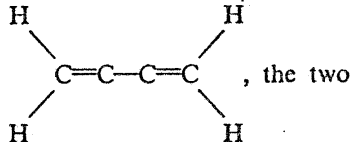


Finally, Chapter 5 on applications of dye lasers by HÄNSCH gives an idea of the broad range of today's applications and offers perspectives for future developments.

The authors have tried to make the chapters as self-contained as possible, so that they can be read independently, albeit at the cost of some slight overlap.

### 1.1. General Properties of Organic Compounds

Organic compounds are defined as hydrocarbons and their derivatives. They can be subdivided into saturated and unsaturated compounds. The latter are characterized by the fact that they contain at least one double or triple bond. These multiple bonds not only have a profound effect on chemical reactivity, they also influence spectroscopic properties. Organic compounds without double or triple bonds usually absorb at wavelengths below 160 nm, corresponding to a photon energy of 180 kcal/mole. This energy is higher than the dissociation energy of most chemical bonds, therefore photochemical decomposition is likely to occur, so such compounds are not very suitable as the active medium in lasers. In unsaturated compounds all bonds are formed by  $\sigma$  electrons; these are characterized by the rotational symmetry of their wave function with respect to the bond direction, i.e. the line connecting the two nuclei that are linked by the bond. Double (and triple) bonds also contain a  $\sigma$  bond, but in addition use  $\pi$  electrons for bonding. The  $\pi$  electrons are characterized by a wave function having a node at the nucleus and rotational symmetry along a line through the nucleus and normal to the plane subtended by the orbitals of the three  $\sigma$  electrons of the carbon or heteroatom (Fig. 1.1). A  $\pi$  bond is formed by the lateral overlap of the  $\pi$ -electron orbitals, which is maximal when the symmetry axes of the orbitals are parallel. Hence, in this position, bond energy is highest and the energy of the molecule minimal, thus giving a planar molecular skeleton of high rigidity. If two double bonds are separated by a single

bond, as in the molecule butadiene, , the two

double bonds are called *conjugated*. Compounds with conjugated double bonds also absorb light at wavelengths above 200 nm. All dyes in the proper sense of the word, meaning compounds having a high absorption in the visible part of the spectrum, possess several conjugated double

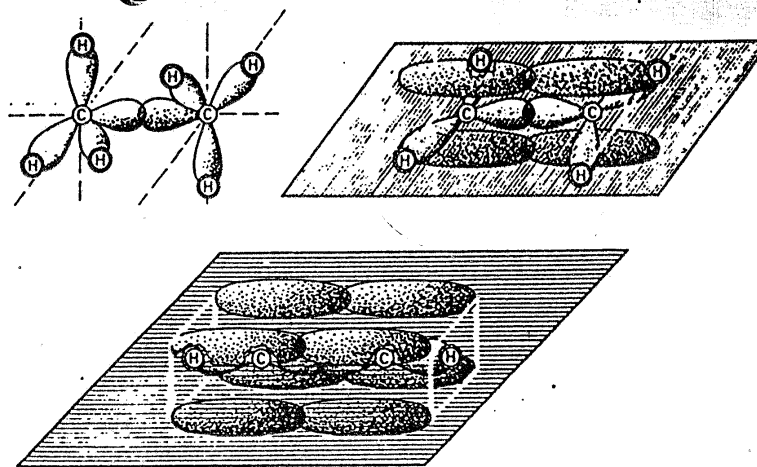


Fig. 1.1. Orbitals and bonds in ethane, ethylene, and acetylene

bonds. The basic mechanism responsible for light absorption by compounds containing conjugated double bonds is the same, in whatever part of the spectrum these compounds have their longest wavelength absorption band, whether near-infrared, visible, or near-ultraviolet. We thus use the term *dye* in the wider sense as *encompassing all substances containing conjugated double bonds*. Whenever the term *dye* is used in this book, it will have this meaning.

For the remainder of this chapter we restrict our discussion of the general properties of organic compounds to dyes, since for the foreseeable future these are the only organic compounds likely to be useful laser-active media.

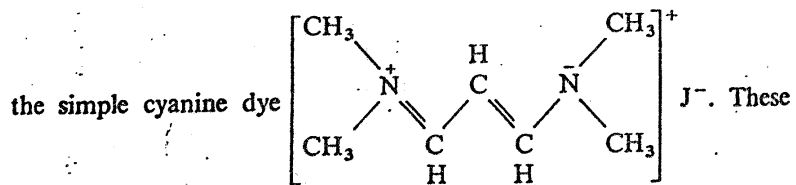
The thermal and photochemical stability of dyes is of utmost importance for laser applications. These properties, however, vary so widely with the almost infinite variety of chemical structure, that practically no generally valid rules can be formulated. Thermal stability is closely related to the long-wavelength limit of absorption. A dye absorbing in the near-infrared has a low-lying excited singlet state and, even slightly lower than that, a metastable triplet state. The triplet state has two unpaired electrons and thus, chemically speaking, biradical character. There is good reason to assume that most of the dye molecules that reach this highly reactive state by thermal excitation will react with solvent molecules, dissolved oxygen, impurities, or other dye molecules to yield decomposition products. The decomposition would be of pseudo-first order with a reaction constant  $k_1 = A \exp(-E_A/RT)$ , where  $A$  is the Arrhenius constant and has most often a value of  $10^{12} \text{ sec}^{-1}$  for reactions

