478. Colour and Constitution. Part I. Basic Dyes.

By M. J. S. Dewar.

The calculation of light absorption by the molecular-orbital method is discussed, and reasons are given for believing that basic dyes should provide a favourable case for its application. This conjecture has been confirmed by agreement between the calculated and experimental absorption frequencies for a number of basic dyes. A general molecular-orbital theory of such dyes is proposed which leads to a comprehensive set of rules for the effect of structural changes on light absorption.

THE relation between colour and constitution has been for decades an outstanding problem in organic chemistry, solution of which became feasible only with the development of the quantum theory. Exact treatment of complex molecules by the new methods is of course out of the question, but qualitative reasoning based on very approximate solutions of the relevant wave equations has provided some understanding of the basic processes involved in light absorption (cf. Forster, *Z. physikal. Chem.*, 1940, **48**, *B*, 12; Herzfeld and Sklar, *Rev. Mod. Physics*, 1942, **14**, 294; Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273; Lewis, *J. Amer. Chem. Soc.*, 1945, **67**, 770; Dewar, " The Electronic Theory of Organic Chemistry," Oxford, 1949). The purpose of the present paper is to put this qualitative treatment on a firmer basis.

Three approximate methods have been used to calculate the light absorption of conjugated organic compounds; the simple MO (molecular-orbital method), the VB (valence-bond method), and the ASMO (anti-symmetricalised molecular-orbital method). Of these the ASMO is the most rigorous and the most satisfactory, since explicit allowance is made for electron spin, and no empirical parameters are involved. The method was devised by Goeppert-Mayer and Sklar (*J. Chem. Physics*, 1938, **6**, 645) and was used by them to interpret the complete electronic spectrum of benzene; it has since been extended to diphenyl (London, *ibid.*, 1945, **13**, 396) and simple Wurster salts (Goeppert-Mayer and McCallum, *Rev. Mod. Physics*, 1942, **14**, 248), and further improved by Craig *et al.* (cf. *Proc. Roy. Soc.*, 1950, **200**, *A*, 474). For the present purpose the method is unsuitable, however, since it would involve prohibitively tedious calculations and would not yield the kind of qualitative generalisations sought. The VB method is unsuitable for calculating light absorption, since it is difficult to include ionic forms, and otherwise the calculated transitions have zero transition moments. No reliable conclusions could be drawn from a model so divorced from reality. Therefore the simple MO method has been used here, for lack of any practicable and better alternative.*

The simple MO method suffers from a number of major theoretical shortcomings (cf. Coulson and Dewar, *Faraday Soc. Discussions*, 1947, **2**, 54) but nevertheless seems quite satisfactory for calculating ground-state energies and electron distributions in hydrocarbons. Apparently the errors are reasonably constant and can be compensated by adjusting the empirical parameter in terms of which the energies are expressed. In molecules containing hetero-atoms, the method is less satisfactory, since the assumption of a self-consistent field breaks down (Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193) but here too the results are reasonable if the additional parameters involved are given suitable values. In the calculation of light absorptions, however, the method often fails very badly. Two effects are probably largely responsible. First, the method neglects electron spin. Therefore it does not distinguish between a corresponding pair of singlet and triplet excited states but gives some kind of average of the two; the calculated excitation energies cannot be brought into correspondence with experiment by adjusting the empirical " resonance integral " since the singlet–triplet separation is neither constant nor in constant ratio to the mean excitation energy. Secondly, the failure of self-consistency will be more serious in excited states where the charge displacements tend to be large.

Now there are reasons for believing that both these effects may be smaller in the case of basic dyes. First, the singlet–triplet separations in such dyes seems to be unusually small (approximetly 6 kcals.; cf. Kasha, *Chem. Reviews*, 1947, **41**, 401). Secondly, the dyes contain more π-electrons than atoms; the accumulation of π-electrons on the terminal hetero-atoms (owing to their relatively high electron affinity) will be compensated by the extra electrons, and the central carbon chain should to a first approximation resemble that in a hydrocarbon. Naturally, these conjectures require confirmation, and so the light absorption of a representative range of basic dyes has been calculated by using one set of theoretically acceptable parameters.

