227. *The Colour of Organic Compounds. Part I. A General Colour Rule.*

By Edward B. Knott.

Förster's colour rule (*Z. Elektrochem.*, 1939, **45**, 548) has been modified to cover non-ionic as well as ionic dyes. An empirical method is given to allow the rule to be applied by organic chemists. It is also shown that this rule can be re-stated in terms consistent with the conclusions of Kuhn (*J. Chem. Physics*, 1949, **17**, 1198) from the electron-gas model.

The closely related colour rules of Lewis and Calvin (*Chem. Rev.*, 1939, **25**, 273) and of Lewis (*J. Amer. Chem. Soc.*, 1945, **67**, 770) are the only ones which have been applied to predict the effect, on the light absorption of a dye, of a structural change at a point in the molecule lying between the auxochromes.* These rules have been found to be unreliable in a number of cases (see later) because they neglect the position of the point of the change in relation to the terminal $\pm M$ atoms and also because they assume that, in an ionic dye, each atom of the chromophoric chain must carry a fractional charge of the same sign as that of the characteristic charge. Moreover, by their definition, they cannot be applied to non-ionic (electrically neutral) molecules. Brooker (with Sklar, *Rev. Mod. Physics*, 1942, **14**, 279) also evolved a rule which might conceivably be applied to such structural changes. It has never been

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* Since the original draft of this paper was submitted in March 1950 a further number of generalizations of this type have been given by Dewar (*J.*, 1950, 2329).

exemplified (the difference in absorption of the two dyes given in that article being caused, it is considered, by an extra-conjugation effect) largely because of the narrow field of its applicability.

It is the purpose of this paper to develop a general rule covering structural changes of this type which may be applied to dyes of any type. As a basis, a much neglected rule given by Förster (*loc. cit.*) is re-interpreted and a method evolved to enable an organic chemist to apply it.

The General Rule.—Förster's rule which can, by definition, only be applied to ionic dyes and which has never been exemplified, considers that $\lambda_{max.}$ of the dye will increase with a decreasing tendency of the chain of atoms (chromophores) lying between the auxochromes to take up the characteristic charge. Its identity with the later rule by Lewis (*loc. cit.*) is obvious. If it is accepted that the resultant charge distribution on the atoms of a resonance hybrid is determined by the relative contributions of all the participating structures, then in any such system the chromophoric atoms carry charges only in the excited structures. The Förster rule can accordingly be re-written in a form which allows its application to non-ionic dyes, namely, $\lambda_{max.}$ will increase as the contributions by any of the interauxochromic,* ionic excited structures decrease. Since the contributions by the various structures depend largely on their relative energies it follows that $\lambda_{max.}$ will be increased by raising the energy of any one interauxochromic, ionic, excited structure. These two derivations of the Förster rule will be referred to as the general rule. The relationship of this rule to the Brooker–Sklar rule, which is concerned with the general alteration in the level of all interauxochromic, excited structures, is clear.

Method of Application.—In order to apply this rule to specific examples it is necessary, in theory, to consider all the possible structures contributing to the hybrid and to assess the effect of a particular structural change on the significance of each structure. It will then be found that this change, in all cases, will increase the contributions of some structures and decrease those of others. Since, therefore, in all cases, the change in $\lambda_{max.}$ following a structural change is a resultant of both hypsochromic and bathochromic shifts a very complicated and tedious procedure is involved because of the absence of quantitative data. The process can, in practice, be simplified considerably by observing the following conditions.

First, it must be assumed that the more significant the structure undergoing a fixed energy change, or the greater the energy change in structures of equal significance resulting from the structural change, the greater will be the effect of that change on the absorption. Two " most likely," *i.e.*, most significant, structures are then selected in which the atom at which the structural change occurs is positively charged in one case and negatively charged in the other. These two structures are chosen, and their relative significance is assessed, by considering such criteria of energy as the number of covalent bonds, the degree of disruption of the conjugated system, the presence of aromaticity, charge separation, or adjacent atoms of like charge (cf. Wheland, " The Theory of Resonance," 1947, p. 15).

If there is a clear-cut difference between the assessed importance of these two structures then the direction of the resultant shift and, after experience, its approximate magnitude can be assessed. This requires the application of further criteria which will determine the direction of the change in the energy level of the more important structure; such criteria include stabilization by the formation of new resonance systems following the introduction of $\pm M$ atoms or groups or a change in the electronegativity of the atom replaced. The magnitude of the shift will in general be greater the larger the difference in the relative significance of the two chosen structures.

