Figure 6. Values of  $\chi_R$  plotted against those of  $\chi_B$ :  $\circ$ , lutidine (L) and lutidine-water mixtures;  $\Delta$ , lutidine and methanol and mixtures of the two; and  $\square$ , pyridine and pyridine-water mixtures. The numbers beside the symbols indicate volume per cent nonhydroxylic solvent in the various mixtures. The large circles containing numbers refer to the other solvents and solvent mixtures: (1) toluene, (2) dichloromethane, (3) acetone, (4) dimethylformamide, (5) acetonitrile, (6) isopropyl alcohol, (7) *n*-butyl alcohol, (8) ethanol, (9) 90% dioxane-10% water, (10) 80% dioxane-20% water, (11) 70% dioxane-30% water, and (12) 60% dioxane-40% water.

XI are the most sensitive, have shorter conjugated chains than VI and VII and consequently show considerably smaller wave-length shifts. The absorption



of X is said to move from 496 in *n*-hexane to 567  $m\mu$  in aniline, so that  $\Delta E_T$  is 7.2 kcal./mole. The corresponding figure for XI is 7.1 kcal./mole.

Of the dyes showing blue shifts, whose absorptions are summarized in Figure 1, IV is the most sensitive. It is therefore suggested that the transition energy, in kcal./mole, of this dye IV in a given solvent, or solvent mixture, be designated  $\chi_B$ , and used as a solvent property criterion of that solvent or solvent mixture. It is further suggested that the transition energy, in kcal./mole, of the red-shifting dye VII in any given solvent, designated  $\chi_R$ , should similarly be used as a criterion of solvent property.

In Table II,  $\chi_B$  and  $\chi_R$  values are listed for a number of pure solvents and solvent mixtures. For strongly stabilizing solvents, however, such as those that are highly aqueous,  $\chi_R$  values cannot be ascertained because of the insolubility of the indicator dye VII in such solvents. Values of  $\chi_B$  are similarly lacking for nonstabilizing solvents (e.g., hydrocarbons) because of the insolubility of IV, hence many of the gaps in Table II.

For the series of solvents comprising lutidine and lutidine-water mixtures, values of  $\chi_R$  are linear with those of  $\chi_B$  (Figure 6), and linearity is likewise found

SSSR, 142, 600 (1962); (b) M. A. Mostoslavskii, V. A. Izmail'skii, and M. M. Shapkina, *J. Gen. Chem. USSR*, 32, 1746 (1962).

Table II. Values of  $\chi_R$  and  $\chi_B$  in Single Solvents and Binary Solvent Mixtures

Solvent	$\chi_R$	$\chi_B$	Solvent	$\chi_R$	$\chi_B$
Isooctane	50.9		2-Butanone	45.4	
<i>n</i> -Hexane	50.9		Chlorobenzene	45.2	
<i>n</i> -Heptane	50.9		Dichloromethane	44.9	47.5
Methylcyclohexane	50.1		2-Butoxyethanol	44.8	
Cyclohexane	50.0		2,6-Lutidine	44.7	43.2
Triethylamine	49.3		Bromobenzene	44.6	
Carbon tetrachloride	48.7		Isopropyl alcohol	44.5	56.1
Isopropyl ether	48.6		<i>n</i> -Butyl alcohol	44.5	56.8
<i>n</i> -Butyl ether	48.6		Diethyl phthalate	44.3	
<i>p</i> -Dioxane	48.4		Cyclohexanone	44.3	
Ethyl ether	48.3		Chloroform	44.2	
<i>p</i> -Cymene	48.0		<i>n</i> -Propyl alcohol	44.1	
<i>m</i> -Xylene	47.8		2-Ethoxyethanol	44.1	
<i>p</i> -Xylene	47.7		Nitromethane	44.0	
Cumene	47.6		Pyridine	43.9	50.0
Mesitylene	47.5		Ethanol	43.9	60.4
<i>n</i> -Butyl acetate	47.5		Dimethylformamide	43.7 <sup>a</sup>	51.5
<i>o</i> -Xylene	47.3		2-Methoxyethanol	43.5	
Toluene	47.2	41.7	Benzonitrile	43.3	
Ethyl acetate	47.2		Methanol	43.1	63.0
Benzene	46.9		Dimethylacetamide	43.0 <sup>a</sup>	
Tetrahydrofuran	46.6		Nitrobenzene	42.6	
Ethyl N,N-dibutylcarbamate	46.0		$\gamma$ -Butyrolactone	42.6	
2-Octanone	45.8		Dimethyl sulfoxide	42.0 <sup>a</sup>	
Acetonitrile	45.7	53.7	Aniline	41.1	
Acetone	45.7	50.1	Ethylene glycol	40.4 <sup>b</sup>	
<i>p</i> -Chlorotoluene	45.6		Propargyl alcohol	38.9	
1-Octanol	45.4		<i>o</i> -Cresol	(35.5) <sup>c</sup>	
Butyronitrile	45.4		<i>m</i> -Cresol	(33.6) <sup>c</sup>	
			Water		68.9