* Kuhn's uniform potential model (cf. *Helv. Chim. Acta*, 1949, **32**, 2247) is even cruder than the simple MO model.

The results are compared with experiment in the Table. It will be seen that the agreement is surprisingly good, particularly since (i) no attempt has been made to choose the best values for

Compound.	λ_{max} (calc.).*	λ_{max} (obs.).*
$Me_2\overset{+}{N}:CH\cdot[CH:CH]_n\cdot NMe_2$; $n = 1$	3160	3090
$n = 2$	$\left\{\begin{array}{l}4390\\2310\end{array}\right.$	$\left\{\begin{array}{l}4090\\2530\end{array}\right.$
$n = 3$	$\left\{\begin{array}{l}5120\\2900\\1950\end{array}\right.$	$\left\{\begin{array}{l}5110\\3050\\2660\end{array}\right.$
Michler's hydrol blue	5850 (*x*) 4020 (*y*) 3440 (*x*)	6100 (*x*) 3600 (*y*) 3000 (*x*)
Malachite-green	6080 (*x*)	6160 (*x*)
Bindschedler's green	7740	7400
Crystal-violet	5590 (*x*) 3680 (*y*) 3250 (*y*) 2590 (*x*)	$\left.\begin{array}{l}5910\\5450\end{array}\right\}(x)$ 3050 (*y*) 2500 (*x*)
Acridine-orange	4320	4910
2 : 7-Diaminophenazinium salts	5520	5130
Sodio-derivative of acetylacetone	2660	2900
Sodium derivative of dihydroresorcinol	2660	2800
$NaO\cdot[CH:CH]_2\cdot CH:N\cdot[CH:CH]_2\cdot CHO$	5680	5500

* Wave-lengths in A., to nearest 10A.

the various empirical parameters, (ii) the change in electron affinity of carbon adjacent to hetero-atoms has for simplicity been neglected, and (iii) the electron affinities of the hetero-atoms can be significantly altered by alkylation. Even the higher excited levels are correctly predicted in many cases; a few examples are given in the Table. The direction of the absorbed electric vector is also correctly predicted in cases when it is known experimentally. In *x*-bands the vector lies along the major axis, in *y*-bands along the minor axis, of the conjugated system [the observed values quoted in the Table are those given by Lewis and Bigeleisen (*J. Amer. Chem. Soc.*, 1943, **65**, 2102, 2107), Simpson (*J. Chem. Physics*, 1948, **16**, 1124), Schwarzenbach, Lutz, and Felder (*Helv. Chim. Acta*, 1944, **27**, 576), and International Critical Tables].

Method.—The calculations followed the standard procedure and require little comment. Overlap was neglected since preliminary calculations showed that its inclusion made little difference. The following values were ascribed to the various Coulomb terms (q relative to carbon) and resonance integrals (γ).

$$q_N \text{ (in } NR_3) = \gamma_{CC} \qquad \gamma_{CN} = \gamma_{CC}$$
$$q_N \text{ (in } RN:C) = 0.5\,\gamma_{CC} \qquad \gamma_{CO} = \gamma_{CC}\cdot\sqrt{2}$$
$$q_O \text{ (terminal)} = \gamma_{CC}$$
$$\gamma_{CC} = 73.2 \text{ kcals.}$$

The calculations are confined to dyes where all the central atoms are carbon or nitrogen, since there is not sufficient evidence to determine the resonance integrals and Coulomb terms of oxygen and sulphur in dyes such as Pyronine G or methylene-blue.