In view of the necessarily rough empiricism of the above procedure it is, none the less, surprising how reliable the rule has proved. The annexed tables give examples of various dye types which illustrate its working. The reason for the choice of the more significant structure of the two given for each dye and the effect of the structural change on its energy level is in most cases obvious from a consideration of the above criteria. For dyes (II) and (IV) the structures involving C^- are considered to be the more stable since, although charge separation is required for their contribution, they each contain two covalent bonds more than those structures involving C^+ and also contain fully aromatic quinoline nuclei. The introduction of a $+M$ group at C^- or a $-M$ group at C^+ will always give rise to a new resonance system with a consequent decrease in the energy of the system. Similarly, owing to the high electronegativity of nitrogen compared with carbon the replacement of ^-CH by N^- will also stabilize the system, whilst a similar replacement of ^+CH by N^+ will raise the energy of the system. The introduction

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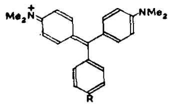
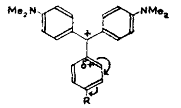
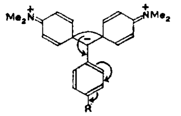
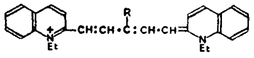
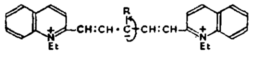
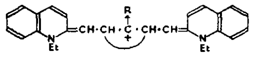
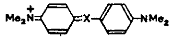
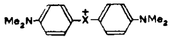
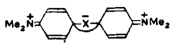
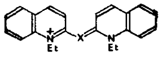
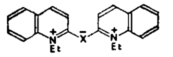
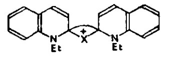
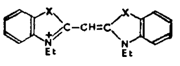
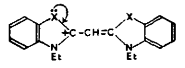
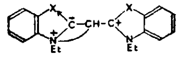
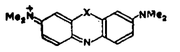
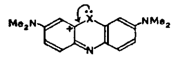
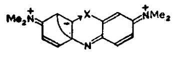
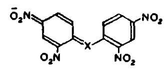
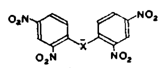
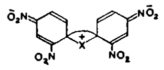
* " Interauxochromic " refers to those structures in which one or more of the atoms lying between the auxochromes is charged.

of a $+I$ atom or group at C$^+$ [*e.g.*, dye (II), less likely structure] or a $-I$ atom or group at C$^-$ will also raise the energy of the structure (relative to the extreme structure) by increasing the amount of charge on the carbon atom. In dye (V) the energy increase is a result of the lower $-M$ effect of sulphur compared with that of oxygen.

It will be found that the Lewis–Calvin or the Lewis rule predicts bathochromic shifts for

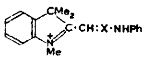
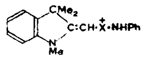
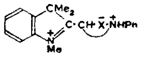
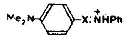
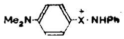
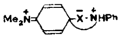
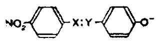
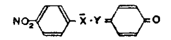
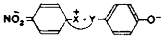
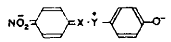
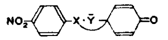
Energetically symmetrical ionic dyes.

	Dye and structural change.	Likely structures (more likely first).	Effect of change on energy level.*	Expected shift.†	Observed absorption.
(I.)			+	B	R = H 621 mμ. R = NO$_2$ 646 mμ. Shift +25 mμ.
	R = H Change to R = NO$_2$		−	—	—
(II.)			−	H	R = H 708 mμ. R = NO$_2$ 580 mμ. Shift −128 mμ.
	R = H Change to R = NO$_2$		+	—	—
(III.)			+	B	X = CH 603 mμ. X = N 725 mμ. Shift +122 mμ.
	X = CH Change to X = N		−	—	—
(IV.)			−	H	X = CH 522 mμ. X = N 424 mμ. Shift −98 mμ.
	X = CH Change to X = N		+	—	—
(V.)			+	B	R = O 372 mμ. R = S 442 mμ. Shift +70 mμ.
	X = O Change to X = S		−	—	—
(VI.)			−	H	R = H 725 mμ. R = S 665 mμ. Shift −60 mμ.
	X = -H H- Change to X = S		−	—	—
(VII.)			−	H	X = CH blue ‡ X = N red Shift, negative
	X = CH Change to X = N		+	—	—

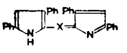
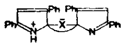
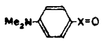
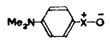
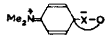
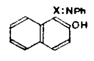
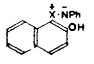
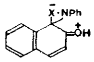
* + = increase; − = decrease. † B = bathochromic; H = hypsochromic.

‡ Wizinger, *J. pr. Chem.*, 1941, **157**, 129.

Energetically asymmetrical ionic dyes.