Vol. % 2,6-lutidine in water <sup>d</sup>	$\chi_R$	$\chi_B$	Vol. % pyridine in water <sup>d</sup>	$\chi_R$	$\chi_B$
90	42.2 <sup>a</sup>	52.1	90	42.1	55.4
80	40.8 <sup>a</sup>	56.8	80	40.8	58.1
70	39.8 <sup>a</sup>	58.8	70	39.9	59.8
60	39.2 <sup>a</sup>	60.1	60	39.3	61.0
50	38.9 <sup>a</sup>	61.1	50	39.2	61.5
40	38.8 <sup>a</sup>	61.8	40		62.3
30	38.6 <sup>a</sup>	62.4	30		63.1
20	38.3 <sup>a</sup>	63.1	20		64.0
10		64.4	10		65.3

Vol. % 2,6-lutidine in methanol <sup>d</sup>	$\chi_R$	$\chi_B$	Vol. % dioxane in water <sup>d</sup>	$\chi_R$	$\chi_B$
90	44.3 <sup>a</sup>	48.4	90	46.4	55.0
80	44.0 <sup>a</sup>	51.9	80	45.0	58.6
70	43.9 <sup>a</sup>	54.9	70	44.0	59.8
60	43.7 <sup>a</sup>	57.4	60	42.3	61.2
50	43.8 <sup>a</sup>	59.2	50		61.0
40	43.7 <sup>a</sup>	60.3	30		63.4
30	43.6 <sup>a</sup>	61.1	10		66.0
20	43.5 <sup>a</sup>	61.6			
10	43.3 <sup>a</sup>	62.2			

Vol. % 2,6-lutidine in methylcyclohexane <sup>d</sup>	$\chi_R$	Vol. % methanol in water <sup>d</sup>	$\chi_B$	Vol % dioxane in isooctane <sup>d</sup>	$\chi_R$
10	49.3	90	63.1	10	50.2
20	48.5	80	63.4	20	50.0
30	47.8	70	64.1	30	49.5
40	47.3	60	64.7	40	49.5
50	46.7	50	65.3	50	49.1
60	46.3	40	66.0	60	49.1
70	45.8	30	66.5	70	48.8
80	45.5	20	67.1	80	48.7
90	45.0	10	67.8	90	48.5

<sup>a</sup> Acetic acid (3–5 drops) was added to the dye solution to stabilize the dye. <sup>b</sup> Solution contained 2% of 2,6-lutidine. <sup>c</sup> Value calculated by extrapolation as described in the Experimental section (Calculations). <sup>d</sup> *N* vol. % A in a mixture of A and B here means *N* volumes of A and (100 – *N*) volumes of B, both at 25° before mixing (*cf.* ref. 12).

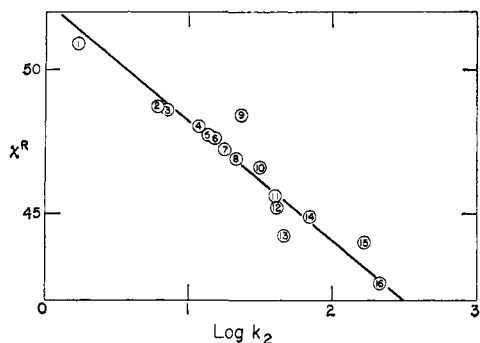


Figure 7.  $\chi_R$  values for the following 16 solvents plotted against  $\log k_2$ , where  $k_2$  is the rate constant of the base-catalyzed decomposition of *t*-butyl peroxyformate<sup>13</sup>: (1) heptane, (2) carbon tetrachloride, (3) butyl ether, (4) *p*-cymene, (5) *p*-xylene, (6) cumene, (7) toluene, (8) benzene, (9) *p*-dioxane, (10) tetrahydrofuran, (11) *p*-chlorotoluene, (12) chlorobenzene, (13) chloroform, (14) dichloromethane, (15) nitromethane, and (16) nitrobenzene.

