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Near-Infrared Absorbing Dyes

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I. Introduction

Due to the recent development of specialized "innovative" or "functional" dyes there has been renewed interest in the area of organic dyes.[1] One area of interest is that of optical recording technology where gallium aluminum arsenide (GaAlAs) and indium phosphide (InP) diode lasers are widely used as a light source. Since dyes absorbing in the near-infrared (near-IR) region (i.e. beyond about 700 nm (= 0.7 μm) in wavelengths and less than about 14 000 cm^{-1} (= 1.4 μm^{-1}) in wavenumbers) are required and the oscillator wavelengths fall in the near-infrared region, they are suitable applicants.

Literature data on near-IR dyes is extremely limited. Recent books on color chemistry[2] contain only sparse information and only a few references have appeared.[3] Some dyes have, however, been discussed in other contexts such as quantum electronics and optoelectronics.[4]

The first near-infrared (near-IR) absorbing organic compounds were synthesized at the beginning of this century. Comparison of the visual color of oxidation products of phenylenediamines and benzidines led J. Piccard to the conclusion that light absorption of them should occur in the near-IR region.[5] This prediction was confirmed decades later when spectral curves were recorded.[6] Various near-IR polymethine dyes became accessible at the beginning of the 1930s and proved very useful in photographic sensitization up to 1300 nm.[7] Some natural porphyrines[8] as well as various related synthetic cyclic chromophores[9] proved to be near-IR absorbing dyes. Compounds absorbing at long wavelengths in the visible and near-infrared region are now generally called "deeply colored" dyes.

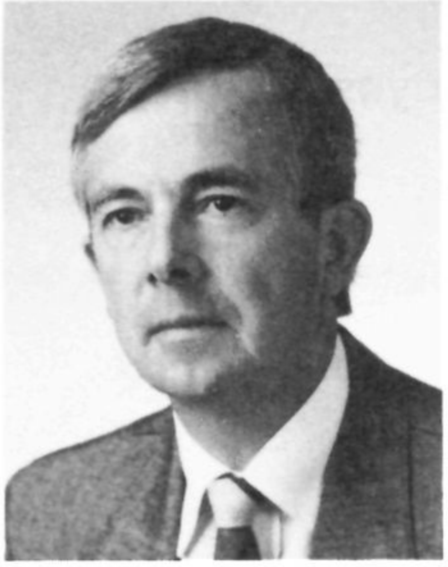
This review includes near-IR chromophores which absorb light due to their π-electronic systems. Both closed- and open-shell structures are discussed. The multitude of spectral data necessarily requires some arbitrary selection. Attempts have been made to select representative examples. In this review attention has also been directed toward the most recent fields of application. Chromophoric systems that are not of practical use because of their low stability or low absorption coefficients are mentioned only in passing.

II. Application of Near-IR Dyes

A. Optical Recording

Near-IR dyes are important in the optical data storage field, particularly, in the DRAW (Direct Reading After Writing) or WORM (Write Once Read Many) disk which is used for recording. The first system using the DRAW disk was developed by Philips in 1978. The DRAW disk in the heat-mode system using organic near-IR dyes is currently available.

The DRAW disk, as shown in Figure 1, consists of a plastic substrate such as transparent polycarbonate or poly(methylmethacrylate) and a recording layer containing near-IR dyes formed through vacuum evaporation or the spin coating technique. The recording (writing) process on a DRAW disk is achieved as follows. A micropit (diameter 1 μm) in the recording layer is formed by thermal energy transformed from the photoenergy of a laser beam of 20–30 W. The diameter of the micropit depends on the spot formed by the laser beam. In the reproducing (reading) process the presence of pits is detected through differences in reflectivity using a laser beam of weak power (approximately one-tenth of that for writing). The signal is picked up by a photodiode for subsequent reproduction. The



Jürgen Fabian was born in Saxony, Germany, in 1936. He studied at the Technical University of Dresden and received his doctoral degree on the synthesis and spectroscopy of sulfur organic compounds in 1965 under the direction of R. Mayer. Stimulated and supported by R. Zahradník and co-workers (Heyrovsky Institute of the Czechoslovak Academy of Sciences in Prague) he worked on applied quantum chemistry in the following years and completed his Habilitation in 1973. His research interests include color chemistry (monograph with H. Hartmann: *Light Absorption of Organic Colorants*; Springer 1980). He is the author or co-author of more than 160 scientific publications. After the recent political changes in East Germany he received the "August-Kekulé-Medaille" from the Chemical Society of the GDR and became Associate Professor at the Technical University of Dresden in 1990.

Hiroyuki Nakazumi was born in Osaka, Japan, in 1950. He received his B.S. from Osaka Prefecture University in 1973 and his Ph.D. degree in 1980 (T. Kitao). His postdoctoral studies were under the direction of H. Zollinger, E.T.H. Zurich, Switzerland, in 1980. He is presently an Assistant Professor at the Osaka Prefecture University and has published more than 60 scientific publications in the fields of dye chemistry and heteroaromatic chemistry of sulfur-containing compounds. His current research interests include the synthesis and characterization of functional dyes and of dyes designed with the aid of quantum chemistry.

Masaru Matsuoka was born in Nara, Japan, in 1942. He received both his B.S. (1966) and Doctorate (1973) degrees in color chemistry from Osaka Prefecture University under the direction of K. Konishi. His thesis was entitled with "The effect of annelation on the characteristics of colorants". In 1967, he joined the Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, as an instructor and has been an Associate Professor since 1979. He was a postdoctoral fellow with H. Zollinger, E.T.H. Zurich, Switzerland from 1973 to 1974. During that time, he worked on color chemistry, in particular, molecular design and the synthesis and applications of special dyes. He is now interested in the chemistry of functional dyes for electrooptical applications. He is the author or coauthor of more than 130 scientific publications. He has recently published two books concerning near-IR dyes: *Infrared Absorbing Dyes* (Plenum 1990) and *Absorption Spectra of Dyes for Diode Lasers* (Bunshin 1990).

wavelength at 780 nm of the commercially available GaAlAs diode laser is used for the writing process and that of 830–840 nm for the reproducing process.

For use in such a DRAW disk, organic colorants need to have an absorption band in the near-infrared region since a GaAlAs diode laser is used as the laser source. The near-IR dyes must also reflect the laser beam in the reproducing process. The reflectivity qualitatively increases with increasing absorbance. Thus, the recording and reproducing sensitivity depends on ϵ, and dyes having a large ϵ give an acceptable signal-to-noise ratio. Another necessary property of organic near-IR dyes is reasonable solubility in the appropriate organic solvents. This is because the recording layer is mainly formed by the spin-coating technique. Since a recorded disk has to have a working lifetime of 10 years or more, photofading of the near-IR dye by the laser beam in the reproducing process and by sunlight has to be minimized.