of this type (ranging from  $10^{10}$  to  $10^{14}$  sec $^{-1}$ ),  $E_A$  is the activation energy,  $R$  is the gas constant and  $T$  the absolute temperature. The half-life of such a dye in solution then is  $t_{1/2} = \ln 2/k_1$ . Assuming as a minimum practical lifetime one day, the above relations yield an activation energy of 24 kcal/mole, corresponding to a wavelength of 1.2  $\mu\text{m}$ . If  $A = 10^{10}$  sec $^{-1}$ , this shifts the wavelength to 1.7  $\mu\text{m}$ , and with  $A = 10^{14}$  sec $^{-1}$  it would correspond to 1.1  $\mu\text{m}$ . If we assume that a year is the minimum useful half-life of the dye (and  $A = 10^{12}$  sec $^{-1}$ ), we get a wavelength of 1.0  $\mu\text{m}$ .

Obviously, it becomes more and more difficult to find stable dyes having the maximum of their long-wavelength band of absorption in the infrared beyond 1.0  $\mu\text{m}$ , and there is little hope of ever preparing a dye absorbing beyond 1.7  $\mu\text{m}$  that will be stable in solution at room temperature. Thus, dye-laser operation at room temperature in the infrared will be restricted to wavelengths not extending far beyond 1.0  $\mu\text{m}$ .

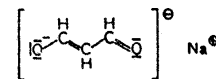
The short-wavelength limit of dye-laser operation, already mentioned implicitly, is given by the absorption of dyes containing only two conjugated double bonds and having their long-wavelength absorption band at wavelengths of about 220 nm. Since the fluorescence, and hence the laser emission, is always red-shifted, dye lasers can hardly be expected to operate at wavelengths below about 250 nm. Even if we were to try to use compounds possessing only one double bond, like ethylene, absorbing at 170 nm, we could at best hope to reach 200 nm in laser emission. At this wavelength, however, photochemical decomposition already competes effectively with radiative deactivation of the molecule, since the energy of the absorbed quantum is higher than the energy of any bond in the molecule.

Another important subdivision of dyes is into ionic and uncharged compounds. This feature mainly determines melting point, vapor pressure, and solubility in various solvents. An uncharged dye already mentioned is butadiene,  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ; other examples are most aromatics: anthracene, pyrene, perylene, etc. They usually have relatively low-lying melting points, relatively high vapor pressures, and good solubility in nonpolar solvents, like benzene, octane, cyclohexane, chloroform, etc. Cationic dyes include the large class of cyanine dyes, e.g.

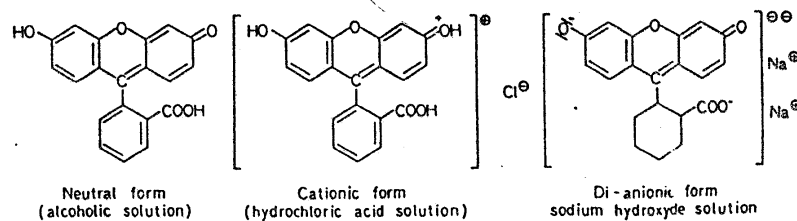


compounds are salts, consisting of cations and anions, so they have high melting points, very low vapor pressure, good solubility in more polar

solvents like alcohols, and only a slight solubility in less polar solvents. Similar statements can be made for anionic dyes, e.g. for the dye



Many dyes can exist as cationic, neutral and anionic molecules depending on the pH of the solution, e.g. fluorescein:



It should be stressed here that dyes are potentially useful as laser-active media in the solid, liquid and vapor phases. The last has not yet been used in a dye laser, but preliminary experiments in several laboratories look promising. Since most dyes form good single crystals, it might be attractive to use them directly in this form. There are two main obstacles to their use in crystal form: The extremely high values attained by the extinction coefficient in dyes, which prevents the pump-light from exciting more than the surface layer a few microns thick; and the concentration quenching of fluorescence that usually sets in whenever the dye molecules approach each other closer than about 10 nm. Doping a suitable host crystal with a small fraction (one thousandth or less) of dye circumvents these difficulties. On the other hand, solid solutions of many different types can be used. For instance, one can dissolve a dye in the liquid monomer of a plastics material and then polymerize it; or one can dissolve it in an inorganic glass (e.g. boric acid glass) or an organic glass (e.g. sucrose glass) or some semirigid material like gelatine or polyvinylalcohol. The utilization of some of these techniques for dye lasers will be discussed later, together with the use of dyes in the liquid and vapor phases.