in the plots of  $\chi_R$  vs.  $\chi_B$  for binary mixtures of pyridine–water and lutidine–methanol. However, the straight lines so obtained are not collinear (Figure 6). Moreover, the plot of  $\chi_R$  against  $\chi_B$  for a number of other solvents and solvent mixtures gives points that are scattered widely about these lines; the correlation coefficient of all points shown in Figure 6 taken together is only 0.620. It follows that  $\chi_R$  does not correlate with  $Z$  values (Table I).

It is thus clear that the order of solvents and solvent mixtures given by  $\chi_B$  values is, in general, not the same as that given by  $\chi_R$  values. It is not unreasonable to associate this behavior with the complex nature of solvent stabilization, where the separate factors of hydrogen bonding and of solvent–solute dipole interaction may be distinguished, as well as solvent–solute polarizability interaction (dispersion forces).<sup>11b</sup> The participation of these and other parameters in proportions which vary from case to case could well give rise to the scatter of points actually observed.

In spite of the imperfect correspondence between  $\chi_B$  and  $\chi_R$  values apparent in Figure 6,  $\chi_B$  values correlate satisfactorily with rate data published by Smith, Fainberg, and Winstein<sup>12</sup> for reactions carried out in seven solvents, all rather strongly polar (Table I). They also correlate well with spectroscopic data on (completely polarized) betaines published by Dimroth and collaborators (Table I) in addition to the  $Z$ -value data of Kosower (Table I and Figure 2). When the solvents used in given comparisons are highly polar, therefore, such as hydroxylic solvents, correlation with  $\chi_B$  values is likely to be good.

On the other hand,  $\chi_R$  values give good linearity (correlation coefficient, 0.958) with the rate data published by Pincock<sup>13</sup> on the influence of nonpolar solvents on the base-catalyzed decomposition of *t*-butyl peroxyformate (Table I and Figure 7) and with the data of Howard and Ingold<sup>14</sup> on the solvent-dependence of the rate of autoxidation of styrene (Table I).

It therefore seems likely that if solvents used in com-

(12) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

(13) R. E. Pincock, Symposium on Solvation Phenomena, Calgary Section, Chemical Institute of Canada, Calgary, Alberta, Aug. 29, 1963.

(14) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044 (1964).

parisons are predominantly of the nonpolar type good correlation with  $\chi_R$  values will be found.

The shielding parameters of Taft for *p*-fluoronitrobenzene showed better correlation with  $\chi_R$  than  $\chi_B$ , though neither was good. This is very plausibly a result of the participation in Taft's experiments of the several parameters which determined solvent behavior in different proportions than in ours.<sup>15</sup>

## Experimental

**3-Methyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole.** *o*-Phenylenediamine (54.0 g., 0.5 mole) and  $\beta$ -methyl- $\delta$ -valerolactone (57.0 g., 0.5 mole) were mixed and heated for 1 hr., during which time water (18 ml.) distilled away. The residue was fractionated and the portion b.p. 160–210° (0.05 mm.) was redistilled, b.p. 160–180° (0.05 mm.). The pale yellow distillate solidified on cooling. The solid was dissolved in acetone (500 ml.). The hydrobromide separated after acidification with 30% hydrobromic acid in acetic acid. After filtration and washing with acetone, the hydrobromide was dissolved in water (500 ml.) and the solution was made alkaline with potassium carbonate. The base separated as cream-colored needles and was used without further purification, yielding 27 g. (29%), m.p. 147–148°.