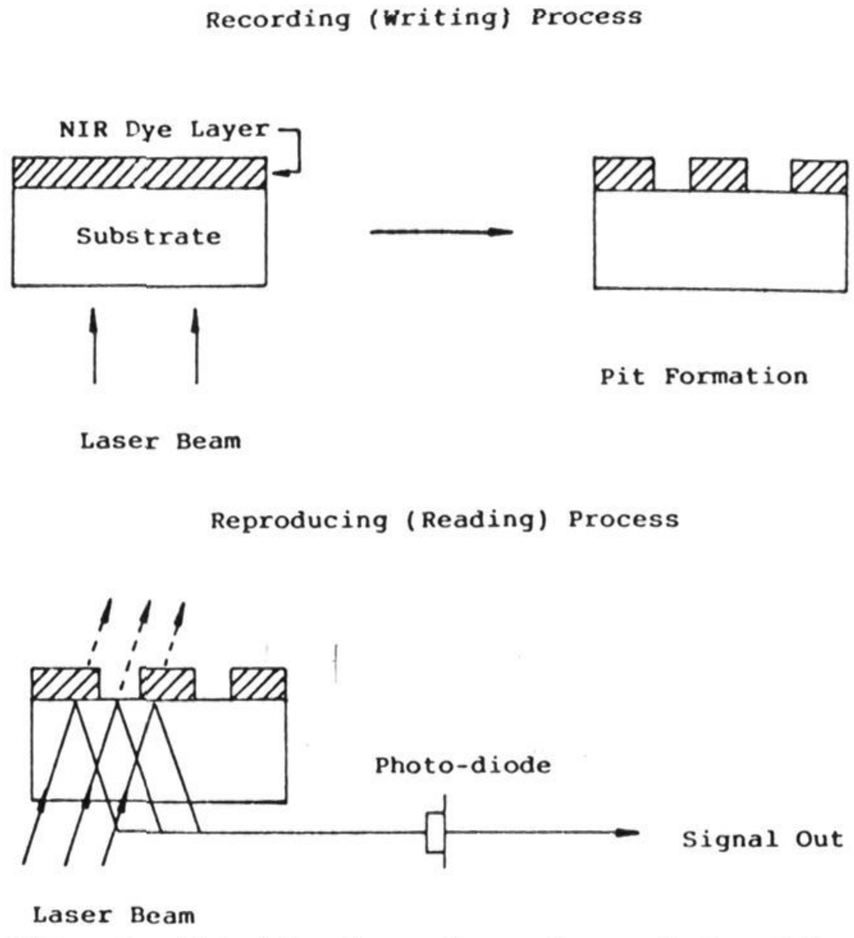
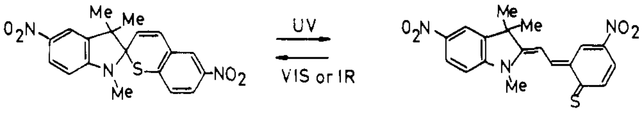


Figure 1. Principle of recording and reproducing of the DRAW disk.

Currently, indolinocyanine dyes, triphenylmethane dyes, naphthalocyanine dyes, and indonaphthol metal complex dyes are commercially available for use as organic colorants in DRAW disks. Several review papers as well as a book on the applications of organic dyes in optical recording systems have been published.[1a,b,4b,d,e,10]

SCHEME I



1 2

Cyanine dyes can only be used if the lightfastness is improved by additives (cf. section IV.B). Phthalocyanine and naphthalocyanine dyes have poor solubility in organic solvents. Their solubility is improved by the introduction of bis(trialkylsiloxy)silyl groups[11] at the central metal atom and of branched- or long-alkyl chains[12] into the naphthalene rings. A thin (100 nm) layer of a sublimable 1,4-naphthoquinone near-IR dyes is applied to the optical disk by vacuum evaporation.[13]

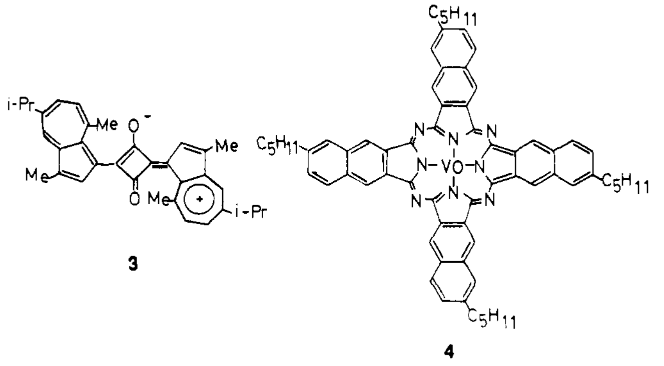
Dyes exhibiting the phenomenon of photochromism may prove important for use in erasable disks. If photochromic dyes are applied to the erasable disk for the diode laser, the colored form should absorb in the near-IR region. Spiropyran derivatives[14] as shown in Scheme I can be applied to the erasable disk system. The colorless spiropyran 1 on a suitable substrate undergoes color generation to 2 (λ_{max} = 750 nm) on irradiation with UV light. Irradiation of 2 with a diode laser or with visible light gives 1. Loss of 50% of the absorbance for colored 2 after 9–10 photochromic cycles however prevents any practical application.[1a,b,15] Fulgide derivatives[15] as well as spiropyran dyes show photochromism through irradiation with both UV and visible light as well as and good recycling characteristics. Their colored forms, however, absorb in the visible region (500–600 nm).

B. Thermal Writing Displays

Thermal addressed displays, where the heat input is provided by a laser beam or heat pulse current, have been known for several years.[16] It is generally accepted that the thermal writing liquid crystal display is most promising because of its intrinsic memory ability. When a laser beam is used to write information onto a liquid crystal panel, the optical energy of the laser beam should be effectively converted into thermal energy. In order to increase writing speed and to decrease laser power, a special absorbing layer made of infrared absorbing dyes is introduced. By using thermo-electro-optical effects of smectic liquid crystal (LC) materials, two types of display systems have been developed, namely, a projection display and a flat panel display.[16]

Urabe et al. discussed the application of near-IR dyes in thermal writing displays.[17] The most common type of infrared dyes are the cyanine dyes, which are known as laser dyes for infrared lasing. Generally they have high absorption coefficients and high dichroic ratios, which in this case are highly desirable characteristics. Some of them can be dissolved in LC materials. However, their lack of durability is a serious problem. Furthermore, the alignment of the LC material is destroyed by decomposed cyanine dyes. Some metal chelate compounds have absorptions in the infrared range and show a very high solubility in LC material. However, the absorption coefficients of these types of dyes are small, so that large amounts of dye would have to be dissolved. This would adversely affect the physical properties of the host LC material. Taking these facts into consideration, the squarylium dyes such as 3 (Scheme II) have been selected for practical application.[17] Squarylium dyes are more durable than cyanine dyes. Moreover, they have absorption characteristics similar to cyanine dyes. The absorption maxima of 3 is at 780 nm, which is close to the wavelengths of the GaAlAs laser used in projection displays. The molar absorption coefficient of 3 is 1.15×10^5 M^{-1} cm^{-1}, and the dichroic ratio in the smectic LC is 6.4. Nagae et al. have also reported the use of an infrared absorbing dye to improve the writing speed of the light pen function.[18] The also used the pleochroic naphthalocyanine dye 4 to improve viewing angle characteristics in a manner similar to that by Lu et al.[19]