## 1.2. Light Absorption by Organic Dyes

The light absorption of dyes can be understood on a semiquantitative basis if we take a highly simplified quantum-mechanical model, such as the free-electron gas model (KUHNS, 1958-59). This model is based on the fact that dye molecules are essentially planar, with all atoms of the

conjugated chain lying in a common plane, linked by  $\sigma$  bonds. By comparison, the  $\pi$  electrons have a node in the plane of the molecule and form a charge cloud above and below this plane along the conjugated chain. The centers of the upper and lower lobes of the  $\pi$ -electron cloud are about one half bond length distant from the molecular plane. Hence, the electrostatic potential for any single  $\pi$  electron moving in the field of the rest of the molecule may be considered constant, provided all bond lengths and atoms are the same (Fig. 1.2). Assume, that the conju-

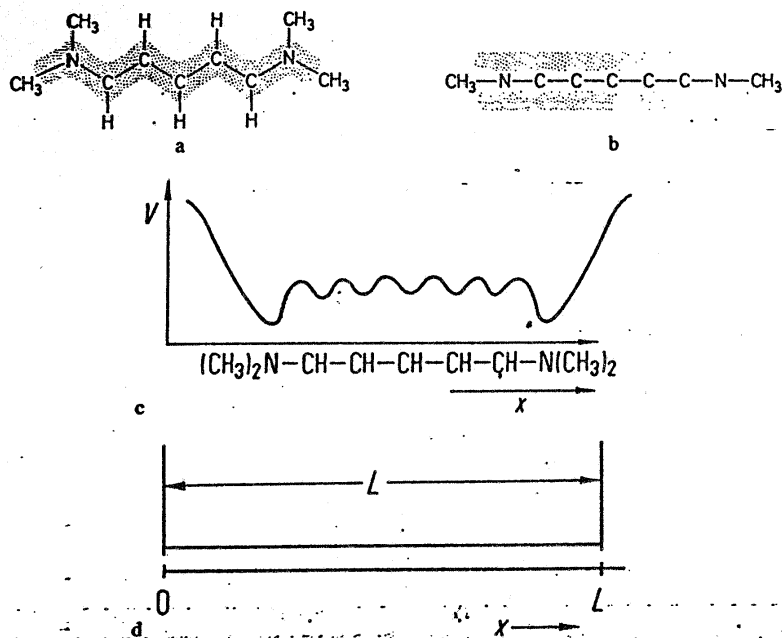


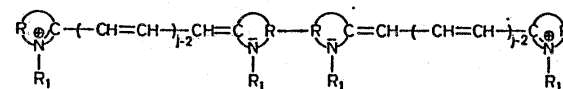
Fig. 1.2 a  $\pi$ -electron cloud of a simple cyanine dye seen from above the molecular plane; b the same as seen from the side; c potential energy  $V$  of a  $\pi$ -electron moving along the zig-zag chain of carbon atoms in the field of the rump molecule; d simplified potential energy trough;  $L$  = length of the  $\pi$ -electron cloud in a as measured along the zig-zag chain. (From FÖRSTERLING and KUHN, 1971)

gated chain which extends approximately one bond length to the left and right beyond the terminal atoms has length  $L$ . Then the energy  $E_n$  of the  $n$ th eigenstate of this electron is given by  $E_n = h^2 n^2 / 8mL^2$ , where  $h$  is PLANCK's constant,  $m$  is the mass of the electron, and  $n$  is the quantum number giving the number of antinodes of the eigenfunction along the

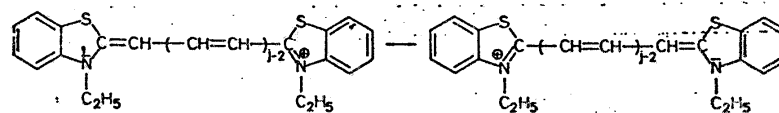
chain. According to the Pauli principle, each state can be occupied by two electrons. Thus, if we have  $N$  electrons, the lower  $1/2N$  states are filled with two electrons each, while all higher states are empty (provided  $N$  is an even number; this is usually the case in stable molecules since only highly reactive radicals possess an unpaired electron). The absorption of one photon of energy  $\Delta E = hc_0/\lambda$  (where  $\lambda$  is the wavelength of the absorbed radiation and  $c_0$  is the velocity of light) raises one electron from an occupied to an empty state. The longest wavelength absorption band then corresponds to a transition from the highest occupied to the lowest empty state with

$$\Delta E_{\min} = \frac{h^2}{8mL^2}(N+1) \quad \text{or} \quad \lambda_{\max} = \frac{8mc_0}{h} \frac{L^2}{N+1}$$

This indicates that to first approximation the position of the absorption band is determined only by the chain length and by the number of  $\pi$  electrons  $N$ . Good examples of this relation are the symmetrical cyanine dyes of the general formula



where  $j$  is the number of conjugated double bonds,  $R_1$  a simple alkyl group like  $C_2H_5$ , and  $R$  indicates that the terminal nitrogen atoms are part of a larger group, as e.g. in the following dye (homologous series of thiacyanines):



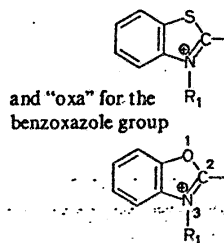
The double-headed arrow means that the two formulae are limiting structures of a resonance hybrid. The  $\pi$  electrons in the phenyl ring can be neglected in first approximation, or treated as a polarizable charge cloud, leading to an apparent enlargement of the chain  $L$ . In the case of the last-mentioned dye, good agreement is found between calculated and experimental absorption wavelength, when the chain length  $L$  is assumed to extend 1.3 bond lengths (instead of 1.0 bond length as above) beyond the terminal atoms. The bond length in cyanines is  $1.40 \text{ \AA}$ . The good agreement between the results of this simple calculation and the

experimental data for the above thiacyanine shown by the following comparison:

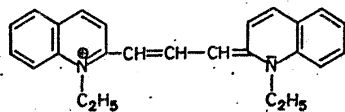
Wavelength (in nm) of absorption maximum for thiacyanines				
	Number of conjugated double bonds $j =$			
	2	3	4	5
Calculated	395	521	649	776
Experimental	422	556	652	760

Similarly good agreement can be found for all the other homologous series of symmetrical cyanines, once the value of the end length extending over the terminal N atoms is found by comparison with the experimentally observed absorption wavelength for one member of the series. Absorption wavelengths have been reported recently for a large number of cyanines (MIYAZOE and MAEDA, 1970).

