Discussion on the Paper Presented by Professor K. Dimroth

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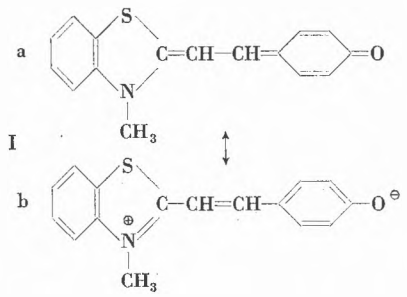
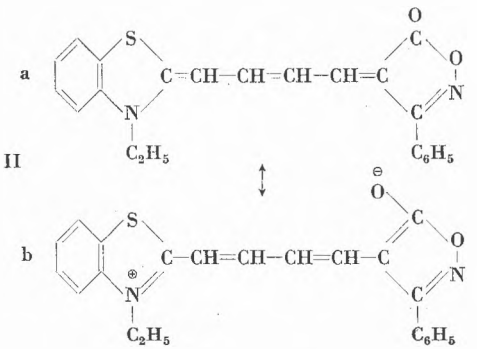
In discussion, Dr. L. Brooker stressed that "solvent sensitivity curves" provide striking evidence of the existence of the "isoenergetic point" of merocyanine dyes, the "Mesomerieschwerpunkt" of Professor Dimroth. Thus, for the merocyanine I, the variation of ab-



sorption with change of solvent indicates that isoenergism, i. e., the point at which Ia and Ib have the same energy when treated by the resonance method, is reached in a water-pyridine mixture containing 92.5 volumes per cent of pyridine. In solvent of this composition the molecular absorption curve of I shows a maximum value of ε_{max}. Using a water-pyridine mixture with a higher concentration of pyridine than that specified, structure Ib is insufficiently stabilized for isoenergism, whereas it is overstabilized for isoenergism if a lower concentration of pyridine than that specified is taken. In both of these latter cases the intensity of absorption at the maximum (ε_{max}) is sharply reduced from that at the isoenergetic point.[1]

The objection has been raised, however, that for certain merocyanines, two principal absorption bands may be distinguished, the relative contributions of which change progressively with change in solvent composition. In such cases, it is as if one were dealing with an equilibrium between two distinct molecular species, although there is no proof that this is the correct explanation.



[1] L. G. S. Brooker *et al.*, *J. Amer. Chem. Soc.* *73* (1951) 5350.

In a great many other instances, however, the absorption curves throughout the range of solvents used are predominantly single-banded. For example, this is true of II, the solvent sensitivity curve for which is shown in Figure 1, together with three of the contributing absorption curves, these being determined in pure 2,6-lutidine, in highly aqueous lutidine and at the isoenergetic point

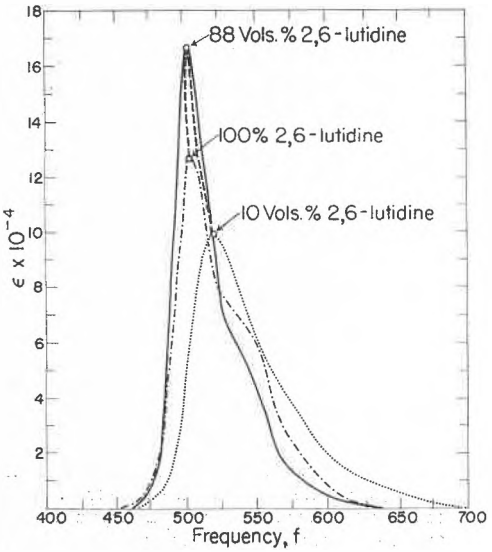


Fig. 1. Solvent sensitivity curve for II (e.g., plot of ε_{max} against frequency, – – – –) with three contributing absorption curves, ———, –·–·–, ····· Solvents comprise 2,6-lutidine and aqueous lutidine mixtures expressed as vols. % lutidine

