

Concepts to design dyes in spectral sensitization

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Abstract. Dyes having desired light absorption can be designed on the basis of five simple, generally valid colour rules within the framework of the triad theory. To engineer dyes having desired relative positions of their frontier molecular orbital (FMO) energies, perturbational molecular orbital (PMO) theory proves to be useful provided that ideal polymethinic fragments are taken as basic structures to be perturbed instead of the hitherto used hydrocarbons or hydrocarbon ions.

Keywords. Colour theory; dyes; molecular engineering; spectral sensitization.

1. Introduction

Spectral sensitization of semiconductors by dyes is mainly governed by both electron transfer and hole injection processes. As demonstrated in figure 1 this has been shown in spectral sensitization of photographic silver halide emulsions already in the sixtieth by Daehne (1965, 1979). One essential precondition of spectral sensitization by electron transfer is that the lowest unoccupied molecular orbital (LUMO) of the sensitizing dye is positioned above the lower limit of the conduction band of the semiconductor under consideration like in groups I and II of figure 1. Molecules whose LUMO lies below this limit can only act as electron trapping agents in their ground state and hence they will desensitize photographic silver halide emulsions by reducing the number of photoelectrons in the conduction band (group IV, figure 1) or by oxidation even the latent image specks (group VI, figure 1).

Another precondition for spectral sensitization is that the highest occupied molecular orbital (HOMO) of the sensitizer be moderately far away from vacuum. Otherwise it may inject electrons in the ground state into the silver halide and thus act as photographic developing or fogging agent (group I, figure 1). Therefore only dyes of group II are real spectral sensitizers. If the position of the HOMO is lowered further, like in groups III and VI of figure 1, it can trap holes from the valence band and thus act as a chemical sensitizer in the ground state. Finally, if the HOMO of the sensitizer is positioned below the upper limit of the valence band, it may effect spectral sensitization by hole injection in its excited state (group V, figure 1). This feature is used in pre-fogged photographic emulsions for direct positive processing.

Similar relationships exist also in the luminescence behaviour of dyes adsorbed at semiconductor surfaces which had been especially elaborated for photographic silver halide emulsions at deep temperatures mainly by Costa *et al* (1974). If the LUMO of the special sensitizing dye lies above the lower limit of the conduction band of the

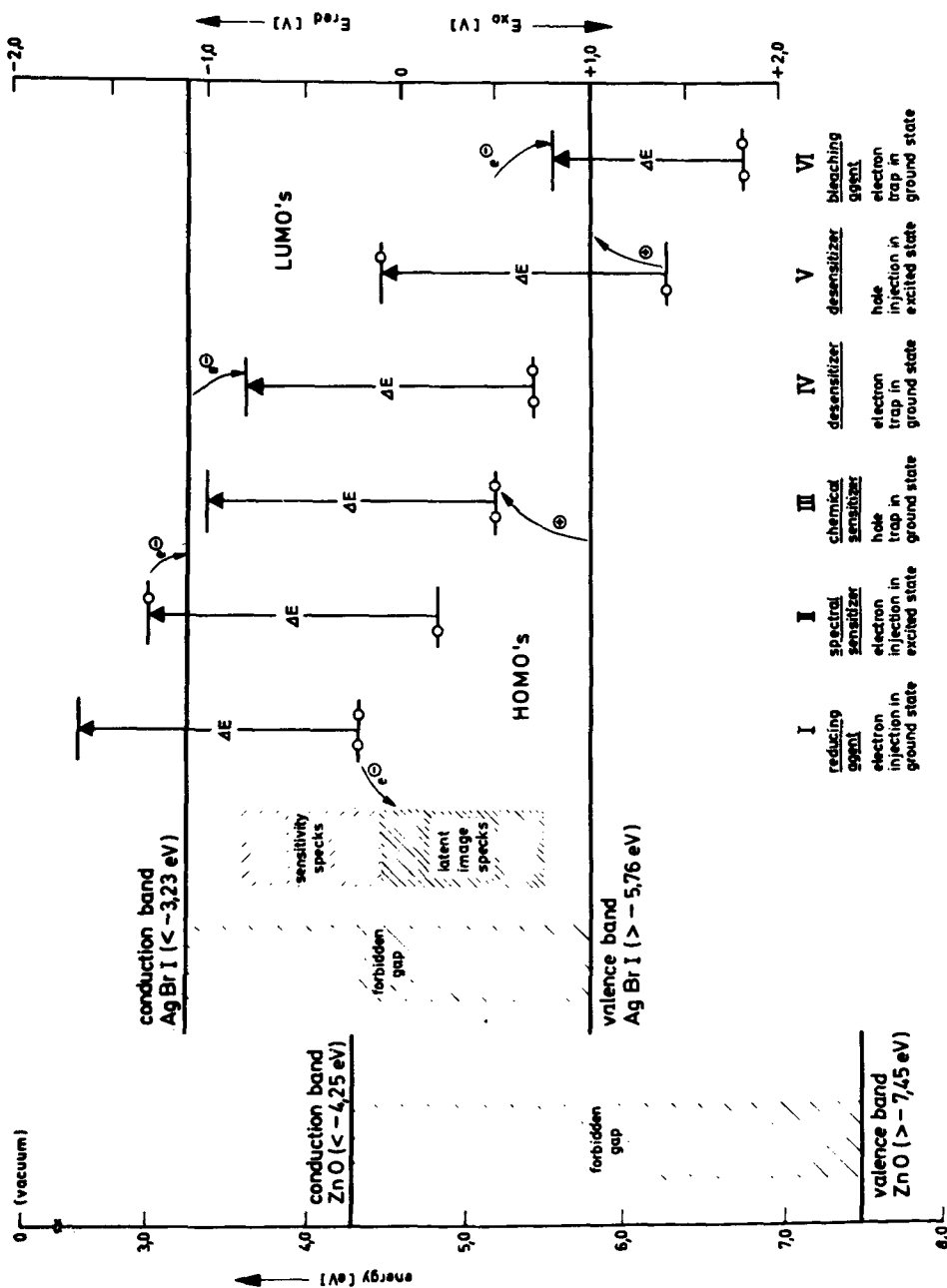


Figure 1. Relationships between the energy levels of spectral sensitizers and band energies of AgBrI and ZnO (after Daehne 1979).