The Coulomb terms (q) require some comment since they are less than the values assumed by other authors. Higher q's lead to excessive calculated dipole moments for simple $>C:N$ and $>C:O$ bonds. The higher values have been assumed in order to get correct calculated moments for more complex molecules; this situation probably arises from the inadequate allowance that has been made for the change in electron affinity of carbon atoms adjacent to hetero-atoms. Investigations by Branch and Calvin (" The Theory of Organic Chemistry," New York, 1946) and McGowan (*Nature*, 1947, **159**, 644; *Chem. and Ind.*, 1948, 632) suggest that if the Coulomb term of a hetero-atom attached to a carbon chain is q, the carbon atoms along the chain should be ascribed Coulomb terms εq, $\varepsilon^2 q$, etc., where $\varepsilon \sim 0.4$—0.5. Most authors have assumed that $\varepsilon \ll 0.1$ in carrying out MO calculations. The use of too small an ε will affect energy calculations little, but it will destroy the value of calculations of dipole moments. Calculations

of rates of benzene substitution, with a more reasonable value of ε ($\frac{1}{4}$), suggest that $q < 2$ for all the usual hetero-atoms (Dewar, *J.*, 1948, 463).

General Theory of Basic Dyes.—The next step, the main purpose of this paper, will be the development of a general qualitative theory of colour in basic dyes.

A basic dye can be formally derived from a mesomeric carbanion by replacing carbon atoms by hetero-atoms and by introducing substituents. It will be assumed that the effects of such changes on the light absorption of the ion are additive (this assumption is equivalent to a first-order perturbation treatment, and it can also be justified empirically; cf. Lewis and Calvin, *loc. cit.*). For instance, Acridine-orange (I) would be formally derived from the carbanion (II) by substitution with NMe and replacement of the terminal CH_2 groups by NMe_2.

$$(I.) \quad Me_2N\text{...}NMe...\overset{+}{N}Me_2 \qquad (II.) \quad \overset{-}{C}H_2\text{...}CH_2$$

The following treatment makes use of some results of Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, A, **191**, 39), and of a modification of the usual MO methods (Dewar, *Proc. Camb. Phil. Soc.*, 1949, **45**, 638). In this LCMO (linear combination of molecular orbitals) modification, the secular equation of a conjugated molecule RS is set up by using the MO's calculated for RH and SH as trial eigenfunctions. The final secular equation must be identical with that given by the usual LCAO method, but the LCMO determinant can be expanded explicitly to give this equation in a particularly convenient form.

Several theorems will now be established for the effect of structural changes on the light absorption of carbanions. It will be assumed that the molecules are alternant (Coulson and Rushbrooke, *loc. cit.*), and that the terminal atoms, *e.g.*, CH_2 in (II), belong to the " starred " set. Only the frequency of the first absorption band (FFAB) will be discussed, since this determines the general colour of a dye.

(a) *The FFAB of the hydrocarbon* R–S *is not greater than the* FFAB *of RH or SH provided that* RH *and* SH *are not both odd.* Denote the π-MO's of RH by Ψ_r, of SH by Φ_s, where

$$\Psi_r = \sum_m a_{rm}\psi_m, \quad \Phi_s = \sum_n b_{sn}\phi_n,$$

and where the total numbers of ψ's and of ϕ's are even. Let the energies of Ψ_r, Φ_s be E_r, F_s respectively, in units of γ_{CC}, the CC resonance integral. Then if, in RS, R and S are linked through atom j in R and atom k in S, the secular equation of RS may be shown to be (Dewar, *loc. cit.*) :

$$\prod_r (W - E_r) \prod_s (W - F_s) \left\{ 1 - \sum_r \frac{a_{rj}^2}{W - E_r} \sum_s \frac{b_{sk}^2}{W - F_s} \right\} = 0 \quad . \quad . \quad . \quad (1)$$

It may be assumed that no root of (1) is equal to an E_r or F_s, since equality can occur only if RH or SH has degenerate levels, or if one of the a_{rj} or b_{sk} vanishes—in either case the identical roots can be explicitly factored out of (1), leaving an equation of the same form.