**5-Ethyl-3-methyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazolium *p*-Toluenesulfonate.** A mixture of 3-methyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (18.6 g., 0.1 mole) and ethyl *p*-toluenesulfonate (20 g., 0.1 mole) was heated overnight in an oil bath at 110°. The viscous product solidified on cooling and was refluxed with acetone (500 ml.). The white solid remaining after filtration was recrystallized from methyl ethyl ketone, yielding colorless crystals, 27 g. (70%), m.p. 156–157°.

*Anal.* Calcd. for  $C_{21}H_{26}N_2O_3S$ : C, 65.2; H, 6.8; N, 7.3. Found: C, 65.5; H, 7.0; N, 7.0.

The following four dyes were required for determinations of deviation.<sup>3,16</sup>

**1,8;1',10-Di(1,3-butylene)-3,3'-diethylbenzimidazolium carbocyanine Perchlorate.** Sodium (1.16 g., 0.05 g-atom) was dissolved in absolute ethanol (100 ml.), followed by 5-ethyl-3-methyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazolium *p*-toluenesulfonate (8.44 g., 0.022 mole). 2,2,2-Trichloro-1-ethoxyethanol (2 g., 0.011 mole) was next added and the mixture was refluxed on a steam bath for 1.5 hr. Solvent was removed under reduced pressure, and the residue was mixed with acetone (300 ml.) and filtered from inorganic material. The filtrate was concentrated, and the red viscous residue was dissolved in absolute ethanol (100 ml.) containing triethylamine (5 ml.). Addition of solid sodium perchlorate (5 g., 0.04 mole) caused the dye to separate as perchlorate. After filtration and drying, the crude dye was dissolved in acetone (150 ml.) and triethylamine (5 ml.), and the filtered solution was poured into water (1 l.) containing concentrated ammonium hydroxide (20 ml.). Dye separated and, after two additional recrystallizations from ethanol containing a few drops of triethylamine, was obtained in minute purplish crystals with a blue reflex, yield

(15) R. W. Taft, E. Price, I. R. Fox, I. R. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(16) Part VII: L. G. S. Brooker, *et al.*, *ibid.*, **67**, 1875 (1945).

0.55 g. (9%), m.p. 245–246° dec.,  $\lambda_{\max}$  in ethanol 250  $m\mu$ .

*Anal.* Calcd. for  $C_{29}H_{35}ClN_4O_4$ : C, 64.6; H, 6.5; N, 10.4. Found: C, 64.4; H, 6.7; N, 10.2.

*4-p-Dimethylaminobenzylidene-5-ethyl-3-methyl-1,2,3,4-tetrahydropyrido[1,2-a]benzimidazolium Perchlorate.* Sodium (1.16 g., 0.05 g.-atom) was dissolved in absolute ethanol (100 ml.), followed by 5-ethyl-3-methyl-1,2,3,4-tetrahydropyrido[1,2-a]benzimidazolium *p*-toluenesulfonate (3.86 g., 0.01 mole) and *p*-dimethylaminobenzaldehyde (2.98 g., 0.02 mole). The mixture was heated under reflux for 45 min. and the filtered solution was treated with sodium perchlorate (4 g., 0.033 mole), stirred, refiltered, and concentrated to dryness. The yellow residue was washed with water, filtered, dissolved in ethanol (60 ml.), and reprecipitated by addition of ether. Recrystallization from absolute ethanol was followed by a thorough washing with water and then three recrystallizations from *n*-butyl alcohol. The yield of yellow-orange felted needles was 0.15 g. (3%), m.p. 188–189°.

*Anal.* Calcd. for  $C_{23}H_{28}ClN_3O_4$ : C, 61.9; H, 6.3; N, 9.4. Found: C, 61.6; H, 6.2; N, 9.2.