silver halide there may occur a spectrally sensitized luminescence of the silver halide by light excitation of the dye (groups I, II, figure 1) where in case of dyes whose LUMO lies below the lower limit of the conduction band the dye fluorescence can be spectrally sensitized by light excitation of the silver halide valence band (groups III, IV, figure 2). Finally the emission of the dye as well as of silver halide is nearly completely quenched if the HOMO of the dye lies below the upper limit of the silver halide's valence band because in that case hole injection from the excited dye into the valence band may occur which prevents any radiative process (group V, VI, Figure 1).

Apart from these thermodynamical preconditions spectral sensitization is doubtlessly a kinetically controlled process which depends on the ratio of all competing electron transfer and hole injection processes both in the valence and conduction band and in the forbidden gap of the semiconductor under consideration as well as in the ground and excited state of the sensitizing dyes (Daehne 1979). Therefore, the relationships between the band energies of the silver halide and the HOMO and LUMO energies of the dyes can be only understood under the assumption that the kinetic parameters, such as the temperature, the preexponential factor and the concentration of the charge carriers and charge trapping centers etc., are nearly equal or constant, respectively, under comparable experimental conditions.

Finally, to realize spectrally sensitized electron or hole transfer by dyes it is necessary that the dye molecules absorb light of the desired wavelengths, i.e., that they have the appropriate colour and transition energy, respectively.

Therefore, to design dyes in spectral sensitization it is necessary to engineer dyes having (i) special colour, (ii) special positions of their HOMO and LUMO energies, i.e., of their frontier molecular orbitals (FMOs), and (iii) special kinetic relaxation properties after light excitation. In the following some recommendations will be made on how to tailor-make dyes having the desired colour and desired FMO energies. First encouraging results to engineer dyes also having desired excited state properties have been recently achieved, among others, by Grabowski *et al* (1983), Tolmachev (1987), and Lippert *et al* (1987).

2. Colour and constitution relationships in spectral sensitization

Although many highly sophisticated quantum chemical methods are now available, which satisfactorily allow the calculation of almost any molecular property, the effect of this state of the art is less successful than expected because of the vast amount of conceivable molecules which have to be calculated to find by chance molecules with certain desired properties. Thus in molecular engineering again empirical or even heuristic guide lines have been proposed enabling chemists how to predict or at least how to estimate desired molecular features.

Concerning colour and constitution relationships such guidelines are now well-elaborated and summed up in the triad theory by Daehne (1978) and Daehne and Moldenhauer (1985) as explained in figure 2. Besides the well-known aromatic and polyenic state there exists at least a third, energetically stabilized state termed ideal polymethine state. This state can be realized by occupying a molecular chain consisting of N atoms with $(N + 1)$ or $(N - 1)$ π -electrons. The ideal polymethine state is characterized among other unique properties by full π -bond order equalization like in the aromatics, but, in contrast to aromatics and polyenes, by strong π -electron

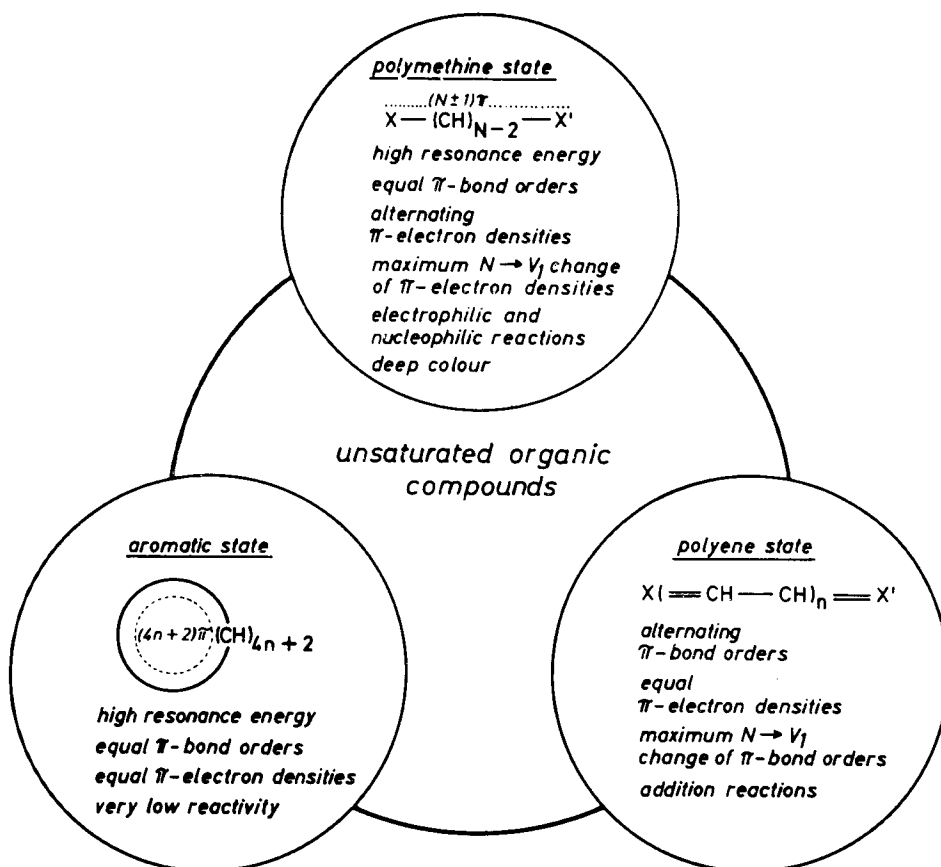
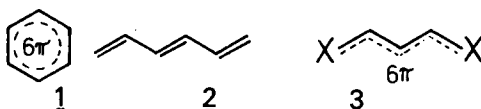