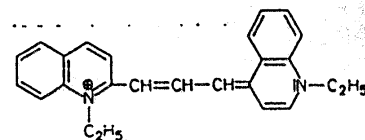
The following nomenclature is customarily used for cyanine dyes. If  $j = 2$ , then the dye is a cyanine in the narrower sense or monomethine dye, since it contains one methine group,  $-\text{CH}-$ , in its chain; if  $j = 3$ , the dye is a carbocyanine or trimethine dye; if  $j = 4, \dots, 7$ , the dye is a di-, tri-, tetra-, or pentacarbocyanine or penta-, hepta-, nona- or undecamethine dye. The heterocyclic terminal groups are indicated in an abridged notation; thus "thia" stands for the benzthiazole group:



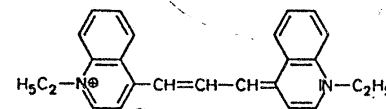
In these groups the atoms are numbered clockwise, starting from the sulfur or oxygen atom. Thus, the name of the last-mentioned thiacyanine dye is 3,3'-diethyl-thiadicarbocyanine for  $j = 4$ . If the terminal group is quinoline, the syllable "quinolyl" indicative of this end group is frequently omitted from the name. In this case, however, the position of linkage of the polymethine chain to the quinoline ring must be given, e.g.



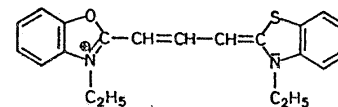
is 1,1'-diethyl-2,2'-carbocyanine (trivial name: pinacyanol), while



is 1,1'-diethyl-2,4'-carbocyanine (trivial name: dicyanine), and



is 1,1'-diethyl-4,4'-carbocyanine (trivial name: cryptocyanine). Where there are two different end groups, these are named in alphabetical order, e.g. 3,3'-diethyl-oxa-thiadicarbocyanine is



It is easy to eliminate the above assumption of identical atoms in the conjugated chain. If, for instance, one CH group is replaced by an N atom, the higher electronegativity of the nitrogen atom adds a small potential well to the constant potential; a simple perturbation treatment shows that every energy level is shifted by  $\epsilon = -B\Psi^2$ , where  $B$  is a constant characteristic of the electronegativity of the heteroatom (in the case of  $=\text{N}-$ ,  $B = 3.9 \times 10^{-20}$  erg·cm) and  $\Psi$  is the value of the normalized wave function at the heteroatom. This means that the shift of an energy level is zero if the wave function has a node at the heteroatom, and maximal if it has an antinode there. The change in absorption wavelength with heterosubstitution calculated in this way is in good agreement with the experimentally observed values. The second of the above assumptions, that of equal bond lengths along the chain, can be eliminated in a similar way. An illustrative example is offered by the polyenes of the general formula  $\text{R}-(\text{CH}=\text{CH})_j-\text{R}$ . These compounds have an even number of atoms. The total charge distribution results in localized double and single bonds (Fig. 1.3) and hence in alternating short and long bond lengths (1.35 Å and 1.47 Å, respectively). A  $\pi$  electron moving along the chain will therefore experience greater attraction to the neighboring atoms in the middle of a double bond than in the middle of a single bond. This fact may be represented by a periodic perturbing potential with minima at the center of the double bonds and maxima at the center of the