The dye absorbs in methanol with  $\lambda_{\max}$  419  $m\mu$  so that the deviation is  $[(606 m\mu + 520 m\mu)/2] - 419 m\mu = 144 m\mu$ , a value greater than any of 25 previously listed.<sup>16</sup> It is, however, slightly less than that of 2-ethyl-3-isquinoline, the deviation of which is 145.5  $m\mu$ .<sup>17</sup>

*Bis[2,2-dimethyl-1,3-cyclobutanedione-(4)]methineoxonol, Sodium Salt.* A mixture of diethoxymethyl acetate (3.24 g., 0.02 mole), 2,2-dimethyl-1,3-cyclobutanedione (2.24 g., 0.02 mole), sodium acetate (0.82 g., 0.01 mole), and acetonitrile (20 ml.) was heated under reflux for 2 min. The dye, which separated on the addition of ether (100 ml.), was dissolved in acetone and purified by column chromatography on neutral alumina. The desired lemon yellow acetone eluate was concentrated under reduced pressure. Recrystallization from acetone and ether gave the dye as yellow crystals; yield 0.24 g. (10%), m.p. 230° (darkening from 190°),  $\lambda_{\max}$  in methanol 418  $m\mu$ .

*Anal.* Calcd. for  $C_{13}H_{13}O_4Na \cdot 0.5H_2O$ : C, 58.9; H, 5.3. Found: C, 58.8; H, 5.1.

*4-p-Dimethylaminobenzylidene-2,2-dimethyl-1,3-cyclobutanedione.* To 2,2-dimethyl-1,3-cyclobutanedione (1.12 g., 0.01 mole) and *p*-dimethylaminobenzaldehyde (2.98 g., 0.02 mole) in ethanol (10 ml.), piperidine (0.85 g., 0.01 mole) was added and the mixture was heated under reflux for 1 hr. Dye separated after chilling and acidification with acetic acid (2 ml.). Two recrystallizations from methanol gave lustrous red plates; m.p. 200–201°, yield 1.5 g. (62%).

*Anal.* Calcd. for  $C_{15}H_{15}NO_2$ : C, 74.0; H, 7.0; N, 5.8. Found: C, 74.2; H, 6.9; N, 5.9.

The dye absorbs in methanol with  $\lambda_{\max}$  500  $m\mu$ . The deviation is thus  $[(606 m\mu + 418 m\mu)/2] - 500 m\mu = 12 m\mu$ , a low value which corresponds to a much higher acidity even than that shown by the 4-linked 3-phenyl-2-isoxazolin-5-one nucleus (deviation, 36  $m\mu$ ).<sup>3</sup>

*4-(5-Acetanilido-2,4-pentadienylidene)-2,2-dimethyl-1,3-cyclobutanedione.* A mixture of 2,2-dimethyl-1,3-

cyclobutanedione (5.6 g., 0.05 mole), 1-anilino-5-phenylimino-1,3-pentadiene hydrochloride (14.2 g., 0.05 mole), sodium acetate (4.19 g., 0.05 mole), and acetic anhydride (25 ml.) was heated rapidly to the refluxing point and held there for 2 min. The reaction mixture was chilled and filtered, and the dye was washed with water, followed by acetic anhydride. Recrystallization from acetic anhydride gave red needles, yield 3.4 g. (22%), m.p. 193–194°.

*Anal.* Calcd. for  $C_{19}H_{19}NO_3$ : C, 73.8; H, 6.2; N, 4.5. Found: C, 73.5; H, 6.4; N, 4.7.

*4-[6-(1-Methyl-4(1H)-pyridylidene)-2,4-hexadienylidene]-2,2-dimethyl-1,3-cyclobutanedione (III).* A mixture of methyl *p*-toluenesulfonate (1.86 g., 0.01 mole) and 4-methylpyridine (0.93 g., 0.01 mole) was allowed to react without external heating. The crude quaternary salt was heated with 4-(5-acetanilido-2,4-pentadienylidene)-2,2-dimethyl-1,3-cyclobutanedione (2.94 g., 0.01 mole) in pyridine (20 ml.) containing triethylamine (2.8 ml., 0.02 mole). After it had been heated under reflux for 5 min., the mixture was cooled and the crude dye was precipitated with ether (150 ml.). The ether was decanted, and the residue was dissolved in chloroform (25 ml.) and separated by column chromatography on neutral alumina. The desired bluish-red chloroform eluate was concentrated to dryness under reduced pressure and the residue was recrystallized from ethanol. The yield of dark blue crystals was 0.25 g. (10%), m.p. 204–205°.

*Anal.* Calcd. for  $C_{18}H_{19}NO_2 \cdot 0.25H_2O$ : C, 75.6; H, 6.9; N, 4.9. Found: C, 75.6; H, 6.8; N, 5.0.