Now Coulson and Rushbrooke (*loc. cit.*) have shown that the roots of the secular equation for a hydrocarbon occur in pairs with energies equal in magnitude but opposite in sign, and that the coefficients of the atomic orbitals in the corresponding MO's again differ at most in sign. Equation (1) may therefore be written

$$1 - \sum_r \left\{ \frac{a_{rj}^2}{W - E_r} + \frac{a_{rj}^2}{W + E_r} \right\} \sum_s \left\{ \frac{b_{sk}^2}{W - F_s} + \frac{b_{sk}^2}{W + F_s} \right\} = 0,$$

or

$$1 - 4W^2 \sum_r \frac{a_{rj}^2}{W^2 - E_r^2} \sum_s \frac{b_{sk}^2}{W^2 - F_s^2} \equiv f(W) = 0 \quad . \quad . \quad . \quad . \quad (2)$$

If the smallest E_r^2 or F_s^2 is e^2, then as W^2 increases from 0 to e^2, $f(W)$ decreases from $+1$ to $-\infty$. Therefore equation (2) has roots $\pm g$ where $g^2 < e^2$. Now the lowest excitation energy of RH or SH is $2|e|$, if overlap is neglected, and the lowest excitation energy of RS is $2|g|$. Since $|g| < |e|$, the FFAB of RS must be less than that of RH or SH. This conclusion is not altered by inclusion of overlap; the excitation energies become :

$$\frac{2|g|}{1 - S^2g^2} < \frac{2|e|}{1 - S^2e^2},$$

and these obey the indicated inequality (since $S^2e^2 < 1$).

The only exception occurs when the lowest level of (RH + SH) factors out of the secular equation for RS; here RS has the same FFAB as the lower FFAB of RH or SH.

This completes the proof of the theorem for normal hydrocarbons; the proof for the case where RH or SH has an odd number of conjugated atoms (*i.e.*, is an ion or radical) is so nearly identical that it need not be given. The theorem does not hold if both RH and SH are odd.

(b) *Replacement of an unstarred carbon atom in the carbanion* R^- *by a hetero-atom lowers the* FFAB. Let the *j*th carbon atom in R^- be replaced to give R_H^-. Let the Coulomb term of the hetero-atom be q relative to carbon. Then, to a first approximation, the change δE_r in the energy level E_r will be given (cf. Coulson and Longuet-Higgins, *loc. cit.*) by :

$$\delta E_r \simeq -q\partial E_r/\partial q_r = -q \cdot a_{rj}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now for the highest occupied orbital in R^-, $a_{rj} = 0$ (Coulson and Rushbrooke, *loc. cit.*). This orbital remains unchanged in R_H^-, to a first approximation. The energy of the first excited level in R_H^- will, from equation (3), be less than that in R^-, since $q > 0$. Therefore the FFAB of R_H^- is less than that of R^-.

(c) *Replacement of a starred atom in* R^- *by a hetero-atom will usually raise the* FFAB. If the highest occupied and the lowest unoccupied MO in R^- are the *r*th and *s*th respectively, it follows from equation (3) that the excitation energies for $R^-(E)$ and $R_H^-(E_H)$ are related by the expression

$$E_H - E \simeq q(a_{rj}^2 - a_{sj}^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Since the *r*th MO is confined to only half of the conjugated atoms in R^-, while the *s*th MO covers the whole molecule, it is likely that $|a_{rj}| > |a_{sj}|$. Therefore as a rule, R_H^- will have a higher FFAB than R^-.

(d) *The effects in* (b) *and* (c) *are roughly proportional to* q. This follows at once from equations (3) and (4).

(e) *A* —E (*anionoid electromeric*) *substituent in* R^- *at an unstarred carbon raises the* FFAB. Consider the case of a monatomic substituent X, with Coulomb term q, attached to atom *j* in R^-. The secular equation for $(RX)^-$ is (Dewar, *loc. cit.*) :

$$W + q - \sum_r \frac{a_{rj}^2}{W - E_r} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Applying a first-order perturbation treatment for the root corresponding to E_r, we have :

$$(E_r)_H \simeq E_r + [a_{rj}^2/(E_r + q)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This shows that addition of the substituent " repels " the roots from the level $-q$. [(RX) will have root approximately equal to $-q$ in addition to the roots approximately equal to E_r.] At an unstarred position, however, if $q > 0$ (as is always the case), $a_{rj} = 0$ for the highest occupied level; this level remains unchanged in $(RX)^-$ to a first approximation. But the lowest unoccupied level is raised [cf. equation (6)]. Therefore the FFAB of (RX^-) is greater than that of R^-. It is easily shown that the same is true if X is attached to two unstarred atoms in R, forming a ring, and that inclusion of overlap does not affect the results.