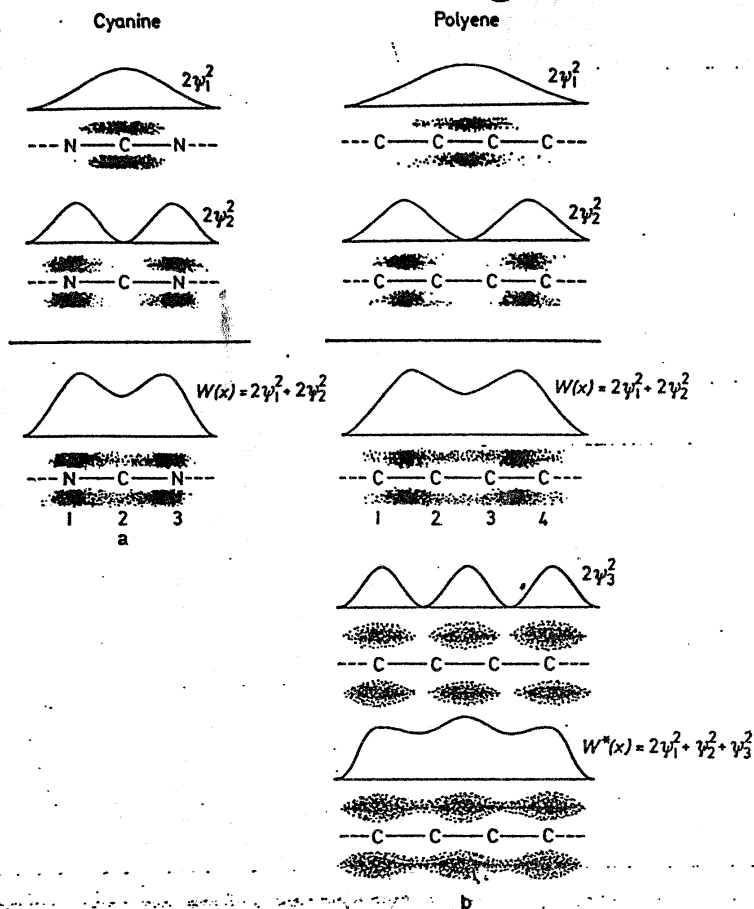


Fig. 1.3. Electron densities (proportional to the square of the wave function,  $\psi^2$ ) along the conjugated chain of a) a cyanine, b) a polyene (butadiene). The symbols  $\psi_1$  and  $\psi_2$  denote the wave functions of the first and second filled  $\pi$ -electron molecular orbital, and  $\psi_3$  that of the lowest orbital normally empty, which is occupied by one electron when excited.  $W(x)$  is the total  $\pi$ -electron density for a molecule in the ground state, and  $W^*(x)$  is the same for butadiene in the first excited state

single bonds (Fig. 1.4). Assuming a sinusoidal potential with an amplitude of 2.4 eV gives good agreement between the calculated and experimental values of the absorption wavelengths. The relation between chain length and absorption wavelength is found to be very different in the cyanines and the polyenes. In symmetrical cyanines the absorption wavelength is

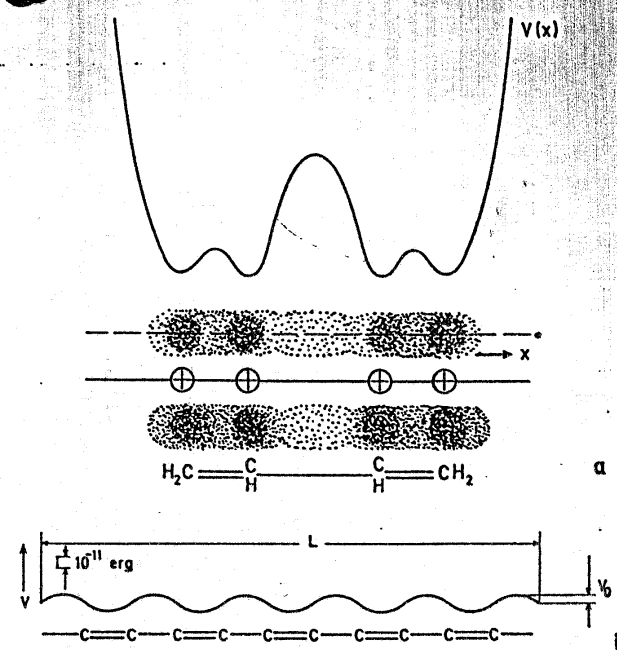
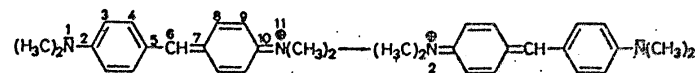


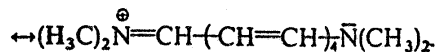
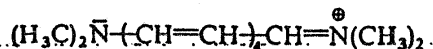
Fig. 1.4. a Potential energy  $V(x)$  of a  $\pi$ -electron moving along the carbon atom chain in the field of the rump molecule of butadiene; b simplified potential energy trough of a long polyene molecule with perturbing sinusoidal potential of amplitude  $V_0 = 2.4$  eV. The energy difference between highest filled and lowest empty orbital is given by  $\Delta E = (\hbar^2/8mL^2)(2j+1) + 0.83(1-1/2j)V_0$ , where  $j$  is the number of conjugated double bonds. (From KUHN, 1959)

shifted by a constant amount of roughly 100 nm on going from one member of a series to the next higher which has one more double bond. In polyenes this shift decreases with increasing number of double bonds. A similar treatment can be applied to unsymmetrical cyanines in which the difference in electronegativity of the different end groups gives a similar polyene-type perturbation. The perturbation is less pronounced when the difference in electronegativity of the end groups is less.

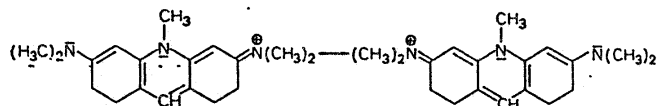
Many dyes containing a branched chain of conjugated double bonds can, in a first approximation, be classified either as symmetrical cyanine-like or polyene-like substances, or as intermediate cases. For example, Michler's hydrol blue



absorbs at practically the same wavelength as the symmetrical cyanine

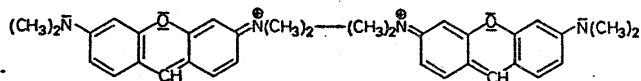


Hence it seems justified to treat it like a cyanine by neglecting the weakly printed bonds in the formula of MICHLER's hydrol blue. If, however, additional branching is introduced by connecting positions 4 and 8 through a  $\left(\begin{array}{c} \text{=N-} \\ | \\ \text{CH}_3 \end{array}\right)$  bridge, this gives acridine orange



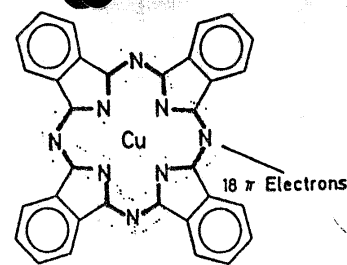
The absorption wavelength is shifted from 603 nm to 491 nm. It indicates that in this case branching cannot be neglected even in a first approximation.