SCHEME II



3 4

C. Laser Printer

Electrophotography has grown in the past two decades from more humble uses as office copier and duplicator applications to surpass other conventional printing methods because of its outstanding characteristics of high speed and high print quality. Now, laser printers based on the same printing principle as electrophotography are widely used for computer printouts or multiple peripheral printers in office workstations and facsimiles.[20] In the case of laser printers, the light source is currently the GaAlAs diode laser which emits near-IR light with wavelengths of around 800 nm. Special photoconductive materials sensitive to near-IR wavelengths are needed. At present, many kinds of organic infrared absorbing dyes are applied as photoreceptors in laser printers. They can be divided into four groups based on their chromophoric systems: phthalocyanines, azo pigments, squarylium pigments, and others. The phthalocyanines have the widest application in practical photoreceptors. They are conventional metal-free or two-valent metal phthalocyanines, transformed into special crystal structures, and three- or four-valent metal phthalocyanines, having intrinsic absorptions in the near-IR region. Special trisazo pigments were designed, synthesized, and used in laser printers. Squarylium dyes are new potentially useful candidates. They show quite strong absorption in the near-IR region and are being marketed. There are problems associated with the use of perylene pigments in diode lasers due to the difficulty in achieving strong absorption. Other types of pyrrolopyrroles or azulenium salts are also being actively developed, and their application in printers is being tested.

The first commercial organic photoconductor (OPC) was the poly(vinylcarbazole) and trinitrofluorenone complex material developed by IBM in 1969.[21] It was a sheet-shaped mono-layered photoreceptor. Presently, dual-layered type OPCs are more popular since they have expanded capabilities.

The dual-layered photoreceptor is composed of a charge transport layer (CTL) and a charge generation layer (CGL), which, alternately, are coated on a conductive substrate. The charging polarity is negative (minus) for this type of OPC in order to make better use of the high hole mobility of the CTL. The imaging light exposure passes through the transparent CTL and reaches the CGL to generate charged photocarriers. The sensitivity of the photoreceptor depends mainly on three characteristics, namely, the charge generation efficiency of the CGL material, the charge transport efficiency of the carrier mobility of the CTL material, and the injection efficiency between the CTL and the CGL.[22,23]

Near-IR absorbing dyes for use in charge generation material (CGM) have been intentionally developed to fit their spectrosensitivities for use with diode lasers emitting a wavelength of about 800 nm. Phthalocyanines are the oldest organic semiconductors known, and many reports have been published concerning their electrical properties.[24] Phthalocyanines show crystal polymorphism and particular special crystal forms show near-IR photoconductivity. The x-form metal-free and copper phthalocyanines,[25] ϵ-form copper phthalocyanine,[26] and a τ-form metal-free phthalocyanine[27] have characteristic strong absorption maxima in the near-IR region and the good photoconductivity has been attributed to this absorption. Aggregated magnesium[28,29] or zinc phthalocyanines[29,30] have also been studied.

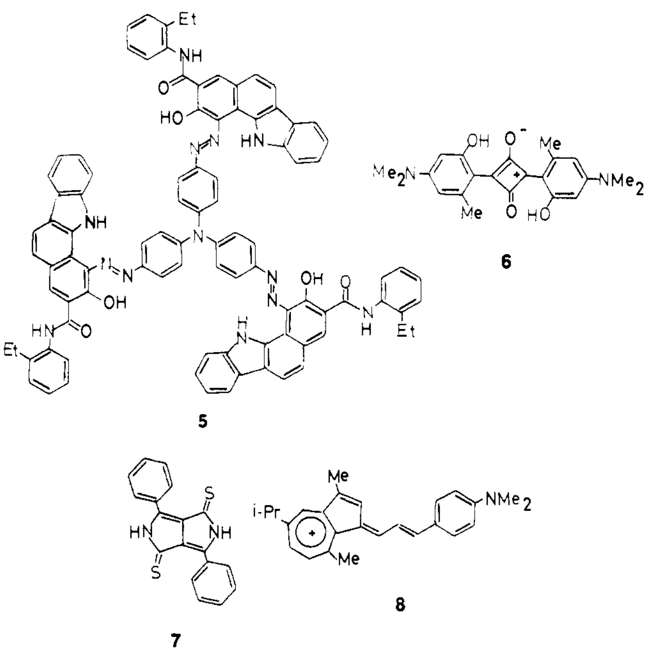
A second type of phthalocyanines used in diode lasers includes three- or four-valent metal complexes. Aluminum, gallium, and indium phthalocyanine chlorides or bromides belong to the three-valent type[31] and vanadyl (VOPc) or titanyl (TiOPc) phthalocyanines[32] to the four-valent type. Naphthalocyanines are currently being evaluated as OPC.

Disazo pigments were adopted as the CGM in an early double-layered photoreceptor for copiers but they were not infrared sensitive. Newly developed trisazo dyes have proven to be sensitive in the near-IR region. Trisazo pigments are generally more difficult to purify than phthalocyanines, and prepurification of the raw materials and a pure synthesis process, preventing degradation of the diazonium salt of the bridging parts, are critical. Azo pigments also show polymorphism, and it is necessary to select a particular crystal structure. A double-layered photoreceptor of the tris-azo pigment 5 of the benzocarbazole type coupler has a high sensitivity at 800 nm and has been applied in marketed printers.[33]

Squarylium dyes or pigments (squaraines) were first examined for solar cell use and later found applications in electrophotography. A symmetrical squarylium dye, bis[4-(dimethylamino)-2-hydroxy-6-methylphenyl]-squaraine (**6**, Scheme III), exhibit photoconductivity at 830 nm.[34]

Other new pigments have been proposed for diode laser use. 3,6-Diphenylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dithione (**7**)[35] exhibits a morphological transformation under solvent vapor accompanied by an enhancement in photoconductivity and a shift in absorption to longer wavelengths. The double-layered photoreceptor of the vapor-treated pyrrolopyrrole pigment has a sensitivity within the 650–850-nm range. 1-[*p*-(Dimethylamino)-cinnamylidene]-5-isopropyl-3,8-dimethylazulenium perchlorate (**8**) also shows quite a broad photosensitivity in the crystalline form, and when incorporated into a double-layered photoreceptor, a high sensitivity of 850 nm is reached.[36]