*4-[5-(5-Ethyl-3-methyl-1,2,3,5-tetrahydropyrido[1,2-a]benzimidazolyl)-2,4-pentadienylidene]-2,2-dimethyl-1,3-cyclobutanedione (IV).* A mixture of 5-ethyl-3-methyl-1,2,3,4-tetrahydropyrido[1,2-a]benzimidazolium *p*-toluenesulfonate (1.93 g., 0.005 mole), 4-(5-acetanilido-2,4-pentadienylidene)-2,2-dimethyl-1,3-cyclobutanedione (1.47 g., 0.005 mole), and triethylamine (1.4 ml., 0.01 mole) in pyridine (15 ml.) was heated under reflux for 10 min. The dye which separated on the addition of ether (100 ml.) was dissolved in chloroform (25 ml.) and purified by column chromatography on neutral alumina. The desired bluish-red chloroform eluate was concentrated to dryness under reduced pressure. After recrystallization from ethanol, the yield of dark blue crystals was 0.154 g. (8%), m.p. 237–240°.

*Anal.* Calcd. for  $C_{25}H_{28}N_3O_2 \cdot \frac{2}{3}H_2O$ : C, 75.0; H, 7.4; N, 7.0. Found: C, 75.0; H, 7.3; N, 7.0.

*3-Phenyl-4-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-2-isoxazolin-5-one (VIII).* Isophorone (15.2 g., 0.11 mole), 3-phenyl-2-isoxazolin-5-one (16.1 g., 0.1 mole), ammonium acetate (2 g.), acetic acid (4 ml.), and chloroform (40 ml.) were combined and the mixture was heated under reflux for 18 hr. in a system designed for the continuous removal of water. The chloroform solution was washed with water (two 20-ml. portions), the chloroform was removed under reduced pressure, and the residue was twice recrystallized from methanol, giving orange-yellow plates (4.5 g., 16%), m.p. 168–170°.

*Anal.* Calcd. for  $C_{18}H_{19}NO_2$ : C, 76.8; H, 6.8; N, 5.0. Found: C, 77.0; H, 6.9; N, 4.8.

*4-[5-(4-Diethylaminophenyl)-1,3-neopentylene-2,4-pentadienylidene]-3-phenyl-2-isoxazolin-5-one (VI).* A

(17) Part IX: L. G. S. Brooker, F. L. White, and R. H. Sprague, *J. Am. Chem. Soc.*, **73**, 1087 (1951).

mixture of *p*-diethylaminobenzaldehyde (3.26 g., 0.02 mole) and VIII (2.81 g., 0.01 mole) in ethanol (25 ml.) containing piperidine (2 ml.) was heated under reflux for 10 min. Acetic acid (4 ml.) was added, with stirring, to the cooled reaction mixture and, after 1 hr., the dye was collected, washed with methanol, and dried. After two recrystallizations from toluene, the yield of purple crystals with a green reflex was 2.03 g. (45%), m.p. 169–170°. The melting point and physical characteristics were unchanged after further recrystallization from methylcyclohexane.

*Anal.* Calcd. for  $C_{30}H_{33}N_2O_2$ : C, 79.4; H, 7.3; N, 6.2. Found: C, 79.3; H, 7.2; N, 6.4.

*1,3-Diethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-2-thiobarbituric Acid (IX).* Isophorone (30 g., 0.22 mole), 1,3-diethyl-2-thiobarbituric acid (40 g., 0.20 mole), ammonium acetate (2.5 g.), acetic acid (4 ml.), and chloroform (100 ml.) were combined and the mixture was heated under reflux for 24 hr. in a system provided for the continuous removal of water. The reaction mixture was washed with water (two 100-ml. portions). The chloroform was removed under reduced pressure, and the crude product was recrystallized twice from methanol, giving yellow needles (35.2 g., 55%), m.p. 108–109°. The melting point was unchanged after two further recrystallizations from ethanol.

*Anal.* Calcd. for  $C_{17}H_{24}N_2O_2S$ : C, 63.7; H, 7.6; N, 8.7. Found: C, 63.9; H, 7.8; N, 8.6.