With an O atom as bridging group instead of the N—CH<sub>3</sub> group, the xanthylium dye pyronine G with an absorption wavelength of 550 nm is obtained:



For a detailed treatment of molecules containing such a branched free-electron gas, the reader is referred to the literature (KUHN, 1958/59).

Another important class of dyes in which the branching of the conjugated chain can be neglected to first approximation, are the phthalocyanines and similar large-ring molecules. In first approximation the benzene rings are separated resonance systems, leaving the 16-membered ring indicated in Fig. 1.5 by heavy lines. Now there are 18  $\pi$  electrons on a ring of circumference  $L=16l$ . In the lowest state ( $n=0$ ) the eigenfunction has no nodes, for  $n \neq 0$  there are two degenerate eigenfunctions for every  $n$ , corresponding to the sine and cosine in the constant-potential approximation. A large perturbation is, however, introduced by the nitrogen atoms, which remove the degeneracy. This effect is most pronounced for  $n=4$ , since one eigenfunction then has its nodes at the N atoms, the other its antinodes. The lowest unfilled levels are again degenerate because of equal perturbation energy. The absorp-



a Cu-Phthalocyanin

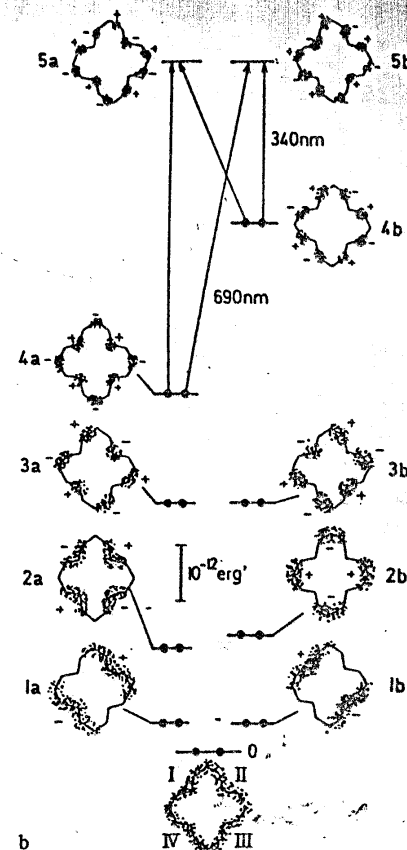


Fig. 1.5. Formula, eigenstates, and eigenfunctions of Cu-phthalocyanine. (From KUHN, 1959)

tion wavelengths for the two transitions from  $n=4$  to  $n=5$  are then readily calculated (with the above value for  $B$ ):  $\lambda_1 = 690$  nm and  $\lambda_2 = 340$  nm (Fig. 1.5). The experimental values are 674 nm and 345 nm.

The free-electron model, even in its simplest form, gives very satisfactory agreement between calculated and experimental values of the absorption wavelength for large dye molecules. Nevertheless, its one-electron functions are not sufficient for a quantitative description of light absorption by small molecules of high symmetry, like benzene, naphthalene and similar molecules, since here the repulsion between the  $\pi$  electrons plays an important role. For the inclusion of electron correlations into the free electron model, the reader is referred to FÖRSTERLING et al. (1966).

The oscillator strength of the absorption bands can also be calculated easily by the free-electron model. Transition moments  $X$  and  $Y$  along and normal to the long molecular axis are connected with the oscillator strength  $f$  of the absorption band by:

$$f = 2 \cdot \frac{8m_0\pi^2}{3h^2} \cdot \Delta E(X^2 + Y^2),$$

and can be calculated using the electron gas wave functions  $\psi_a$  and  $\psi_b$  of the eigenstates between which the transition occurs:

$$X = \int_{\text{molecule}} \psi_a x \psi_b dx, \quad Y = \int_{\text{molecule}} \psi_a y \psi_b dy.$$

The relative strengths of the  $x$  and  $y$  component also yield the orientation of the transition moment in the molecule. One finds good agreement on comparing the  $f$  values obtained from the absorption spectrum of the dye using the relation

$$f = 4.32 \cdot 10^{-9} \int_{\text{absorption band}} \epsilon(\tilde{\nu}) d\tilde{\nu},$$

where  $\epsilon$  is the numerical value of the molar decadic extinction coefficient measured in liter/(cm · mole), and  $\tilde{\nu}$  is the numerical value of the wave number measured in  $\text{cm}^{-1}$ .