Figure 2. Principle of triad theory (after Daehne 1978).

density alternation which is reversed in the first excited singlet state and which is responsible for the high disposition of polymethines for electrophilic and nucleophilic substitution reactions. Molecules in the ideal polymethine state have the longest wavelength absorption and (apart from exceptional cases of forbidden transitions) the most intense absorption meaning that they are deepest in colour in comparison to aromatic or polyenic molecules of comparable size.

This is the first colour rule in the framework of triad theory. For example the transition energies, calculated by the HMO- β_{sc} method of benzene **1**, hexatriene **2**, and the trimethine cyanine **3** ($X = \text{nitrogene}$) each having 6π -electrons, decrease in the order **1** > **2** > **3** (Daehne and Moldenhauer 1985).



As explained in figure 2 polymethinic structures can be realized by filling a molecular chain with one more or one less π -electron than the number of the chain's constituent atoms where usually the donor substituent provides the excess π -electron.

In practice, this condition can be realized by substituting an aromatic entity like

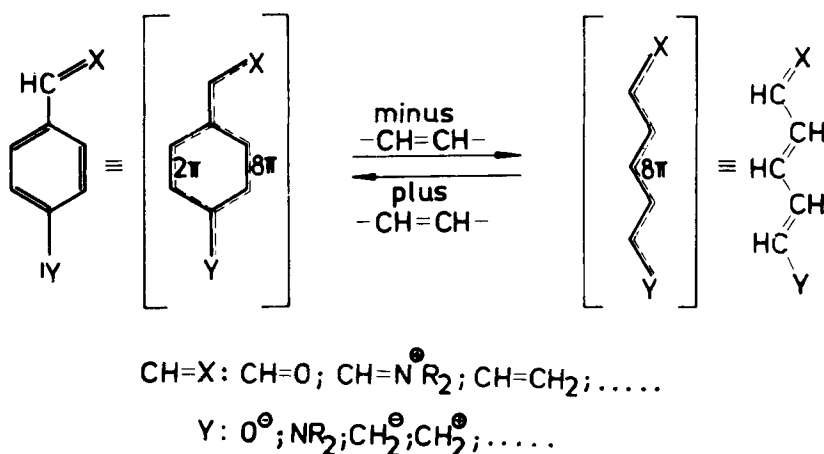


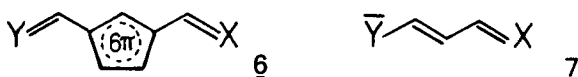
Figure 3. Interrelationship between donor-, acceptor-substituted benzene, pentamethine, and donor-, acceptor-substituted butadiene according to Daehne and Hoffmann (1990).

benzene or a polyenic chain like butadiene by an acceptor group and a donor group as exemplified in figure 3. If both terminal atoms of the substituents are identical, one would get, e.g., a cyanine dye in case of combining the carbimmonium acceptor group with the amino donor group, or one would get an oxonol dye by combining the aldehyde group with the hydroxylate anion group (Daehne and Hoffmann 1990).

Starting with ideal polymethinic building blocks it is only necessary to introduce four additional colour rules in organic chemistry to fully understand the essential colour and constitution relationships. The second colour rule reads: if the characteristic π -electron density alternation in polymethines is maintained on structural modifications as in **4** only a slight blue shift of the light absorption is caused, whereas the third colour rule reads: if the characteristic π -electron density alternation in polymethines is perturbed on structural modifications as in **5** a strong red shift of the light absorption is brought about.



The last two colour rules only fix the limits of validity of the two preceding ones in accordance with the first colour rule, namely, the fourth rule: aromatization within molecules as in **6**, originates a strong blue shift of the light absorption, and fifth rule: polyene-formation in consequence of the nonsymmetric localization of the π -electron system as in **7** causes a moderate blue shift. All deviations from these five basic colour rules could be explained so far by second order effects such as *cis-trans* isomerization, steric hindrances, intermolecular interactions etc.



Some examples explaining the second and third colour rule are given in figure 4. On alternating substitution of the indolinodicarbocyanine at the *meso*-position with