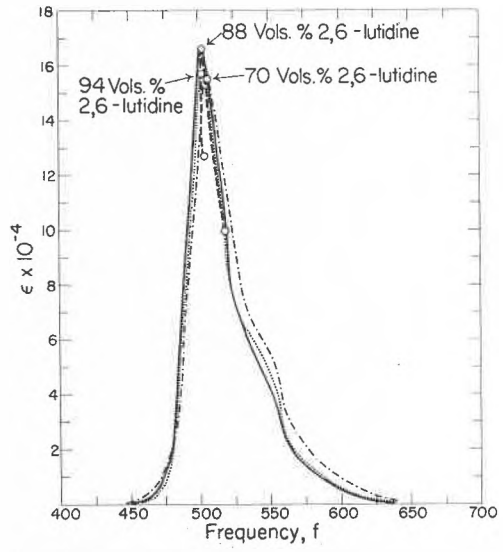


Fig. 2. Solvent sensitivity curve of II (for lutidine-water mixtures, – – –) with three contributing absorption curves, one at the apex and one on either side

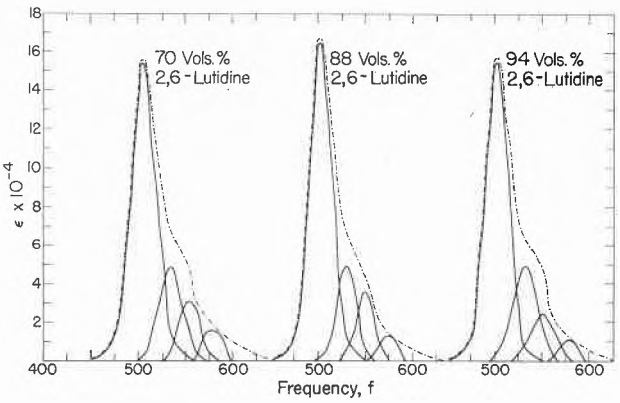


Fig. 3. Resolution of the three contributing absorption curves of Figure 2 into principal and subsidiary bands

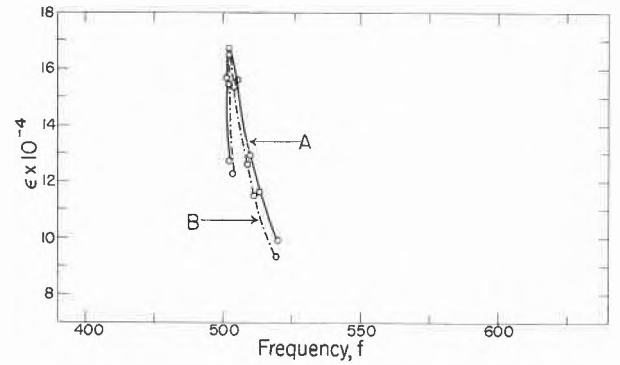
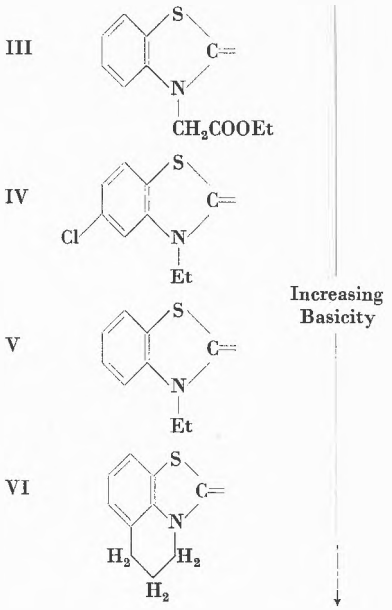


Fig. 4. Solvent sensitivity curves of II for 2,6-lutidine-water mixtures. *A*, plot of ε_{max} *versus* frequency for the unresolved band envelopes of the contributing absorption curves; *B*, drawn using values for the principal bands obtained by resolution, as in Figure 3



(88 volumes per cent of lutidine). For this and many similar dyes, the predominantly single-banded character of the absorption curves is especially pronounced at and near to the isoenergetic point (Fig. 2).