*1,3-Diethyl-5-[5-(2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizin-9-yl)-1,3-neopentylene-2,4-pentadienylidene]-2-thiobarbituric Acid (VII).* A mixture of 9-formyljulolidine (4.0 g., 0.02 mole) and IX (3.2 g., 0.01 mole) in ethanol (25 ml.) containing piperidine (2 ml.) was heated under reflux for 13 min., after which methanol (100 ml.) was added and then acetic acid (4 ml.). The reaction mixture was chilled overnight and a first crop of dye was obtained (1.54 g., 31%). A second crop (2.2 g., 44%; total yield, 74%) separated on further standing. The first crop was recrystallized from methylcyclohexane, and was obtained as dark green crystals with a gold reflex, m.p. 217–218°, yield 1.04 g. (20%).

*Anal.* Calcd. for  $C_{30}H_{37}N_3O_2S$ : C, 71.5; H, 7.4; N, 8.3. Found: C, 71.8; H, 7.6; N, 8.0.

*Solvents.* When available, Eastman Spectro Grade solvents were employed (20 solvents, including *p*-dioxane and dimethyl sulfoxide). Most of the remaining solvents (31) were Eastman Grade; toluene (from the sulfonic acid) was used, and the aniline was freshly distilled. *n*-Butyl ether, 2-octanone, and 2-butoxyethanol, all Eastman Practical Grade, were employed without purification. Eastman Practical Grade *o*-

and *m*-cresol were distilled before use. Commercial absolute ethanol was used. Propargyl alcohol was obtained from Farchan Research Laboratories. All solvents except *o*- and *m*-cresol, propargyl alcohol, ethyl *N,N*-dibutylcarbamate, and aniline were dried over Linde Type 3A molecular sieves ( $1/16$ -in. pellets).

Karl Fischer titrations were carried out on all solvents except triethylamine, mesitylene, ethyl acetate, acetone, 2-octanone, 2-butanone, bromobenzene, cyclohexanone, nitromethane, ethanol, benzonitrile, propargyl alcohol, and ethyl *N,N*-dibutylcarbamate. The amount of water present in the solvents was, in general, less than 0.05% and exceeded 0.10% in only three cases: pyridine (0.12%), dimethylformamide (0.14%), and methanol (0.40%).

*Absorption Measurements.* Absorption curves were obtained with a Perkin-Elmer Model 350 recording spectrophotometer, using 1-cm. Beckman ultraviolet matched silica cells with the appropriate solvent or solvent mixture in the reference cell. The concentration of dye solutions was of the order of  $10^{-5}$  *M*. When the solvent exhibited basic properties, small amounts of glacial acetic acid (3 to 5 drops to a 50-ml. solution) were used to stabilize the dye, though the addition did not affect  $\lambda_{max}$ .

*Calculations.* The calculation of the regression lines and of other statistical data was carried out by the method of least squares outlined by Jaffé,<sup>18</sup> and discussed by Snedecor.<sup>19</sup> These data are summarized in Table I. The experimentally determined  $E_T$  values for VII in *o*- and *m*-cresol were 37.6 and 37.2 kcal./mole, respectively, while those for VI for the same two solvents were 43.5 and 42.0 kcal./mole, respectively. Although a plot of  $E_T$  values for VII for a large number of solvents against corresponding values for VI showed good linearity (Figure 5 and regressions 7, 8, and 9, Table I), the points for *o*- and *m*-cresol fall away from the line shown in Figure 5 in a way that suggests that in highly stabilizing *o*- and *m*-cresol, VII, though not VI, is approaching isoenergism<sup>20</sup> with consequent loss of sensitivity to environmental change as reflected by  $\lambda_{max}$ . The calculated  $\chi_R$  values for *o*- and *m*-cresol given in Table II were obtained from regression 9, Table I, by means of the appropriate prediction equation (see ref. 18, p. 253).

*Acknowledgments.* We wish to thank Mr. Donald F. Ketchum and his department for the microanalyses and Mrs. Florence Wagner Lohwater for the absorptions.

(18) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(19) G. W. Snedecor, "Statistical Methods," 4th Ed., The Collegiate Press, Inc., Ames, Iowa, 1946.

(20) Reference 4; see also L. G. S. Brooker, *Chimia*, **15**, 87 (1961).