SCHEME III

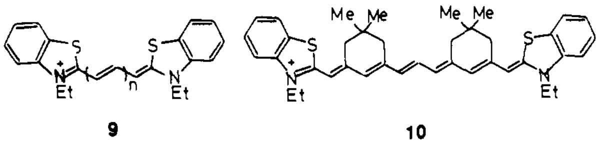


D. Laser Filter

Lasers are sources of light possessing properties which differ from conventional light sources. Laser light can be highly monochromatic, very well collimated and coherent, and in some cases lasers are extremely powerful. These characteristics make the laser a very useful light source with a variety of applications in science and industry. Optical filters are widely used in engineering and research. The spectral distribution of the incident laser energy must be either selectively or nonselectively altered or precisely controlled.[37] Here the discussion is confined to absorption filters for lasers that produce light at wavelengths in the infrared spectrum. The most common types of absorption filters are made of glass, gelatin, or plastic in which coloring agents are dissolved or suspended. Plastic filters are very inexpensive and generally stable. Gelatin or plastic filters can be readily cut to the desired size and shape and are flexible and convenient to use. Although such filters are generally less stable than glass filters, their spectral features are often much sharper. Plastic filters consist of infrared-absorbing dyes dissolved in some transparent host medium in amounts such as to provide the desired optical properties. Some of the most important technical requirements for infrared-absorbing dyes within the plastic are[37] as follows:

1. Excellent lightfastness of the infrared-absorbing dye.
2. High thermal stability.
3. High solubility.

SCHEME IV



4. A particular plastic and dye must be stable in the chemical reactions at processing temperature.
5. No loss of the dye from the plastic through exudation, volatilization, or other processes.
6. Low dye toxicity.

Because many organic infrared-absorbing dyes show low lightfastness properties they are not used as materials in laser filters. Metal complexes are generally much more stable to light and heat and are therefore very important practically as dyes for laser filters. Recently, active research on near-IR absorbing metal phthalocyanines and naphthalocyanines which are very soluble in organic solvents has been undertaken (section IV.A). Some infrared-absorbing dyes used in laser filters are as follows: cyanine, pyrylium and thiapyrylium, squarylium, indoaniline, azo, anthraquinone, naphthoquinone, aminium radical salt, charge-transfer complex, metalated azo, phthalocyanine, naphthalocyanine, and bis(dithiolene) and related complexes.

E. Infrared Photography

Silver halide microcrystals are the photosensitive elements in photographic materials.[38] However, the spectral sensitivity of silver halide microcrystals is limited to ultraviolet and blue light, and "spectral sensitization" is necessary to make photographic materials sensitive to green, red, and infrared light.[39] This requires sensitizing dyes, which are absorbed on the surface of the silver halide microcrystals, to inject electrons into the conduction band of the silver halide when they absorb light.

Since the discovery of spectral sensitization by Vogel in 1873, the portion of the spectrum which can be photographed has been gradually extended to longer wavelengths. It was extended to beyond 700 nm through the discovery of monocarbocyanine dyes **9** ($n = 1$) and to beyond 1300 nm by pentacarbocyanines **9** ($n = 5$) (Scheme IV).

The applicability of IR-sensitizing dyes depends on their stability during storage, their ability to absorb IR light, and their efficiency in spectral sensitization. Infrared-sensitizing polymethine dyes generally have a low stability during storage and low spectral sensitization efficiency.[40] Enhancement of the rigidity of the polymethine chain through alicyclic rings is very effective in improving the stability and hence applicability of infrared sensitizing dyes, e.g. **10**.

Various kinds of infrared-sensitive photographic materials are now produced for recording systems: (a) with new light sources such as diode lasers and (b) with detecting and discriminating capabilities which are enhanced by their sensitivity to IR light.[41] In case a, infrared-sensitive black and white films and papers are used as recording materials for scanners with laser diodes in the field of graphic arts and medical diagnosis. Infrared color negative film is composed of three emulsion layers sensitive to green, red, and infrared light, respectively. A yellow filter is used to absorb blue light incident to the film, since all the emulsion layers are sensitive to blue light. Infrared, red, and green light incident to the film form cyan, magenta, and yellow dyes, respectively. A color given by an IR color film is completely different from that in the original image and is called "false color". It is obvious that the introduction of IR light sensitivity into photographic materials, to which human beings are not sensitive, enhances their detecting and discriminating ability.[41]

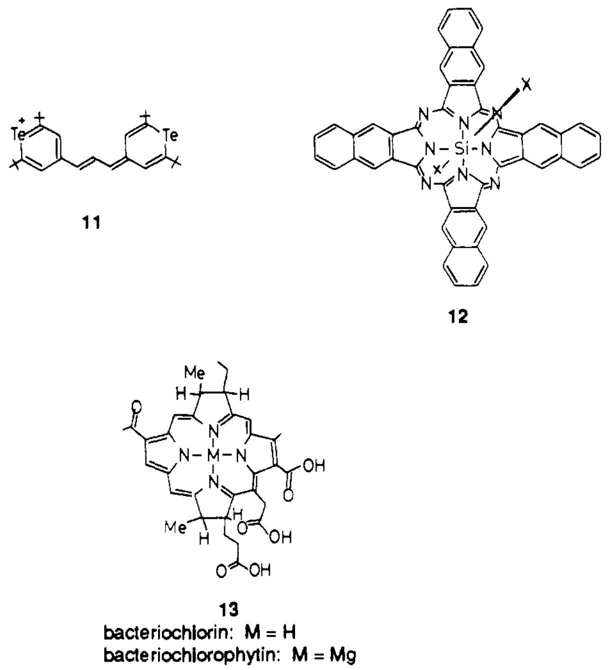
F. Medical Applications[42]

In 1942, Auler and Banzer reported that hematoporphyrin could be absorbed into cancerous tissue.[43] In 1964 Lipson et al. recognized that an oligomerized derivative of hematoporphyrin (HpD) accumulated preferentially into cancerous tissue rather than the surrounding tissue.[44] A purified version of this derivative, Photofrin II,[45] has been shown by Dougherty to possess certain clinical advantages over HpD in photodynamic therapy (PDT).[46] Singlet oxygen has the ability to react with a wide variety of biochemical molecules[47] and can cause significant damage and even death to any species unfortunate enough to ingest a sensitizer and consequently be exposed to light. Many compounds that absorb in the near-ultraviolet and the visible regions of the spectrum act as photosensitizers and accomplish the triplet–singlet interconversion of oxygen from their long-lived triplet excited state.[48] Until recently, little was known about this ability with regard to compounds which absorb in the near-IR region. Photofrin II, which has its absorption edge at 633 nm, is the only singlet oxygen photosensitizer approved for clinical studies in humans by the United States Food and Drug Administration. New compounds for use in PDT which absorb both on the edge of the near-IR region and into it are being investigated by a number of groups throughout the world. Unlike Photofrin II, they all have definite structural integrity, thus facilitating both in vitro and in vivo studies. Three categories are generally known: cationic dyes, phthalocyanines, and modified natural porphyrins, chlorins, and bacteriochlorins. The chalgenopyrylium dye **11** (Scheme V) first developed by Detty et al.[49] at Eastman Kodak absorbs at ideal wavelengths (780–820 nm, molar extinction coefficients of up to 300 000 M^{-1} cm^{-1}) for excitation by diode lasers. Metalated and sulfonated phthalocyanines have been the most extensively studied for use in PDT. Various metal complexes are effective to varying levels. Metalated naphthalocyanines **12** have recently been tested for effectiveness in PDT. Early in vitro studies using silicon dihexylalkoxynaphthalocyanine have shown it to be very effective in photolytic cell destruction.[50] Very early in vivo studies with these compounds utilizing a diode laser as a light source have found good efficiency.[51] Bacteriochlorin a (**13**, 770 nm) has also been investigated for use in phototherapy.[52] In vitro studies showed that **13** seemed to be more effective than HpD at killing cells.

