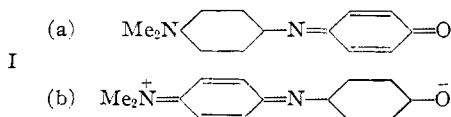


[CONTRIBUTION NO. 820 FROM THE KODAK RESEARCH LABORATORIES]

Color and Constitution. IV.¹ The Absorption of Phenol Blue

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Phenol blue is an un-ionized dye that may be represented by the resonance scheme Ia \longleftrightarrow Ib.



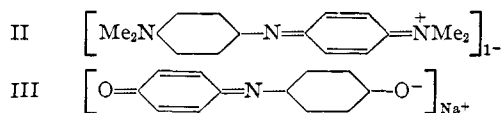
It is of special interest from the theoretical standpoint, because the two extreme resonance configurations, Ia and Ib, differ only as regards the terminal auxochromic atoms, the chromophoric chain being the same in each. Any difference of stability that exists between the two configurations, therefore, may be ascribed solely to the greater or less stability of $\text{Me}_2\text{N}-$ and $=\text{O}$ in Ia compared to $\text{Me}_2\text{N}^+=$ and $-\text{O}^-$ in Ib, bearing in mind that the opposite poles in Ib will exert a considerable electrostatic attraction on each other which will tend to make the configuration relatively unstable.

It is well known that the absorption of an un-ionized dye is strongly affected by the solvent, and thus phenol blue gives solutions which vary in color from reddish-violet in cyclohexane to deep blue in water. The values of λ_{max} are given in Table I for four solvents, and it is seen that the absorption is shifted to progressively longer wave lengths as the dielectric constant of the solvent is increased. The most reasonable explanation of this is that although Ib is, in the absence of solvent effects, less stable than Ia because of the coulombic interaction of the opposite charges of the dipole, the polar arrangement in Ib is increasingly stabilized by the dipole orientation of the surrounding solvent molecules as the polarity of the solvent is increased. Thus stabilized, Ib tends to approach Ia in stability, and the increasing degeneracy of the resonance structures is accompanied by absorption at longer wave lengths.

The above argument has the limitation that it gives no idea as to how nearly Ia and Ib approach each other in absolute terms. Further insight into this problem, however, is gained by using the technique of comparing the absorptions of unsymmetrical dyes with those of the related sym-

metrical dyes, employed in previous papers.^{1,2,3}

For such a comparison I must be regarded as the structural cross between the cation of Bindschledler's green (II) and the anion of phenol indophenol (III), the iodide and the sodium salt of which are shown in the formulas. Both of these ions are symmetrical, each being represented by two identical extreme resonance configurations, only one of which is shown in each case.



If it were found that I absorbed exactly midway between II and III, it could reasonably be argued that the degeneracy of the configurations in I was as complete as in the parent symmetrical dyes, and that Ia and Ib were of equal stability. If the observed absorption occurred at shorter wave length than that calculated from II and III, however, the interpretation would be that Ia and Ib differed in stability, and the amount of the difference between $\lambda_{\text{max. obsd.}}$ and $\lambda_{\text{max. calcd.}}$ could be used as a measure of this energy difference.

Compared with I, the absorptions of II and III are relatively little affected by change of solvent. This is readily understandable, for since the extreme resonance configurations of any symmetrical dye are identical, one cannot be stabilized by any particular solvent more than the other. The values for $\lambda_{\text{max.}}$ are given in Table I and the points are plotted in Fig. 1.

TABLE I

Solvent	Approx. dielectric constant	$\lambda_{\text{max.}}$ I	$\lambda_{\text{max.}}$ II	$\lambda_{\text{max.}}$ III	$\lambda_{\text{max.}}$ I calcd.	Deviation
Cyclohexane	2	5520
Acetone	21	5820	7290	6420	6825	1005
Methyl alc.	31	6120	7260	6400	6805	685
Water	80	6680	7280	6280	6745	65

The ionized dyes are both insoluble in cyclohexane, and comparisons of all three dyes were restricted to acetone, methyl alcohol and water.

(2) Brooker, Sprague, Smyth and Lewis, *ibid.*, **62**, 1116 (1940).(3) Brooker, White, Keyes, Smyth and Oesper, *ibid.*, **63**, 3192 (1941).(1) Part III, THIS JOURNAL, **63**, 3203 (1941).