A peculiarity of the spectra of organic dyes as opposed to atomic and ionic spectra is the width of the absorption bands, which usually covers several tens of nanometers. This is immediately comprehensible when one recalls that a typical dye molecule may possess fifty or more atoms, giving rise to about 150 normal vibrations of the molecular skeleton. These vibrations, together with their overtones, densely cover the spectrum between a few wave numbers and  $3000 \text{ cm}^{-1}$ . Many of these vibrations are closely coupled to the electronic transitions by the change in electron densities over the bonds constituting the conjugated chain. After the electronic excitation has occurred, there is a change in bond length due to the change in electron density. If, e.g. in Fig. 1.3, the bond length connecting atoms 1 and 2 is  $r$  (typically  $1.35 \text{ \AA}$ ) and this bond is lengthened in the excited molecule, the new equilibrium distance being  $r^*$ , atoms 1 and 2 will start to oscillate, classically speaking, around this new position with an amplitude  $r^* - r$  (typically  $0.02 \text{ \AA}$ ) after the electronic transition has occurred. A molecular skeletal vibration is excited in this way. The new equilibrium total  $\pi$  electron density  $W^*(x)$  for the excited state is given in Fig. 1.3c. demonstrating the large increase in  $\pi$  electron density over the bond connecting atoms 2 and 3. Quantum-mechanically this means that transitions have occurred from the electronic and

vibrational ground state  $S_0$  of the molecule to an electronically and vibrationally excited state  $S_1$ , as depicted in Fig. 1.6. This results in spectra like Fig. 1.6b or c, depending on how many of the vibrational sublevels, spaced at  $h\nu_0 \cdot (v + 1/2)$ , with  $v = 0, 1, 2, 3, \dots$ , are reached and what the transition moments to these sublevels are.

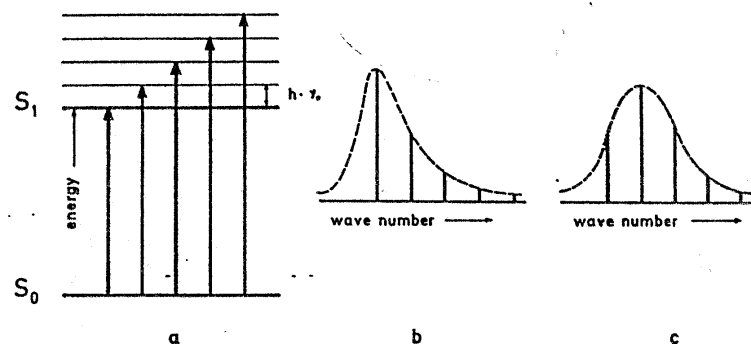


Fig. 1.6. a Electronic and vibronic energy levels of a dye molecule;  $S_0$ : ground state,  $S_1$ : excited state, and absorptive transitions from  $S_0$  to  $S_1$ ; b and c two possible forms of concomitant spectra

In the general case of a large dye molecule, many normal vibrations of differing frequencies are coupled to the electronic transition. Furthermore, collisional and electrostatic perturbations, caused by the surrounding solvent molecules broaden the individual lines of such vibrational series as that given in Fig. 1.6. As a further complication, every vibronic sublevel of every electronic state, including the ground state, has superimposed on it a ladder of rotationally excited sublevels. These are extremely broadened because of the frequent collisions with solvent molecules which hinder the rotational movement so that there is a quasicontinuum of states superimposed on every electronic level. The population of these levels in contact with thermalized solvent molecules is determined by a Boltzmann distribution. After an electronic transition, which, as described above, leads to a nonequilibrium state (Franck-Condon state) the approach to thermal equilibrium is very fast in liquid solutions at room temperature. The reason is that a large molecule experiences at least  $10^{12}$  collisions/sec with solvent molecules, so that equilibrium is reached in a time of the order of one picosecond. Thus the absorption is practically continuous all over the absorption band. The same is true for the fluorescence emission corresponding to the transition from the electronically excited state of the molecule to the ground state.

This results in a mirror image of the absorption band displaced towards lower wave numbers by reflection at the wave number of the purely electronic transition. This condition exists, since the emissive transitions start from the vibrational ground state of the first excited electronic state  $S_1$  and end in vibrationally excited sublevels of the electronic ground state. The resulting typical form of the absorption and fluorescence spectrum of an organic dye is given in Fig. 1.7.

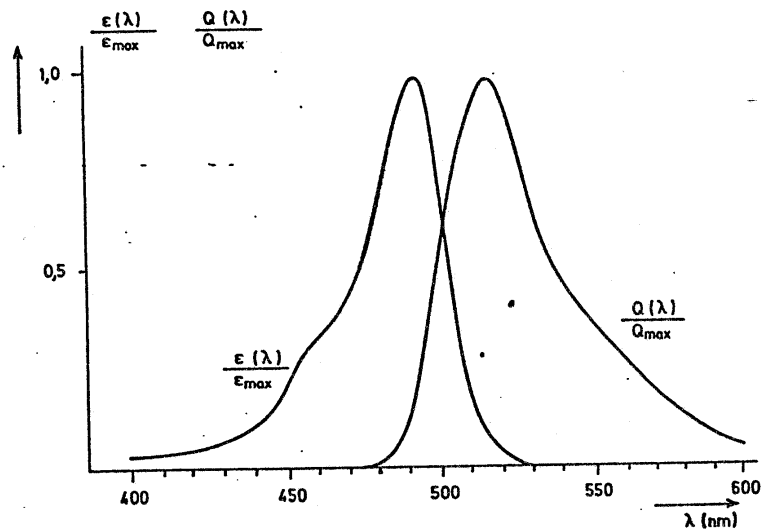


Fig. 1.7. Absorption spectrum,  $\epsilon(\lambda)/\epsilon_{\max}$ , and fluorescence spectrum,  $Q(\lambda)/Q_{\max}$ , of a typical dye molecule (fluorescein-Na in water).