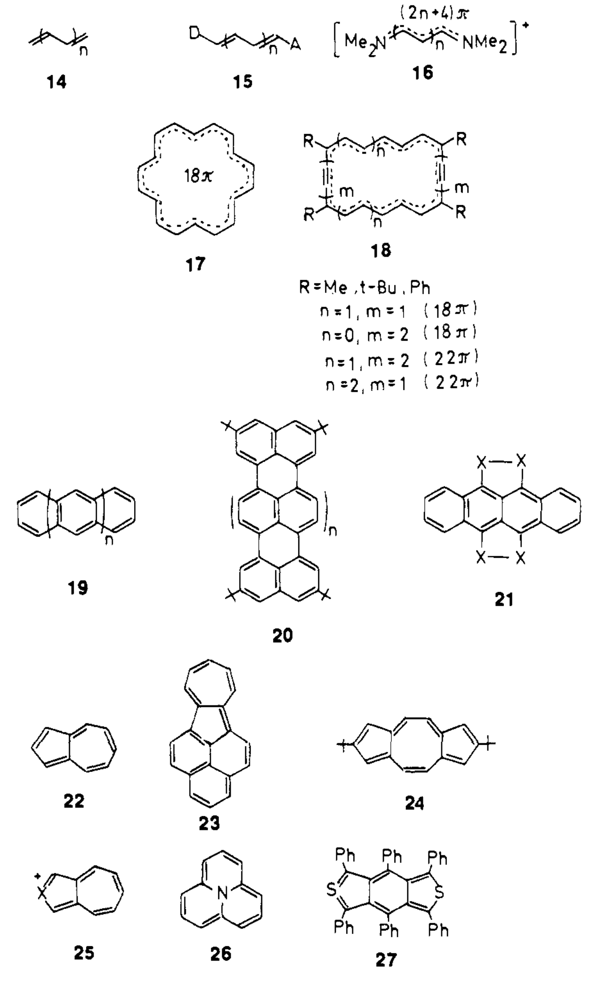
III. Basic Near-IR Chromophores and Origin of the Light Absorption

All those organic compounds that absorb intensively in the near-IR are conjugated systems. Long wave-

SCHEME V



SCHEME VI



length absorptions are mostly observed if the conjugated systems are strongly delocalized. Whereas polyenes **14** (Scheme VI) display bond fixation resulting in convergence in absorption wavelengths at about 600 nm at longer chain lengths (carotinoides, polyacetylene),[2,53] push-pull-substituted polyenes **15** (D = donor substituents, A = acceptor substituents) and similarly substituted carotinoides are more bathochromic than unsubstituted polyenes.[54] Donor-acceptor-substituted polyenes are in principle meropolymethine dyes (e.g. **15**, D = NR_2, A = C=O). Chain molecules may be near-IR chromophores at long chain length if the terminal heteroatoms are the same (e.g. **15**, D = NR_2, A = $C{=}NR_2^+$). They are known as polymethine dyes (**16**). In contrast to meropolymethines polymethines are charged molecules. The cations **16** with noncyclic end groups (streptocyanines) are simple representatives of these series. These streptopolymethines are characterized by $[N + 1]\pi$ electrons distributed over N atoms along the conjugated chain rather than the $[N]\pi$ electrons found in a polyenic structure (N = 2, 4, ...).[55]

In contrast to **14** the carbon-carbon bonds of **16** are nearly equal in length. The λ_{max} values of **16** ($n \geq 5$) amounts to more than 700 nm, and the molar absorption coefficients are large ($\log \epsilon > 4.5$).

Polymethine dyes with various noncyclic, carbocyclic, and heterocyclic end groups are discussed at length in section IV.C. There are also series of cationic and anionic polymethines that do not contain any heteroatom in the end group.[2d] The more recently described deeply colored vinylogous (cyclopentadienyl)-pentafulvenes[56a] and (tropylium)heptafulvenes[56b] belong to them.

Another class of basic chromophores can contain a cyclic structure.[57] In turn, light absorption in the near-IR occurs with highly delocalized bond systems rather than with cyclopolyenes. Aromatic [N]annulenes absorb at more than 700 nm if $N \geq 18$. The long wavelength absorptions of [18]annulene (**17**) and of various substituted compounds are relatively weak ($\log \epsilon \approx 3$). Near-IR absorptions have also been found for the conformationally more rigid dehydroannulenes **18**[58] and structurally fixed benzoannulenes.[59]

Annelation of benzene requires relatively large π-electronic systems to shift the color band to more than 700 nm. This wavelength region is reached with n = 5 in the series **19**[60] and n = 3 in the series **20** (746 nm[61]). Near-IR absorption is also produced on substitution of the hydrocarbons e.g. on going from tetracene (**19**, n = 2) to the tetrachalcogenotetracenes **21** (X = S, Se, Te).[62] The first absorption band of the latter is intense ($\log \epsilon \sim 4$).

The deeply colored porphyrins are related to annulenes and near-IR absorption has been found for tetrahydroporphyrins,[63a] vinylogous porphyrins,[63b,e] and related compounds[63c,d] as well as various natural dyes such as bacterochlorin a (**13**).[64]

Another series of deeply colored hydrocarbons is exemplified by **22**–**24** (Scheme VI). In contrast to **17** and **18** these compounds are nonalternant hydrocarbons. These hydrocarbons have a very broad weak absorption band at long wavelengths which may be extended to more than 1000 nm.[65] In general, this absorption band displays fine structure. Numerous heterocycles isoconjugated with **22** (e.g. **25**, X = NPh, S)[66] or with larger nonalternant hydrocarbons[67] also absorb at more than 700 nm.

For the sake of clarity, the formulae **19** to **25** are given by a single limiting formula with localized bonds. These and many other formulae in this review reflect neither the true bonding situation nor the symmetry of the molecules. In addition, any charge localization in the formulae of the ionic dyes fails to describe the true electron distribution.