TABLE II

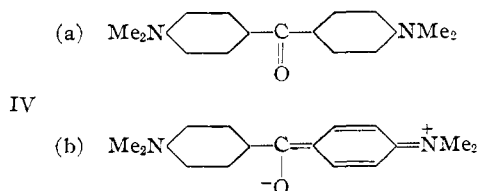
Mole fractions (C_2), dielectric constants (D), densities of solutions in benzene (d), polarizations at 25° (P_2), molar refractions (MR_D), polarizations at 25° (P_∞), observed moment (μ) and calculated moment (μ calcd.)

Compound	C_2	D	d	P_2	MR_D	$P_\infty(25^\circ)$	$\mu (\times 10^{18})$	μ calcd. ($\times 10^{18})$
I	0.000000	2.2807	0.87233	$P_1 = 26.789$				
	.001226	2.3382	.87317	736	67	765 ± 40	5.80 ± 0.17	2.4 ± 0.5
	.002475	2.4014	.87406	753				
	.003119	2.4415	.87448	787				
	.005855	2.5582	.87635	713				

The difference between $\lambda_{\max. \text{ obsd.}}$ for I and that calculated as the harmonic mean between II and III may be called the "deviation," and this varies considerably from solvent to solvent. In acetone, configuration Ib is less stabilized by the solvent than it is in solvents of higher polarity, and the deviation is considerable, amounting to 1005 Å. This is reduced to 685 Å. in methyl alcohol and to only 65 Å. in water. In this latter solvent, therefore, the stabilization of Ib is so great that the degeneracy of configurations Ia and Ib is nearly complete. Thus, if the phenol blue molecule is sufficiently shielded against the effect of the attraction of the opposite poles in Ib, the degeneracy of the configurations reaches a very high level indeed, a conclusion which is interesting and perhaps surprising.

The contribution of Ib even in benzene is brought out by the fact that the observed dipole moment of 5.80 ± 0.07 is much greater than the value of 2.4 ± 0.5 calculated from Ia. We are greatly indebted to Professor C. P. Smyth and Mr. P. Oesper for these values. Their data are given in Table II.

From the above conclusions it would appear that the lack of color of Michler ketone (IV), even in strongly polar solvents, is in all probability not due to the electrostatic attraction of



the charges in configurations of the type of IVb, but rather to the heavy stabilization of IVa be-

cause of the benzenoid arrangement of both benzene nuclei.¹

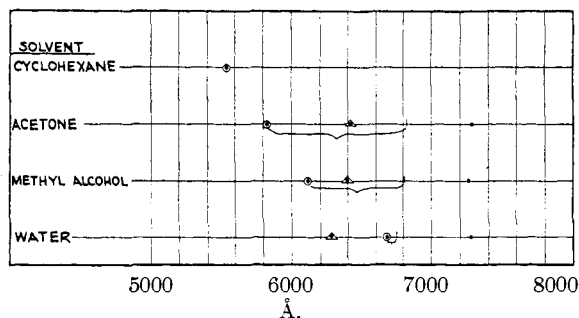


Fig. 1.—Values of $\lambda_{\max.}$ of phenol blue and related dyes in various solvents: \circ , phenol blue (I); \bullet , Bind-schedler's green iodide (II); Δ , sodium phenol indophenol (III); $|$, calcd. (harmonic) mean between II and III. The brackets indicate the deviations.

Summary

1. Solutions of phenol blue (I) are deeper in color the greater the polarity of the solvent. It is suggested that this is because the stabilization of the dipolar configuration Ib by dipole orientation of the solvent molecules is greater with the more strongly polar solvents and the degeneracy of the resonance scheme $Ia \longleftrightarrow Ib$ is correspondingly increased.

2. Phenol blue is the structural cross between the ionized dyes II and III. Their absorptions have been compared in three solvents. In water $\lambda_{\max.}$ of I lies at only 65 Å. shorter wave length than that calculated from II and III. Here the stabilization of Ib by the solvent is so great that it approaches Ia in stability. In methyl alcohol, the corresponding deviation is 685 Å., and in acetone it is 1005 Å., due to progressively less polarization stabilization by the solvents.

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