

ABSORPTION SPECTRA OF SOME IMIDAZOLID-4-ONE DERIVATIVES,  
THE DIMEROCYANINES. IV. EFFECT OF TEMPERATURE ON DYE  
ABSORPTION SPECTRUM IN THE VISIBLE REGION

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Observation at different temperatures of uv absorption spectra of a number of imidazolid-4-one derivatives, dimerocyanines, shows that change in temperature of the solution causes considerable alterations in the absorption curves. In agreement with previous results, this corresponds to a displacement of equilibrium between two dye conformations in solution. One conformation has the  $\beta$ -dicarbonyl group more coplanar with respect to the plane of the molecule than the other. The transition energy required to convert one form into the other ( $\Delta H$ ) is found from a plot of the logarithms of the equilibrium constants against the reciprocal of the temperature. It is shown that  $\Delta H$  depends on the substituent at the nitrogen atom in position 3 of the imidazolidone ring.

Study of the electronic and ir absorption spectra of dimerocyanines, derivatives of 1,3-disubstituted imidazolid-4-ones [1-3], made it possible to show that in solutions of dyes containing the phenyl group in position 1 of the ketomethylene ring and a  $\beta$ -dicarbonyl group in position 2 of the same ring, there exists an equilibrium between the two forms that depends on the position of the  $\beta$ -dicarbonyl group relative to the plane of the ketomethylene ring. Solvation promotes formation of the form with the dicarbonyl group more rotated. In the absence of a solvating solvent, equilibrium between the two forms can be displaced by varying the temperature of the solution [4]. Thus, measurement of absorption spectra of dimerocyanines at different temperatures made it possible not only to confirm the existence of the conformational equilibrium independently, but also to determine the energy of transition from one dye form to the other.

The subjects of investigation were the dyes I and II, giving two forms in aprotic solvents and two absorption bands in the visible region, the intensity ratio depending on the solvent  $D_k$ , or the relative content of solvating component [1]. For comparison, dyes III and IV were also investigated; their absorption curves are simple, corresponding to the existence of only one form in solution.

The spectra were measured on an SF-4 spectrophotometer, with a special thermostatted jacket connected to a water thermostat. Over the range from room temperature to 70° the temperature in the cells was maintained constant to within  $\pm 0.05^\circ$ .

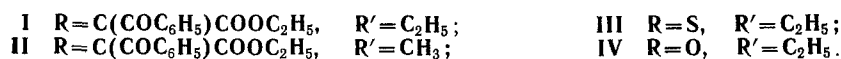
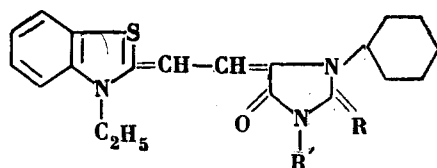


Figure 1 shows the absorption spectra of  $5 \times 10^{-5}$  M dye solutions in benzene, obtained at different temperatures. It can be seen (Fig. 1, a and b) that with dyes I and II raising of the temperature of the solution leads to a marked change in the shape of the absorption curve. The position of the maximum for the dye I is displaced from 555 m $\mu$  at 23° to 545 m $\mu$  at 63°. Especially marked is the change in the absorption curve on heating dye II (Fig. 1, b). The curve for 43° has two distinct absorption maxima at 565 and 550 m $\mu$ , corresponding to the two conformations of the dye molecule, which are present at about the same concentrations in the dye solution, while the absorption spectra of the solutions of dyes III and IV (Fig. 1, c and d) are practically unchanged for the temperature range investigated. This confirms that these two dyes have the same molecular form.

Bad resolution of the two maxima makes it difficult to determine accurately the concentrations  $C_1$  and  $C_2$  of each form of dyes I and II present in solution at a particular temperature. However, the concentrations  $C_1$  and  $C_2$  can be found from the experimental absorption curve, if it is split into two curves corresponding to the two conformations, provided that the positions of the absorption maxima of the dyes are known and that the extinction coefficients of each form are equal.