The previously mentioned linear and cyclic chromophores are important basic chromophores. Most of the dyes under discussion are more or less complex derivatives of them. Less symmetric compounds may, however, be considered as being composed of two (or more) molecular fragments which differ in their electron donor and electron acceptor strength. Composite molecules such as these give rise to weak intramolecular charge transfer bands at very long wavelengths (CT chromophores).

Conjugated π-type organic radicals are often deeply colored. They are less inclined to form σ-dimers if the π-system and the spin densities are highly delocalized in the open chain or ring closed structure. The polymethine violene radicals are the congeners of the polymethine cyanines.[68] Both classes of these compounds belong to the $[N+1]\pi$-streptopolymethines.[69]

Although there is increasing information available concerning near-IR absorbing triplet molecules (e.g. retinal,[70a] merocyanines,[70b] cyanines,[70c,d] porphyrins[70e]) these chromophores are not included in this review. It should only be mentioned that the increase in λ_{max} of vinylogous triplet cyanine dyes is similar to that found for these dyes in the singlet state.[70c]

Some organic compounds owe their weak near-IR absorption bands to electronic excitation which are only in part due to the π-electronic systems. This gives rise to weak absorption bands (log $\epsilon \sim 2$). These are the σ–π^* (n–π^*) or π–σ^* transitions whereas π–π^* transitions occur in all the forementioned cases.

In this classification the simple MO model is used for a qualitative interpretation of the color determining electronic transitions. Kuhn's empirical MO-FE and Hückel's empirical MO-LCAO (HMO) method permit a surprisingly accurate prediction of near-IR absorption maxima in series of related linear chromophores that are strongly delocalized (e.g. ref 71). Useful results have been achieved for closed- as well as open-shell polymethines. In search of deeply colored dyes, Dyadyusha and co-workers refined the topological approach by defining the contribution of the end groups to the absorption wavelength.[72]

Explicit consideration of electron–electron interactions rationalizes the relatively low excitation energy of azulene[73] and other nonalternant hydrocarbons. Due to the significant redistribution of charge after excitation, the electron exchange repulsion is low in this series. The same effect is operative for CT-type transitions. Concomitantly, however, the transition density is low and the absorption intensity is consequently weak.

Configuration interaction between singly excited configurations has to be taken into account in order to understand both the position and intensity of the first absorption band of cyclic hydrocarbons and related chromophores. Electron and configuration interaction is considered semiempirically using the PPP method at the π-level and by various XNDO/S methods at the all-valence-electron level.[74a] The LHP method permits prediction of absorption features of organic radicals at the π-level.[74b] Both the PPP and LHP methods have been used to estimate λ_{max} values of near-IR dyes.[74,75] These values are systematically underestimated for closed shell cyanine dyes by about 100 nm in the 800-nm region if standard parametrizations are used.[75] Less is known about the calculation to triplet excited states.[76]

In order to better understand the electronic excitation of composite molecules in terms of their fragments, the electronically excited state has to be defined by the configuration interaction between locally excited (LE) configurations and intramolecular charge transfer (CT) configurations. The charge resonance (CR) configuration describes a mixture of two configurations resulting from oppositely directed CT excitation between identical subchromophores. The molecular exciton theory works well if the electron delocalization between the subchromophores is small. The excited state then corresponds to a configuration of the molecular exciton (MX) type. Configuration analysis allows PPP-calculation results to be analyzed in terms of LE-, CT-, CR-, and MX-type configurations for the excited states.

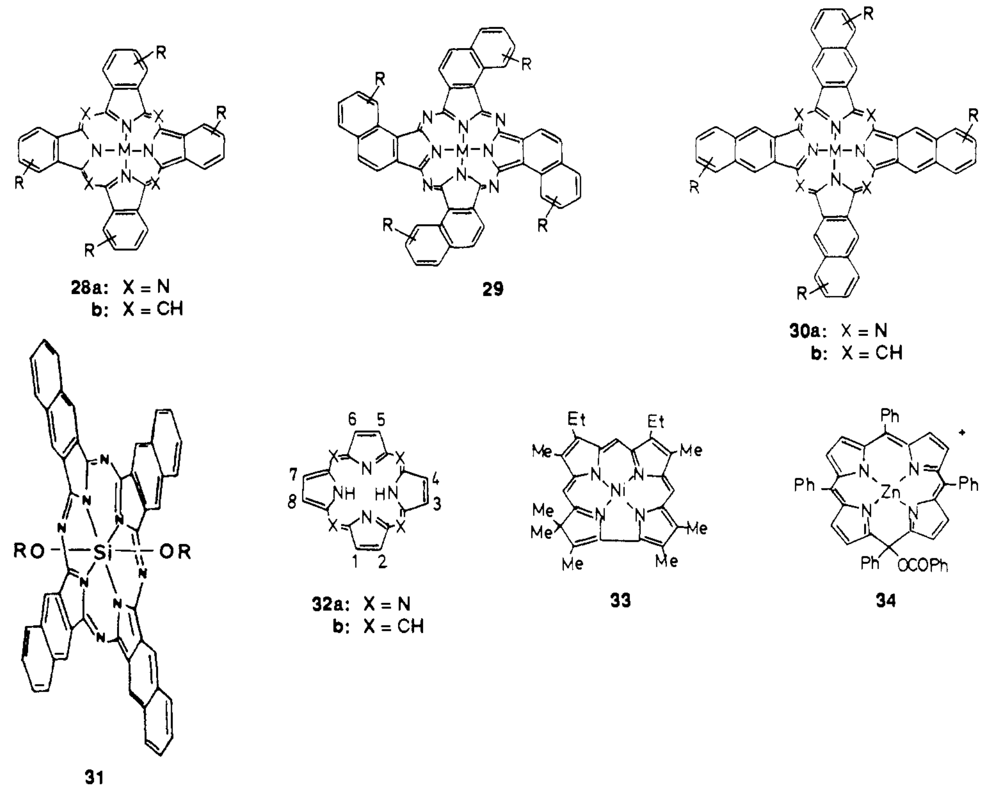
The question has been raised as to whether or not the conventional PPP method is reliable for compounds which absorb at extremely long wavelengths.[77] These compounds have some biradicaloid character, and this requires, in principle, an extension of the configurational space. Consideration of deeply colored compounds as perturbed biradicals has drawn attention to various relatively small compounds absorbing at long wavelengths, for example **26** and **27**. In the first case nitrogen has been introduced into an antiaromatic [12]annulene and in the second case, two sulfur atoms into the non-Kekulé hydrocarbon 1,2,4,5-tetramethylene benzene. The resulting heterocycles, cycl[3.3.3]azine and hexaphenylthieno[3,4-*f*]isothionaphthene, absorb at 1290 nm (λ_∞ value)[78] and 793 nm (λ_{max} value, log ϵ = 4.06), respectively.[79] Whereas derivatives of antiaromatics only produce weak long wavelength absorptions such as found for conformationally fixed dehydroannulenes,[80] more intense absorption may occur with structural modification of some non-Kekulé-type hydrocarbons, such as found for derivatives of tetramethylene ethene[81] and 1,2,4,5-tetramethylene benzene.[79] Conventional PPP-type calculations normally overestimate the absorption intensity (oscillator strength), but the agreement is improved by including higher excited configurations.