	Dye and structural change.	Likely structures (more likely first).	Effect of change on energy level.	Expected shift.	Observed absorption.
(VIII.)	 X = CH Change to X = N		+	B	X = CH 409 mμ. X = N 438 mμ. Shift +29 mμ.
			−	—	—
(IX.)	 X = CH Change to X = N		+	B	X = CH 435 mμ. X = N 516 mμ. Shift +81 mμ.
			−	—	—
(X.)	 X = Y = CH Change to (a) X = N, Y = CH (b) X = CH, Y = N	(a) 	−	H	X = CH 437 mμ. X = N 406 mμ. Shift −31 mμ.
			+	—	—
		(b) 	+	B	Y = CH 437 mμ. Y = N 448 mμ. Shift +11 mμ.
			−	—	—

Non-ionic dyes.

	Dye and structural change.	Likely structures (more likely first).	Effect of change on energy level.	Expected shift.	Observed absorption.
(XI.)	 X = CH Change to X = N		+	B	X = CH 550 mμ.¶ X = N 614 mμ. Shift +64 mμ.
			−	—	—
(XII.)	 X = CH Change to X = N		+	B	X = CH 342 mμ. X = N 423 mμ. Shift +81 mμ.
			−	—	—
(XIII.)	 X = CH Change to X = N		+	B	X = CH 437 mμ. X = N 498 mμ. Shift +61 mμ.
			−	—	—

The author thanks Dr. M. A. T. Rogers for samples of some of these dyes.

¶ In pyridine.

dyes (II) * and (IV). This failure which also occurs in many related dyes is believed to be caused by the unusually strong $-M$ effect of the heterocyclic rings which has the effect of building up a negative charge on certain chain atoms in spite of the positive nature of the characteristic charge.

It will be noted that the replacement of ⁻CH⁼ by ⁻N⁼ in these dyes may cause either a hypsochromic or a bathochromic shift. A simple rule which can be applied in these cases is that, if the carbon atom at which the replacement takes place is separated from the active $\pm M$ centres of the auxochromes by an odd number of conjugated atoms,† then a hypsochromic shift results whilst a separation by an even number of atoms results in a bathochromic shift.‡

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[*] A bathochromic shift is also predicted by Dewar (*loc. cit.*, generalization 4).

[†] This generalization was reached also by Förster (*loc. cit.*).

[‡] Cf. Dewar (*loc. cit.*), also Kuhn, *Chimia*, 1950, **9**, 203.

Application to the Electron-gas Model of Absorption.—Kuhn (*loc. cit.*) in applying the electron-gas model to the absorption of energetically unsymmetrical dyes regards the potential field of the conjugated system as approximating to a sine wave. A decrease in the amplitude of this wave resulting from decreasing non-degeneracy of the system results in a bathochromic shift. Similarly he suggests that even in symmetrical dyes the alternate bonds of the chromophoric system may not be quite of the same order since contributions to the hybrid by excited structures may disturb the uniformity. The conclusion can thus be drawn that for any particular length of conjugation the more uniform the potential field of the system the larger will be the calculated value of $\lambda_{max.}$.

In comparing the Förster and the general rule with the above it is at once clear that the smaller the tendency of the chromophoric atoms to take up the characteristic charge in ionic dyes, or the smaller the importance of the excited structures in dyes of any type, the smaller will be the probability of variations in charge on the chromophoric atoms (and hence in potential field of these atoms) and, in symmetrical dyes, the smaller will be the disturbance in the uniformity of the bond order of alternate links.

FIG. 1.

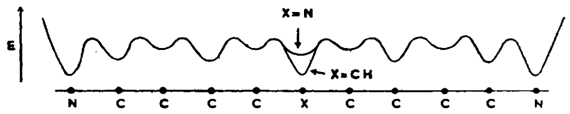
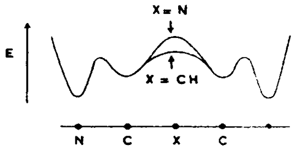


FIG. 2.



Although, for his treatment, Kuhn regards the dyes as containing a uniformly fluctuating potential field it is clear that in certain cases this is not so. Thus dye (III) must contain a big dip in the field at the point X owing to the great significance of the excited structure containing X^+. On the other hand, in dye (IV) there must be a hump corresponding to the importance of structures containing X^-. The field diagrams of these dyes may be represented by Figs. 1 and 2. The replacement of X=CH by X=N in (III), and of X=N by X=CH in (IV), will then cause an increase in the uniformity of the field by reducing the irregularity as shown.

The conclusions to be drawn from the Förster and the general rule are thus seen to accord fully with the findings of Kuhn.

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