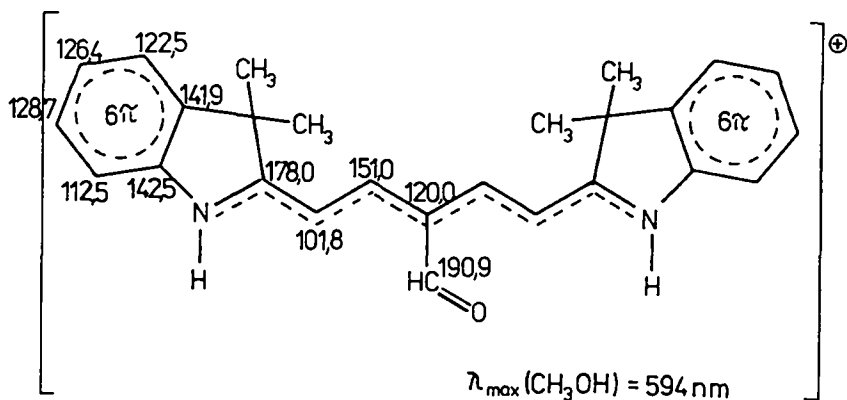
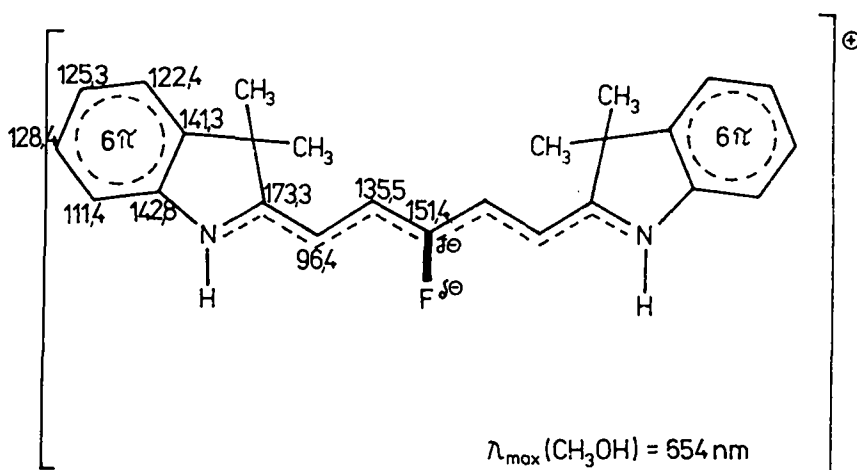
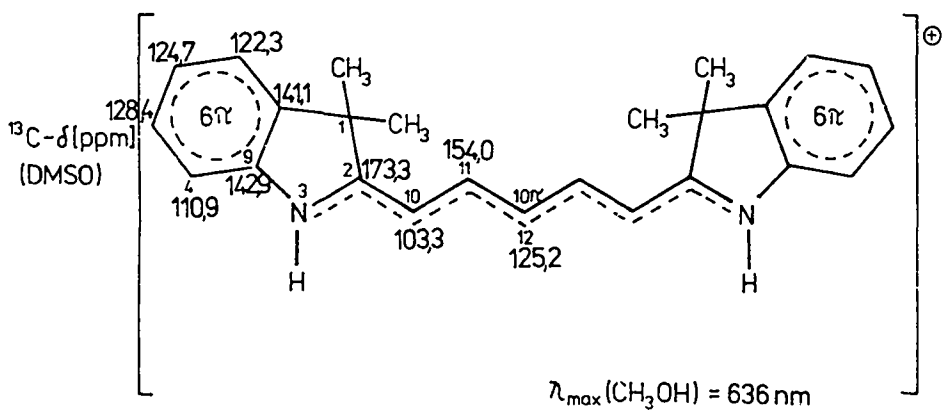
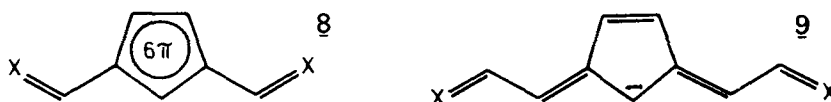


Figure 4. Spectral substituent effect in the indolinodicarbocyanine according to Grahn and Reichardt (1976). The numbers at the atoms are ^{13}C chemical shifts indicating perturbation or maintenance of π -electron density alternation within the heptamethine chain.

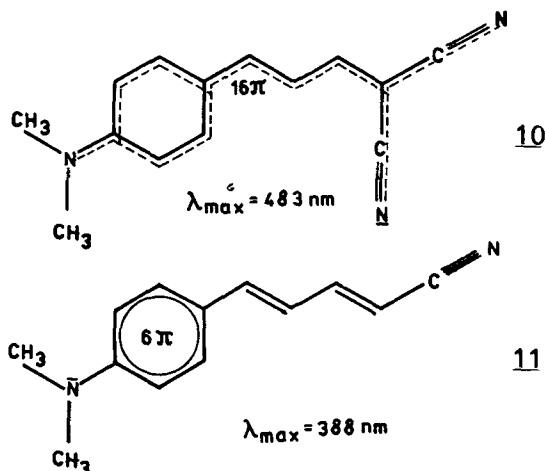
an acceptor group (figure 4, below) the π -electron density alternation is maintained and originates a blue shift whereas a donor substituent at the same position disturbs the π -electron density alternation and hence causes a relatively strong red shift (Grahn and Reichardt 1976).

Structures **8** and **9** demonstrate how to recognize the formation of aromatic structures in ring systems effecting blue shift according to colour rule 4. Aromatization only takes place in **8** containing a pentamethine unit because the prerequisite for aromatization is that an isolated six π -electron system [or $(2n + 4)$ π -electron systems, respectively] can be formulated which has exclusively singly-bonded substituents.



This is no longer the case in the ethylene-bridged heptamethine chain **9** in which the five-membered ring system contains two exocyclic double bonds if a resonance structure with 6 π -electrons within the ring is formulated. Therefore, a blue shift is to be expected for the upper case but a strong red shift for the lower one. The experimental proof of this prediction is given in figure 5. The light absorption of the centrally bridged benzthiadicyanobenzene having no aromatic structure is strongly red-shifted according to the third colour rule whereas the nonsymmetrically bridged dye in the lower part of figure 5 absorbs at shorter wavelengths than the unsubstituted dye according to colour rule 4 because the ring system within the polymethine chain can now form an aromatic ten π -electron system (Ficken and Kendall 1961).

Finally, polyene formation by nonsymmetric localization of the π -electrons can be studied in the dicyanomercyanine **10** whose light absorption is blue-shifted if one cyano group is omitted giving the vinylogous para-dimethylaminobenzonitrile **11**.