IV. Near-IR Absorbing Organic Compounds

A. Phthalocyanine and Naphthalocyanine Dyes

Phthalocyanine chromophores were first synthesized by chance in 1928 during the preparation of phthalimide from phthalic anhydride and ammonia in a reaction vessel made of iron. The iron phthalocyanine obtained was isolated and identified by Linstead in 1934.[82] Its structure was confirmed by Robertson[83] using X-ray analysis in 1935. Since then, phthalocyanines (Pc) have become important colorants as dyes and pigments. Their structural analogy to natural pigments such as the porphyrins is of great interest in academic research, in particular with regard to their application as colorants. The chemistry of phthalocyanine compounds was reviewed by Moser and Thomas[84a] in 1936. Further advances in the color chemistry of phthalocyanines were reviewed by Booth[84b] in 1971 and Gordon and Gregory[84c] in 1983. Recently,

SCHEME VII



Luk'yanets[9] surveyed and summarized the absorption spectra of phthalocyanines, naphthalocyanines, and related compounds.

In the search for suitable near-IR dyes for use in the optical recording media, phthalocyanines (**28a**, Scheme VII) were first investigated. Metal-free phthalocyanines absorb at 698 nm in a 1-chloronaphthalene solution and at 772 nm in the solid state. The metal complexes generally absorb at much shorter wavelengths, but some, such as lead phthalocyanine, absorb at much longer wavelengths than the metal-free phthalocyanine.[85] Multiple substitution[86a] and complexation with Lewis acids[86b-d] can cause a shift to the near-IR region. This is more generally observed with annelation.[9,86e-g] The bathochromic shift produced on passing from phthalocyanines to 1,2-naphthalocyanines (**29**, R = H) and 2,3-naphthalocyanines (**30a**, R = H) amounts to 22 and 67 nm, respectively. The photophysics of some derivatives is discussed in refs 86d,h,i. Annelated phthalocyanines are fluorescent at room temperature.[86i] Some spectral absorptions are given as follows. Pc (**28a**): R = *tert*-heptyl, M = VO (809 nm[87]), R = 1,4-$(OMe)_2$-2,3-Cl_2, M = H,H (750 nm[88]), R = 1,4-$(OBu)_2$, M = $Sn(OSiEt_3)_2$ [695 nm(log ϵ = 4.64)[89], 779 nm(log ϵ = 5.27)]. Nc(**30a**): R = H, M = $Ge(OSiEt_3)_2$ (780 nm[90]), R = 2-heptylundecanoyl, M = $Si(OR_3)_2$ (798 nm[91]), R = SiR_3 or $(CO_2R)_n$, M = $Si(OR_3)_2$ (800 nm[92]), R = H, M = AlCl (774 nm[93]).

The series of 2,3-naphthalocyanine derivatives is potentially very important with electrooptical applications in areas such as optical recording media, organic photoconductors, color filter dyes, and photosensors. They have been modified to improve solubility through the introduction of branched long-chain alkyl groups into the naphthalene rings and/or of trialkylsiloxysilane into the central core.

There are many synthetic methods for the preparation of phthalocyanines but, in general, four main processes are employed.[84a] Recently, a new route to unsymmetrical phthalocyanines via subphthalocyanine was reported.[86e]

2,3-Naphthalocyanine was first synthesized by Luk'yanets et al. from 2,3-dicyanonaphthalene.[94a] Substituted naphthalocyanines (Nc)[94b] are generally synthesized from substituted dicyanonaphthalenes. Tetrabromination of substituted *o*-xylene with NBS using UV light followed by condensation with fumaronitrile gives dicyanonaphthalenes. Kenney et al. prepared new types of bis(alkylsiloxy)silyl naphthalocyanines **31**.[94c] 2,3-Dicyanonaphthalene is converted to 1,3-diiminobenz[*f*]isoindoline which tetramerizes to give dichlorosilylnaphthalocyanine ($SiNcCl_2$) in the presence of tetrachlorosilane. The acid hydrolysis of $SiNcCl_2$ results in $SiNc(OH)_2$, which reacts with trialkylsilyl chloride to give $SiNc(OSiR_3)_2$ (**31**). The two isomers of magnesium 1,2-naphthalocyanine, the α and β form, were first obtained by Bradbrook and Linstead[95] in 1936. The zinc and copper complexes are also known,[95] but their absorption spectra have so far not been described.

The color–structure relationship of phthalocyanine chromophores has been studied using MO calculations.[2c,84c] λ_{max} values, molar absorptivities, and changes in π-electron density accompanying the first transition were calculated. The calculations indicated that a charge-transfer occurs from the center toward the outside. Metalation, which reduces the electron density at the inner nitrogen atoms, is predicted to produce a hypsochromic shift. This is in fact observed experimentally. The extent of the λ_{max} shift to shorter wavelength depends on the electronegativity of the metal. In contrast, electron-withdrawing groups such as halogens at the periphery of the molecule are

Table I. Spectral Data of Porphines, Corroles, Phthalocyanines, and Naphthalocyanines

compound	λ_{max}[a]	$10^{-4}\epsilon$[b]	solvent	ref
porphine **32b**	619, 529	0.46, 0.76	pyridine	84c
corrole **33**	825, 746	1.01, 0.54	$CHCl_3$	99c
isoporphyrin **34**	857, 775	1.51, 0.89	CH_2Cl_2	100
tetraazaporphine **32a**	624, 556	8.13, 4.68	pyridine	84c
tetrabenzoporphine **28b**, R = H, M = H,H	662, 596	1.58, 2.19	THF[c]	102a
phthalocyanine **28a**, R = H, M = H,H	698, 665	16.22, 15.14	*d*	84c
tetraaza(2,3-naphtho)-porphine **30b**, R = H, M = H,H	722, 703		DMF	101
2,3-naphthalocyanine **30a**, R = H, M = H,H	765	18.20		3a
tert-octyl-VO-2,3-naphthalocyanine	809	24.55	toluene	87
1,2-naphthalocyanine **29**, R = H, M = H,H	720, 677		*d*	102b

[a] In nm. [b] In M^{-1} cm^{-1}. [c] Addition of pyridine (5%). [d] In 1-chloronaphthalene.

SCHEME VIII

35

$z = 0, -1, -2$

predicted to give rise to a bathochromic shift. In principle, however, the 18π-electron inner ring system of the phthalocyanines determines the bathochromicity and substitution at the benzene rings has only a minor effect on the λ_{max} of the phthalocyanine chromophores.