Figure 2 gives the relation between the reciprocal of the temperature and the log of the equilibrium constants for the two forms calculated in this way. It may be seen that the points correspond rather well to a linear relation. From the

slopes of the straight lines, the calculated heats of transition  $\Delta H$  from one form of dye to the other is  $2.5 \pm 0.5$  kcal/mole for dye I and  $4 \pm 0.5$  kcal/mole for dye II. If it is assumed, as in [1-3], that in dimerocyanines I and II the conformational isomers are conditioned by rotation of the  $\beta$ -dicarbonyl group around the  $C=C$  bond connecting it with the imidazolidone ring, the values of  $\Delta H$  obtained are a measure of the bond energy of the oxygen of the carbonyl group of the radical and the  $\pi$ -electron system of the benzene ring at position 1 of the ketomethylene ring. Actually, the steric hindrances [1] in dye molecules I and II strive to rotate the  $\beta$ -dicarbonyl group in such a way that the dye form obtained

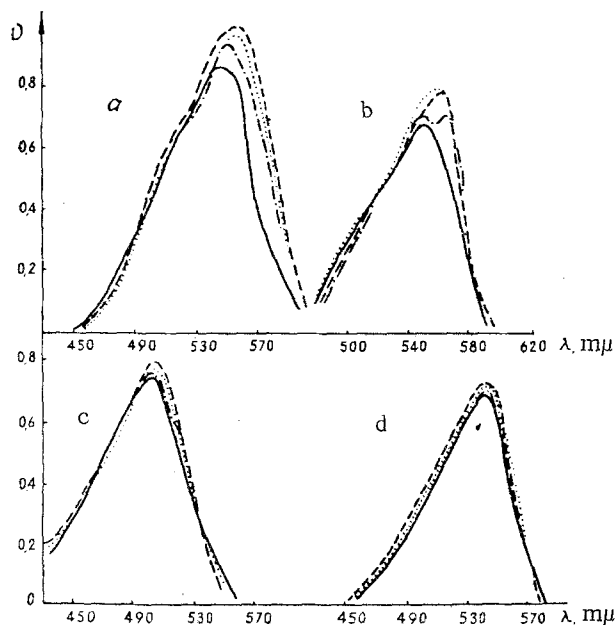


Fig. 1. Dye absorption curves I(a), II(b), III(c) and IV(d), measured at 23° - - - -, 33° · · · ·, 43° - · - · - and 63° ———.

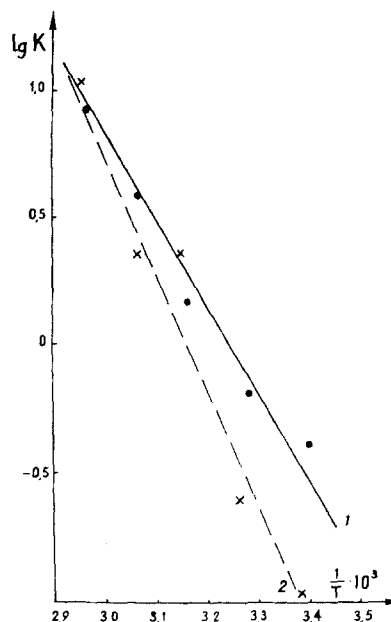


Fig. 2. Relation between temperature and the equilibrium constants of the two dye forms: 1 - I, and 2 - II.

is that with the maximally rotated radical. On the other hand, interaction between the oxygen atom of the carbonyl group and the phenyl ring stops the ethyl benzoyl acetate group from being rotated. This gives rise to the dye form characterized by a smaller angle of rotation, and hence by greater coplanarity of this part of the molecule. Evidently, the smaller the steric hindrance, the greater this interaction energy, and hence the value of  $\Delta H$ . In agreement with previous work [1], it follows from the measurements of  $\Delta H$  given that the methyl group in position 3 of the ketomethylene ring creates less steric hindrance than the ethyl group. Obviously, the heat of solvation of the dimerocyanines I and II, or of hydrogen bonding between the solvent and the carbonyl group of the ethylbenzoylacetate group, must be greater than the values of  $\Delta H$  found for transition between the two dye forms. This condition is also in agreement with the usual heats of hydrogen bonding, namely 5-10 kcal/mole.

#### REFERENCES

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