The three contributing absorption curves in Figure 2 are shown resolved in Figure 3 into principal and subsidiary bands. These latter contribute very little at the frequency of maximum absorption of the principal bands. In fact, a strongly cuspidated solvent sensitivity curve is obtained either by using values of ε_{max} *versus* frequency obtained from the unresolved band envelopes

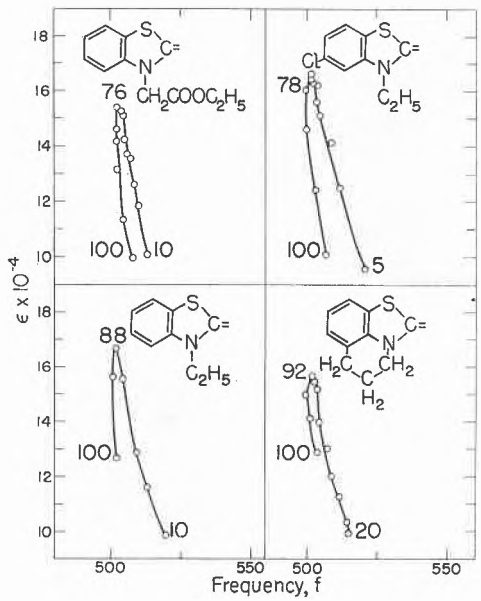


Fig. 5. Solvent sensitivity curves of dyes of the type of II containing the basic nuclei shown. Numbers on the curves indicate vols. % of lutidine in lutidine-water mixtures used as solvents at the "ends" of the curves and at the apices. The points on the curves were obtained from unresolved absorption-band envelopes

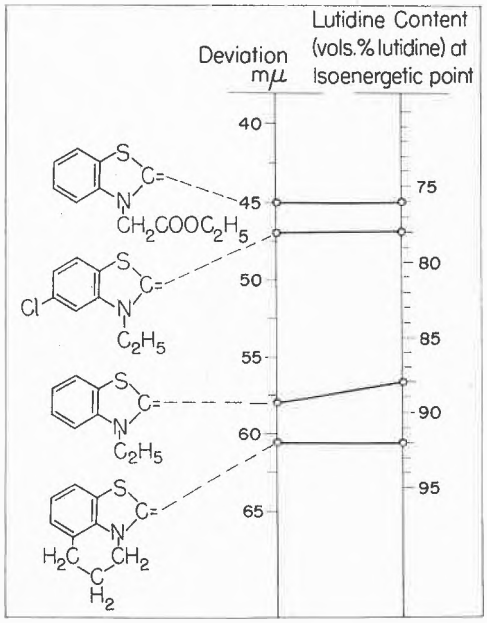


Fig. 6. Deviations of *p*-dimethylaminostyryl dyes with nuclei III → VI, plotted against solvent composition at the isoenergetic point for dyes of type II. The scales are adjusted so that the lines joining the points in the two columns for nuclei III and VI are horizontal

or from the principal bands obtained by resolution (Fig. 4).

Evidence which further supports the authenticity of the concept of the isoenergetic point is provided by a study of dyes similar to II but containing nuclei III, IV and VI in place of the nucleus V which is present in II. The relative basicities of these benzothiazolylidene nuclei have been shown to be in the order shown.[2] It follows that the four merocarbocyanines would show increasing polarity in the same order. This leads, in turn, to the expectation that somewhat more highly aqueous lutidine would be required to bring about isoenergism for the dye with IV than for that with V, while still more highly aqueous lutidine would be required for the dye with III. On the other hand, the dye with VI should require less aqueous lutidine for isoenergism than II. These expectations have been fully realized, as shown in Figure 5.

The order of basicity of the nuclei III → VI was originally arrived at from a study of "deviations" in λ_{max} ("Abweichungen") of unsymmetrical dyes such as those containing the *p*-dimethylaminostyryl group, in which series a large deviation corresponds to high basicity of the heterocyclic nucleus.[2] In Figure 6 the deviations shown by the *p*-dimethylaminostyryl dyes from nuclei III → VI are plotted against the lutidine content of the water-lutidine mixture at the isoenergetic points of the corresponding dyes of type II. The agreement between the two sets of values is excellent.

[2] Brooker *et al.*, *J. Amer. Chem. Soc. 67* (1945) 1884.