As Griffiths (1981) has stressed, the experimentally found result contradicts colour rule 2 which predicts red shift on cancelling the alternating branching by the cyano group in **10**. Therefore, one has to assume that the observed blue shift is caused by

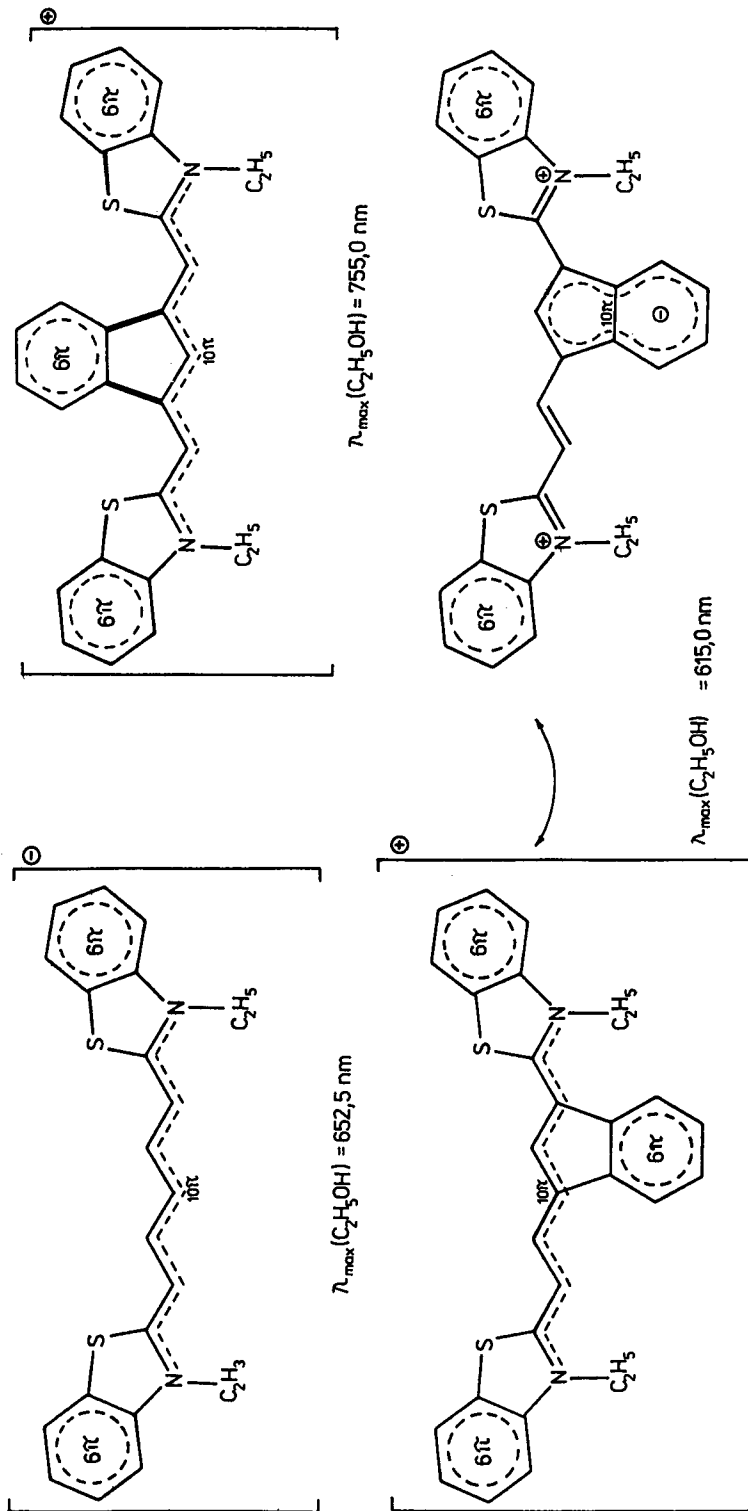


Figure 5. Spectral substituent effect in the benzthiadiazocyanine according to Ficken and Kendall (1961).

strengthening the polyene structure indicated in **11** in accordance with colour rule 5. This could be indeed confirmed by quantum chemical calculations and ir and nmr spectroscopical measurements by Daehne (1991).

3. Engineering of the relative positions of the frontier molecular orbitals (FMOs) of spectral sensitizers

Experimentally the relative position of the HOMO of a spectral sensitizer can be determined by its electrochemical anodic halfwave potential and that of the LUMO by its cathodic one. Both potentials correlate well with the quantum-chemically accessible FMO energies (Daehne 1965, 1979). Absolute values of the dye energy levels are in principle available by esca measurements. This method, however, has some shortcomings in respect to sensitizer molecules because of the dye's instability and degradation on evaporation in vacuum. Therefore, one would again have to undertake a lot of extensive synthesis, measurements, or at least quantum chemical calculations to find dyes with special FMO energies. This would be, however, against the pretension of molecular engineering.

As the triad theory and its colour rules do not provide any information about molecular state energies the perturbational molecular orbital theory (PMO theory) mainly developed by Dewar and Dougherty (1975) must be used to design dyes having certain MO energies.