Further complications of dye spectra arise from temperature and concentration dependence and acid-base equilibria with the solvent. If the temperature of a dye solution is increased, higher vibrational levels of the ground state are populated according to a Boltzmann-distribution, and more and more transitions occur from these to higher sublevels of the first excited singlet state. Consequently, the absorption spectrum becomes broader and the superposition of so many levels blurs most of the vibrational fine structure of the band, while cooling of the solution usually reduces the spectral width and enhances any vibrational features that may be present. Thus, spectra of solid solutions of dyes in EPA, a mixture of 5 parts ethyl ether, 5 parts isopentane, and 5 parts ethanol that forms a clear organic glass when cooled down to 77°K, are often used for comparison with calculated spectra because of their well-

resolved vibrational structure. Further cooling below the glass point, when the free movement of solvent molecules or parts thereof is inhibited, usually brings about no further sharpening of the spectral features (Fig. 1.8). The many possible different configurations of the solvated molecule in the cage of solvent molecules cannot be attained when the temperature is lowered because the activation energy required to reach the new equilibrium positions is too high. A very special case is the

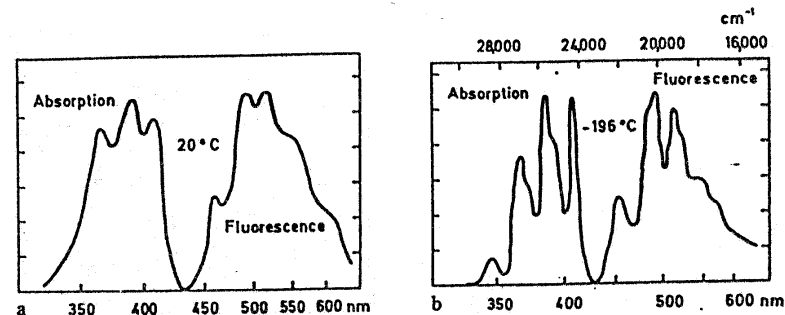


Fig. 1.8. Absorption and fluorescence spectra of diphenyloctatetraene in xylene. a at 20° C, b at -196° C. (From HAUSSER et al., 1935)

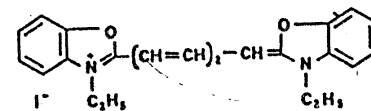
Shpol'ski effect (SHPOLSKI, 1962): This refers to the appearance of very sharp, line-like spectra (often termed quasi-line spectra in the Russian literature) of about one  $\text{cm}^{-1}$  width instead of the usual diffuse band spectra of dye molecules (most often aromatics) in a matrix of  $\eta$ -paraffins at low temperature (usually below 20°K). Evidently this is because there are only few different possibilities of solvation of the molecule in that matrix, and each of the different sites causes a series of spectral lines in absorption as well as in emission. Analyzing these series gives the energy difference of the different sites, usually a few hundred  $\text{cm}^{-1}$  (Fig. 1.9). The Shpol'ski effect has also been called the optical analog of the Mössbauer effect (REBANE and KHIZHNYAKOV, 1963), since here also the recoil of the interacting photons seems to be taken up by the matrix as a whole.

The concentration dependence of dye spectra is most pronounced in solutions where the solvent consists of small, highly polar molecules, notably water. Dispersion forces between the large dye molecules tend to bring the dye molecules together in a position with the planes of the molecules parallel, where the interaction energy usually is highest. This is counteracted by the repulsive Coulomb forces if the dye molecules are charged. In solvents of high dielectric constants this repulsion is lowered and the monomer-dimer equilibrium is far to the side of the dimer. The



D O D C I

**3,3'-Diethyloxadicarbocyanine Iodide**  
NK 1533



$C_{23}H_{23}N_2O_2I$   
MW: 486.35

Lambdachrome number: 6550.  
Appearance: Blue solid  
Absorption  $\lambda_{max}$  (in ethanol): 582 nm  
Molar absorptivity:  $22.3 \times 10^4$  L mole<sup>-1</sup> cm<sup>-1</sup>

For research and development purpose only.

**Application:**  
Laser dye for pulsed operation; tunable around 660 nm.  
Most frequently used saturable absorber for flashlamp and cw pumped Rhodamine 6G and Rhodamine B dye lasers; applicable around 580 nm<sup>2-4,5</sup>

Pump Source	Wavelength (nm)	Dye Laser Characteristics				Solvent	Ref.
		Peak (nm)	Range (nm)	Effic. (%)	Conc. (g/l)		
Nd:YAG, 2nd	532	-	-	-	0.49	Ethanol	1
Flashlamp	-	662	-	-	0.10	DMSO	2

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