(f) *A* —E *substituent at a starred atom will tend to lower the* FFAB. This result follows from equation (6) in the same way that (c) follows from equation (3).

(g) *The effects in* (e) *and* (f) *decrease with increasing* q. This follows at once from equation (6).

(h) *A* +E (*cationoid electromeric*) *substituent should tend to lower the* FFAB. The introduction of such a substituent ·X:Y can be supposed to take place in stages. First introduce ·CH:CH$_2$, then replace CH by X, then CH$_2$ by Y. The first step will lower the FFAB [(a) above]. Of the other two steps, one will raise, and one will lower, the FFAB, but the latter, a first-order effect [(b) above] should in general be greater than the former, a second-order effect [(c) above]. Therefore the net effect of the +E substitutent should be to lower the FFAB. The relative effects of such substituents in starred and unstarred positions can be predicted, using the rules already given. Thus ·COR should have a greater bathochromic effect in an unstarred position, since the oxygen is then unstarred. There do not seem to be any suitable data available to check such predictions.

General Conclusions.—The results of the foregoing analysis may be summed up in the following generalisations. It is assumed that the dye is formally derived from a carbanion by

substitution or replacement, and that the terminal atoms in the carbanion are starred.   Then the FFAB will in general be lowered by (1) extension of the conjugated system, (2) replacement of unstarred carbon by a hetero-atom, (3) substitution of starred carbon by a $-E$ group, or (4) $+E$ substituents.   In (2) the effect should be greater, in (3) less, the greater the electron affinity (q) of the hetero-element or $-E$ group.   (It is of course assumed that replacement does not alter the total number of π-electrons; thus only terminal carbon can be replaced by hetero-elements other than nitrogen.)
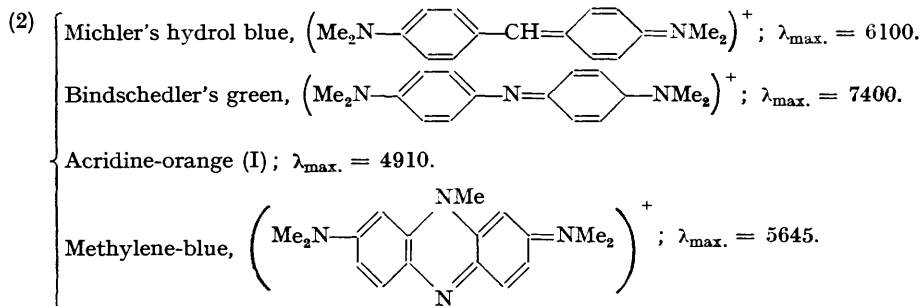
The FFAB will be raised by (5) replacement of starred carbon by a hetero-atom or (6) substitution of unstarred carbon by a $-E$ group.   The effect in (5) should be greater, in (6) less, the greater the electron affinity of the hetero-element or $-E$ group.

Comparison with Experiment.—All these conclusions seem to agree with experiment, and many of them are already known empirically.   One or two examples will suffice in each case.
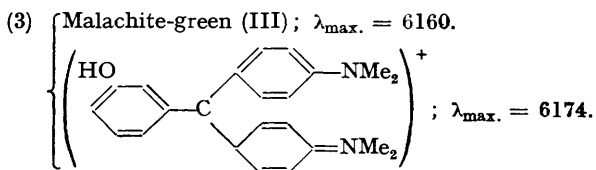
(1) This well-known effect is seen most clearly in the cyanine dyes, where the FFAB falls as n increases in the sereies $[R \cdot [CH\dot:CH]_n \cdot S]^+$.   An interesting further example is the decrease in

$$\left(Me_2N - \text{---} - CPh = \text{---} = NMe_2\right)^+ \qquad \left(Ph \cdot NH - \text{---} - CPh = \text{---} = NHPh\right)^+$$