Usually, Dewar's formalism starts with hydrocarbons as the basic structural units to be perturbed. This frequently fails, however, in colour chemistry because the FMO

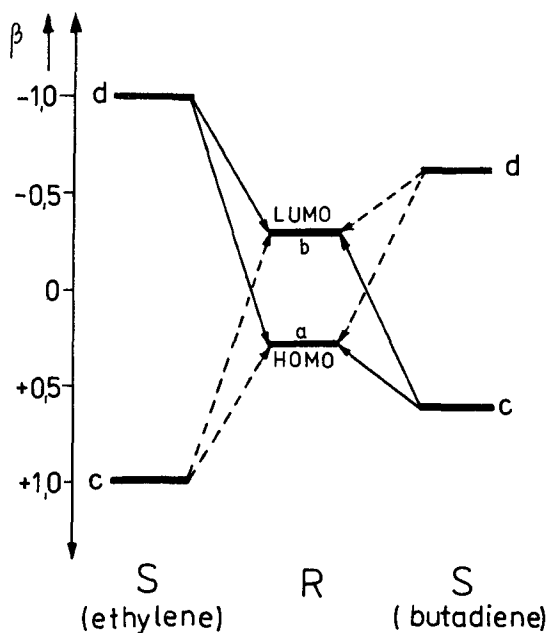


Figure 6. Correlation diagram between the FMOs of a polymethine R and a substituent S, like ethylene or butadiene (after Daehne and Hartmann 1986).

wavefunctions of the hydrocarbons and hydrocarbon ions, respectively, have many nodes at atomic positions with coefficients of the value zero which do not allow any prediction of energetical changes if these positions interact with substituents or other molecular building blocks.

Hartmann (1979) has found that such difficulties can usually be avoided by using the ideal polymethine units as the basic structures in molecular engineering of more complicated dyes. It was shown by Fabian and Hartmann (1975) that the molecular parameters of the ideal polymethines can be described within the HOMO formalism by simple analytical functions same as with the ideal polyenes and aromatics. The function of the coefficients $C_{i,r}$ of ideal polymethines at position r in the molecular orbital i reads:

$$C_{i,r} = (2/N)^{1/2} \cos[\pi(2r-1)(i-1)/2N], \quad \text{for } i = 2, 3, \dots, N \quad (1)$$

where N is the number of constituent atomic orbitals and $r = 1, 2, \dots$

The coefficients at nearly each atom have finite values and hence perturbation by certain linkage with other atoms will cause definite energetical changes of the MO energies according to PMO theory. These changes depend on the size and the sign of the coefficients of the interacting atoms and can be described by rather simple analytical functions (Hartmann 1979; Daehne and Hartmann 1986).

Figure 6 demonstrates as an example the possible effect if an ideal polymethine unit R with its HOMO a and LUMO b (having the smallest transition energy according to the first colour rule) is linked at the positions μ and ν with a certain building block S with its HOMO c and its LUMO d at the positions μ' and ν' . In this case the energetical changes δ_ϵ of the FMOs are given by (2), and (3) below:

$$\begin{aligned} \delta_{\epsilon_a} &= \frac{H_{ac}^2}{\epsilon_a - \epsilon_c} + \frac{H_{ad}^2}{\epsilon_a - \epsilon_d} \\ &= \frac{[(C_{a\mu} \cdot C_{c\mu'} + C_{a\nu} \cdot C_{c\nu'})\beta]^2}{\epsilon_a - \epsilon_c} + \frac{[(C_{a\mu} \cdot C_{d\mu'} + C_{a\nu} \cdot C_{d\nu'})\beta]^2}{\epsilon_a - \epsilon_d} \end{aligned} \quad (2)$$

$$\begin{aligned} \delta_{\epsilon_b} &= \frac{H_{bc}^2}{\epsilon_b - \epsilon_c} + \frac{H_{bd}^2}{\epsilon_b - \epsilon_d} \\ &= \frac{[(C_{b\mu} \cdot C_{c\mu'} + C_{b\nu} \cdot C_{c\nu'})\beta]^2}{\epsilon_b - \epsilon_c} + \frac{[(C_{b\mu} \cdot C_{d\mu'} + C_{b\nu} \cdot C_{d\nu'})\beta]^2}{\epsilon_b - \epsilon_d} \end{aligned} \quad (3)$$

If both linkages μ, μ' and ν, ν' have the same sign, the numerators of (2) and (3) will be large and therefore the perturbational effect will be strong. The opposite will be the case if the two linkages have different signs and thus cancel each other.

As can be seen the energy changes depend furthermore on the distance between the FMOs of the interacting molecular orbitals a with c or d , and b with c or d , respectively. The shorter this distance, the smaller is the denominator and hence the larger the energy change.

As an example in figure 7 the coefficients of an ideal nonamethine unit together with those of an ethylene and a butadiene fragment are depicted, where their size is marked by the radius of the circles and their sign by open or full circles. For example, on combination of two ethylene groups in the 1,2-position with the 1,4- and 8,11-position of the nonamethine yielding a γ, γ' -pyridocarbocyanine dye, the interactions of the HOMO a of R with the HOMO c of S are both positive and, hence

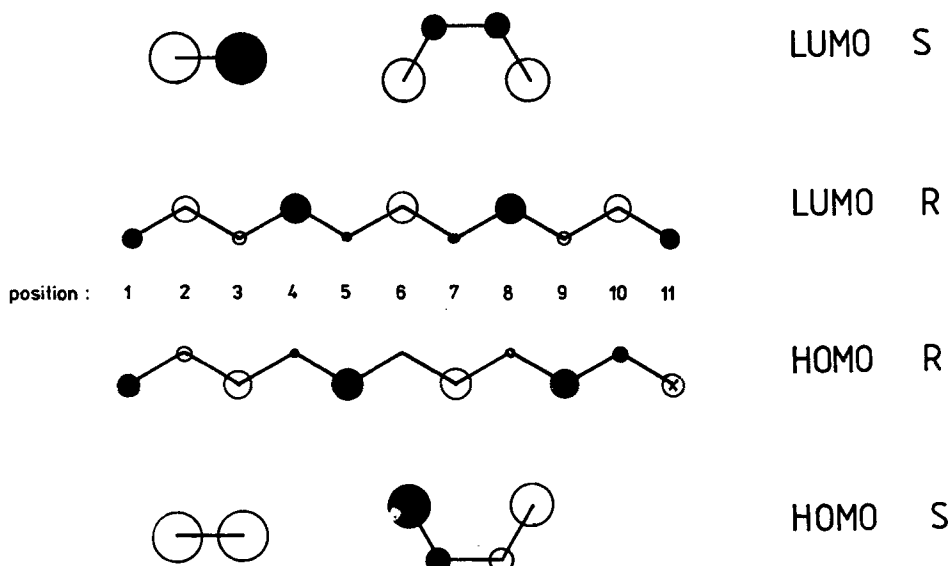


Figure 7. Representation of the FMO coefficients of a nonamethine chain R, ethylene, and butadiene (after Daehne and Hartmann 1986). See text for explanation.

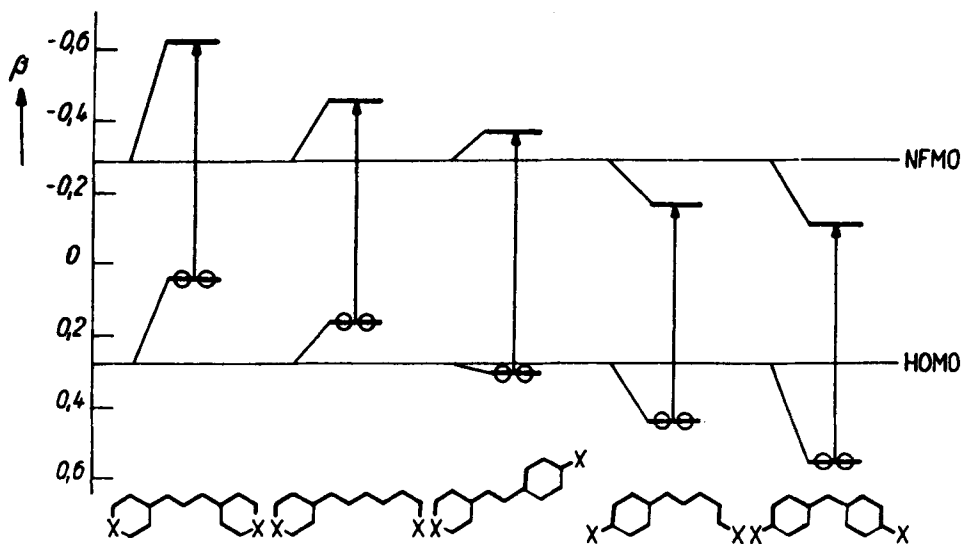


Figure 8. Perturbational changes of the FMO energies of a nonamethine linked with one or two ethylene groups at different positions.

summed up, whereas the interactions of the HOMO *a* of R with the LUMO *d* of S at the same position have different signs and therefore, they will, roughly speaking, cancel each other. The same is true with the LUMO *b* of R. The overall effect will be that both FMOs of R will be shifted upwards in direction to vacuum. On the other hand there is the opposite situation on combination of the ethylene fragment

with the nonamethine unit in its 2,5- and 7,10-positions giving a diphenylmethane dye known as Michlers Hydrole Blue. The FMOs are now shifted downwards. This is shown together with some other combinations in figure 8.

The well-known fact that pyridocarbocyanines are excellent spectral sensitizers of silver halide emulsions whereas diphenylmethane dyes are strong desensitizers confirm these theoretical conclusions (cf. figure 1). As the butadiene moiety shown in figure 7 has, in comparison to ethylene in its 1,4-position, inverse symmetry of its atomic orbitals, the opposite effect is to be expected if the nonamethine unit is linked at the same positions with a butadiene fragment.

In this way nearly any dye molecule can be designed with high or low lying FMOs by combination of polymethine units of different lengths with any conceivable building blocks. Some of them are shown in figure 9.

Their terminal positions have either the same or a different symmetry of their atomic orbitals enabling chemists to select any necessary combination with suitable polymethinic building blocks. Especially interesting may be the last example of figure 9 whose FMOs are both positioned above that of the nonamethine unit. Consequently, this will produce only a more or less strong downward shift of the FMOs of the nonamethine depending on the sign of the interacting atomic orbitals, as shown in figure 10.

As is to be expected, only the combinations at the 2,3- and 9,10-, or 4,5- and 7,8-positions of the nonamethine give an appreciable effect.

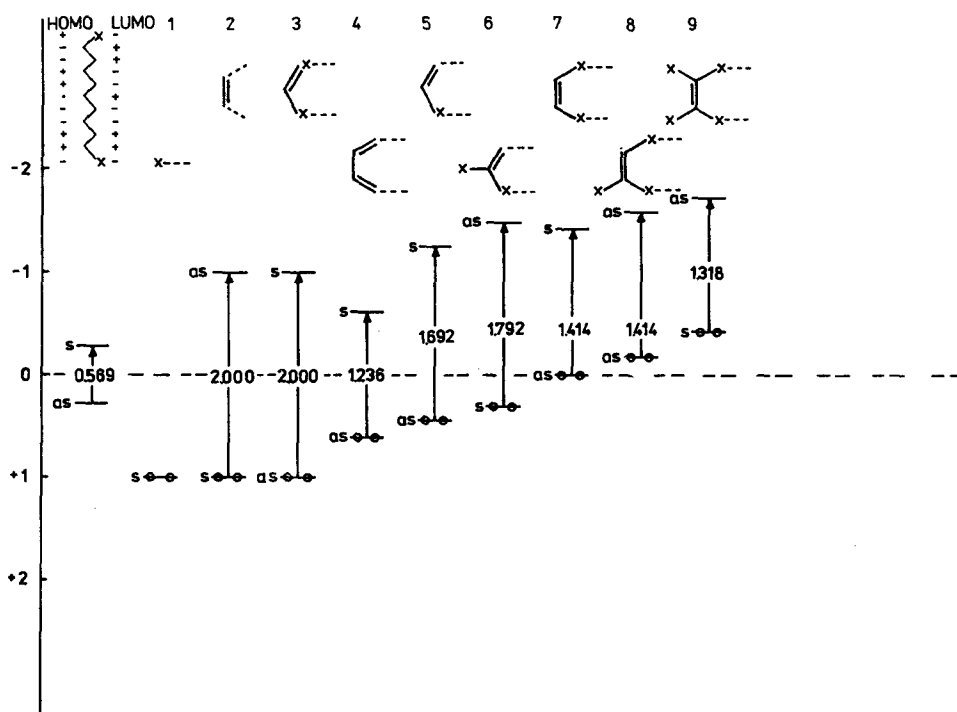


Figure 9. Several building blocks for molecular engineering (after Daehne and Hartmann 1986).