(III.) $\lambda_{max.} = 6160.$ (IV.) $\lambda_{max.} = 6370.$
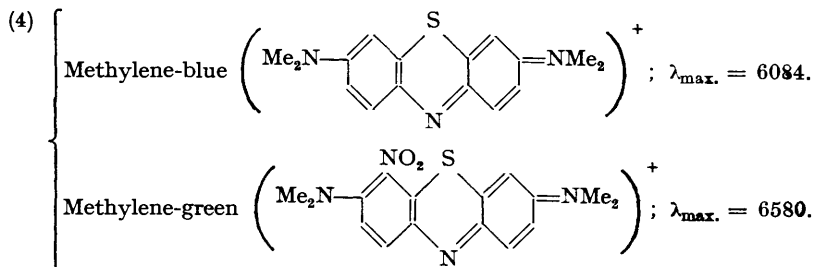
FFAB brought about by terminal arylation, *e.g.*, in the pair Malachite-green (III) and Viridine-green (IV).   Here the effect of additional conjugation outweighs the effect of increasing the electron affinity of the nitrogen atoms.

(2) Michler's hydrol blue, $\left(Me_2N - \text{---} - CH = \text{---} = NMe_2\right)^+$; $\lambda_{max.} = 6100.$

Bindschedler's green, $\left(Me_2N - \text{---} - N = \text{---} - NMe_2\right)^+$; $\lambda_{max.} = 7400.$

Acridine-orange (I) ; $\lambda_{max.} = 4910.$

Methylene-blue, $\left(Me_2N - \text{---} - \overset{NMe}{\text{---}} - \underset{N}{\text{---}} = NMe_2\right)^+$; $\lambda_{max.} = 5645.$

In each case replacement of unstarred C by N lowers the FFAB.

(3) Malachite-green (III) ; $\lambda_{max.} = 6160.$

$\left(\overset{HO}{\text{---}} - C \overset{-NMe_2}{\underset{=NMe_2}{\text{---}}}\right)^+$; $\lambda_{max.} = 6174.$

Addition of a $-E$ substituent (OH) at a starred position lowers the FFAB.

(4) Methylene-blue $\left(Me_2N - \text{---} - \overset{S}{\underset{N}{\text{---}}} = NMe_2\right)^+$; $\lambda_{max.} = 6084.$

Methylene-green $\left(Me_2N - \overset{NO_2 \; S}{\underset{N}{\text{---}}} = NMe_2\right)^+$; $\lambda_{max.} = 6580.$
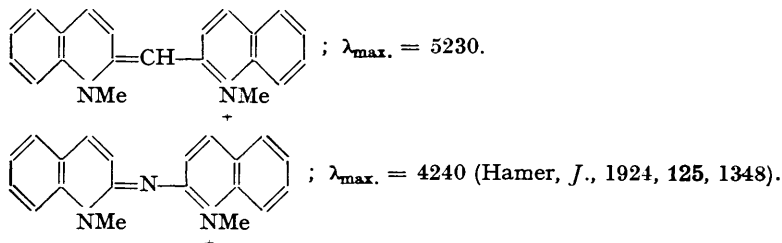
The $+E$ substituent (NO_2) lowers the FFAB.

(5) Since the terminal groups in a dye are starred, this rule implies that the FFAB should be raised by increasing the electron affinity (decreasing the basicity) of the terminal groups.   This
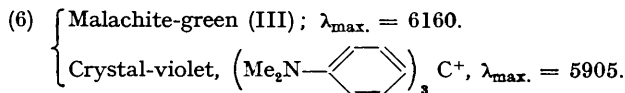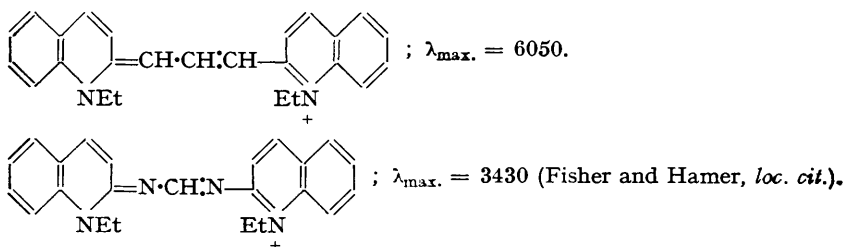
effect is qualitatively very well known (see Dewar, *op. cit.*, for numerous examples). The effect of replacing central starred atoms is seen in the following comparisons :
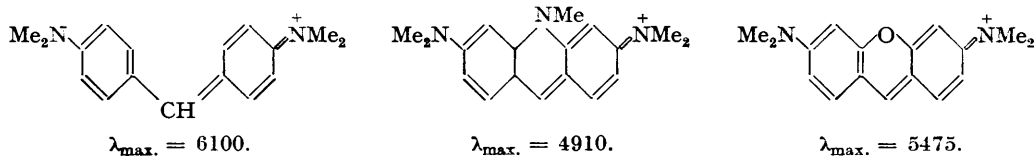
$$\text{(naphthalene-NEt}^+\text{)}-CH\!:\!CH-\text{(phenyl)}-NMe_2; \quad \lambda_{max.} = 5300.$$