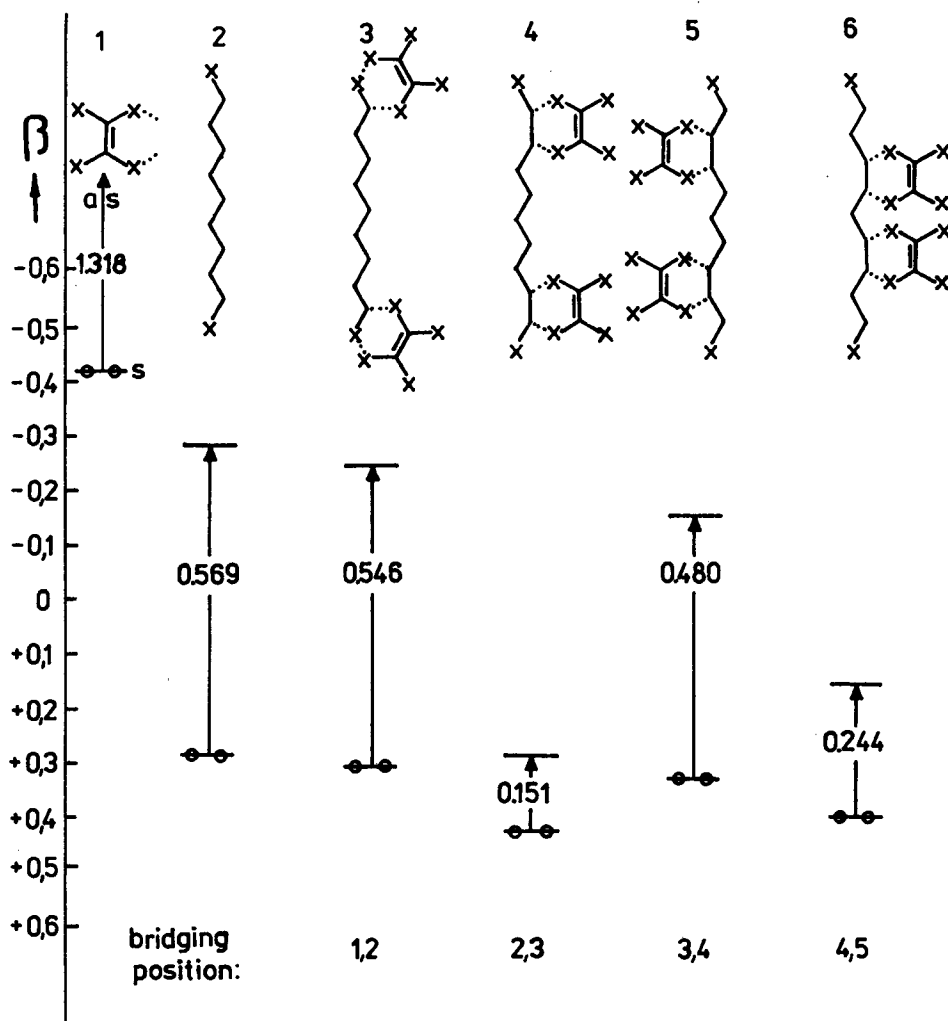


Figure 10. Perturbational changes of the FMO energies of a nonamethine by bridging its chain with two tetradonor substituted ethylene groups.

References

- Costa L F, Grum F and Gilman P B 1974 *Photogr. Sci. Eng.* **18** 261
 Daehne S 1965 *Z. Wiss. Photogr., Photophys., Photochem.* **59** 113
 Daehne S 1978 *Science (Washington)* **199** 1163
 Daehne S 1979 *Photogr. Sci. Eng.* **23** 219
 Daehne S 1991 (to be published)
 Daehne S and Hartmann H 1986 *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **31** 312
 Daehne S and Hoffmann K 1990 *Prog. Phys. Org. Chem.* **18** 1
 Daehne S and Moldenhauer F 1985 *Prog. Phys. Org. Chem.* **15** 1
 Dewar M J S and Dougherty R C 1975 *The PMO theory of organic chemistry* (New York: Plenum)

- Fabian J and Hartmann H 1975a *Theor. Chim. Acta.* **36** 351
Fabian J and Hartmann H 1975b *J. Mol. Struct.* **27** 67
Ficken G E and Kendall J D 1961 *Chimia* **15** 110
Grabowski Z R and Dobkowski J 1983 *Pure Appl. Chem.* **55** 245
Grahn W and Reichardt C 1976 *Tetrahedron* **32** 125
Griffiths J 1981 *Rev. Prog. Color. Relat. Top.* **11** 37
Hartmann H 1979 *J. Signalaufzeichnungs materialien* **7** 101, 181
Lippert E, Rettig W, Bonacic-Koutecky V, Heisel F and Mische J A 1987 *Adv. Chem. Phys.* **68** 1
Tolmachev A I 1987 *Progress and trends in applied optical spectroscopy (SOS-86)*, Teubner Texte zur Physik **13** 115