$$\text{(naphthalene-NEt}^+\text{)}-CH\!:\!N-\text{(phenyl)}-NMe_2; \quad \lambda_{max.} = 5800.$$
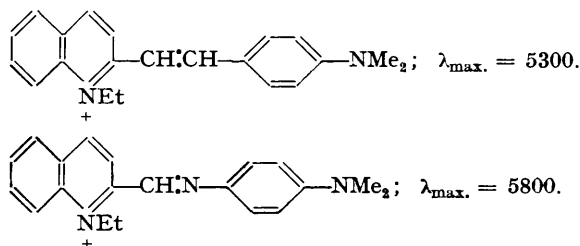
(the mean shift for ten such pairs is 400 A.; Bloch and Hamer, *Phot. J.*, 1930, **54**, 374).

$$\text{(naphthalene-NMe)}=CH-\text{(naphthalene-NMe}^+\text{)}; \quad \lambda_{max.} = 5230.$$

$$\text{(naphthalene-NMe)}=N-\text{(naphthalene-NMe}^+\text{)}; \quad \lambda_{max.} = 4240 \text{ (Hamer, } J., 1924, \textbf{125}, 1348).}$$

(The mean shift for three such pairs is 900 A.; Fisher and Hamer, *ibid.*, 1927, 907).

$$\text{(naphthalene-NEt)}=CH\cdot CH\!:\!CH-\text{(naphthalene-EtN}^+\text{)}; \quad \lambda_{max.} = 6050.$$

$$\text{(naphthalene-NEt)}=N\cdot CH\!:\!N-\text{(naphthalene-EtN}^+\text{)}; \quad \lambda_{max.} = 3430 \text{ (Fisher and Hamer, } loc.\ cit.).}$$

(6) $\begin{cases} \text{Malachite-green (III); } \lambda_{max.} = 6160. \\ \text{Crystal-violet, } \left(Me_2N-\text{(phenyl)}\right)_3 C^+, \lambda_{max.} = 5905. \end{cases}$

Addition of a $-E$ group (NMe_2) at an unstarred position raises the FFAB. The effect of increasing the electron affinity of the substituent is seen in the comparison :

$$Me_2N-\text{(phenyl)}-CH=\text{(phenyl)}-\overset{+}{N}Me_2$$
$$\lambda_{max.} = 6100.$$

$$Me_2N-\text{(xanthene-NMe)}-\overset{+}{N}Me_2$$
$$\lambda_{max.} = 4910.$$

$$Me_2N-\text{(xanthene-O)}-\overset{+}{N}Me_2$$
$$\lambda_{max.} = 5475.$$

Conclusions.—Some of the rules given above have previously been put forward on qualitative grounds but the present discussion is more complete and also rests on a much firmer theoretical basis. The alternating effect of substituents, etc., in starred or unstarred positions has not been noticed previously as a general phenomenon; its nature is brought out very clearly in the present treatment. The striking increase in FFAB from Malachite-green to Crystal-violet is also well interpreted, and also of course the still greater differences between Michler's hydrol blue and analogous tricyclic dyes such as Acridine-orange or Pyronine G.