Applications of phthalocyanines and naphthalocyanines have been summarized in ref 3a. Phthalocyanine compounds have attracted attention as functional dyes in various fields, and much interesting research has been reported.[96] Their semiconductor or dielectric properties are useful in diode, piezoelectric, and electrochromic devices. Their optical properties make them suitable for practical applications in xerography, photochemical hole burning, laser disk memory, and photodiodes. Their catalytic activities have led to their utilization in photovoltaic cells and chemical sensors.

Naphthalocyanines absorb in the near-infrared region and are interesting as recording media for laser optical recording systems. The most important question is how to achieve good solubility in nonpolar organic solvents. Dye media are dissolved in high concentration and then applied onto the substrate made of polycarbonate or other polymers to produce the recording disk. Good solubility has been achieved by the introduction of a long alkyl chain into the naphthalene ring. Solubility in organic solvents is increased by preventing aggregation of Nc caused by steric interaction between the bulky and long-chain alkyl substituents.

Kenney et al.[94c] synthesized the silicon naphthalocyanines **31**, which opened up a new field of Nc chemistry. Silicon naphthalocyanines have been developed because of interest in their use as photodynamic sensitizers for the electrolysis of water and the photodynamic therapy of tumors.[89] Their redox behavior, reversible energy-transfer reactions, and electrical conductivity has been investigated in relation to their structures and spectral properties. Photoproperties of metal octabutoxyphthalocyanines with deep red optical absorbance have been recently reported.[97]

Table II. Spectral Data of Metal Complexes 36 and 37

no.	M	R	λ_{max}[a]	$10^{-4}\epsilon$[b]	solvent	ref(s)
36	Ni	H	720	1.43	MeOH	103, 104
36	Ni	*n*-BuS	1000	4.70	CH_2Cl_2	106a
36	Ni	C_6H_5	866	3.09	$CHCl_3$	104
36	Ni	4-OMeC_6H_4[c]	925	2.51	$CHCl_3$	104
36	Ni	4-julolidinyl	1298	4.8	$(ClCH_2)_2$	107
36	Ni	4-$(CF_3)C_6H_4$	832	2.99	CH_2Cl_2	108c
36	Ni	2-ClC_6H_4	783	2.56	CH_2Cl_2	108c
36	Pt	C_6H_5	802	4.27	$CHCl_3$	104
36	Pd[d]	C_6H_5	885	3.97	CH_2Cl_2	104, 105
37	Ni	CN	848	0.80	MeCN	114
37	Ni	C_6H_5	940	1.34	CH_2Cl_2	104, 108a
37	Ni	4-$(CF_3)C_6H_4$	923	1.26	CH_2Cl_2	108a
37	Ni	-SC(S)S-(*R*,*R*)	1150	1.99	CH_2Cl_2	106
37	Pt	CN	855	1.17	$CHCl_3$	115
37	Pd[e]	CN	1100	1.38	$CHCl_3$	115

[a] In nm. [b] In M^{-1} cm^{-1}. [c] For numerous nonsymmetric **36** with different substituent groups see refs 109 and 108–111. [d] Molybdenum complex with two additional carbonyl ligands (R = 4-$(NMe_2)C_6H_4$): λ_{max} = 750 nm (log ϵ = 4.19).[112] [e] Cobalt complex (n = −1, R = H): λ_{max} = 731 nm in DMF (log ϵ = 3.08).[113]

Another field of current research is the electrolysis of water,[98] in which a new type of molybdenum 1,2-naphthalocyanine played an effective catalytic role.

Various alkylated metal corroles are known to strongly absorb light over 700 nm.[99] In a more recent study, attention has been directed to near-IR absorptions of isoporphyrins because of their noticeable photochemical and redox properties.[100] Some spectral data of phthalocyanines and naphthalocyanines are collected in Table I along with those of porphyrins, isoporphyrins, and corroles (**32**–**34**). Because of their interrupted cyclic conjugation, the cationic isoporphyrins, however, belong to the branched conjugated polymethine dyes rather than to the porphyrins.

B. Metal Complex Dyes

The electronic structure of dithiolene metal complexes in which the metals are transition metals such as Ni (or Pt and Pd) are described by two equivalent resonance forms **35** (cf. Scheme VIII).

The chelate component is a stable aromatic 10π-electron system.[103,104] The neutral metal complex (z = 0) can be reduced to anions with the charges $z = -1$ or −2. The neutral and mono anion complexes have an intense absorption band in the near-IR region (log $\epsilon \approx$ 4). The near-IR absorption maxima of the complexes **36**–**39** selected from refs 105–123 are summarized in Tables II and III.

The spectra of the nickel complexes have been discussed using HMO,[103] PPP,[124a] as well as more refined quantum chemical methods.[104] The longest wavelength absorption band of the neutral complex has been assigned to a b_{1u}–b_{2g} (π–π*) transition.[103,104] According to INDO/S calculations[104a] the highest occupied MO (b_{1u}) is virtually a pure ligand orbital and the lowest empty MO (b_{2g}) has some Ni as well as ligand character.

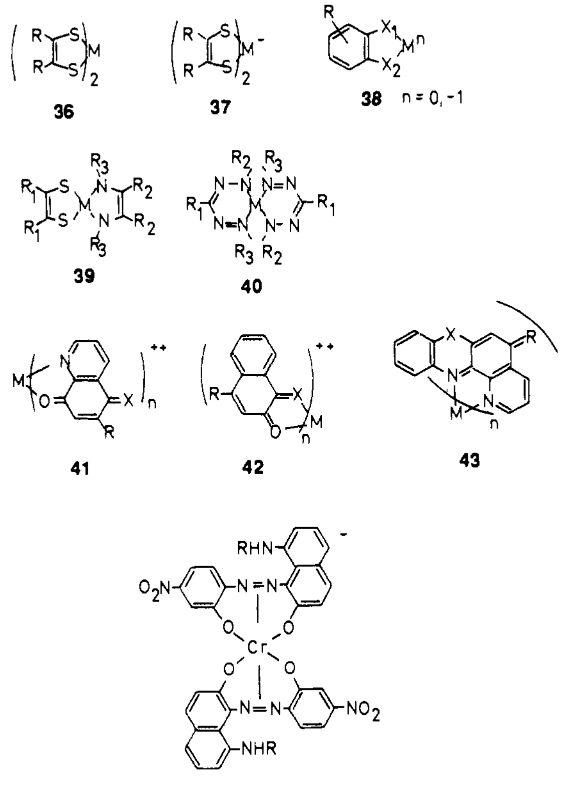
The absorption band of **36** in the near-IR region is sensitive to substituent groups. In the presence of more powerful electron-donating substituents in **36**, **37**, and **38** such as NR_2, SR, and thiapentalene residues (Scheme IX) the absorption band is shifted to wavelengths up to 1000 nm longer. A good linear relationship[124b] has been found between λ_{max} values and modified Hammett substituent constants, δ_p^+, in the case of substi-

Table III. Spectral Data of Metal Complexes 38–40

no.	M	charges, substituents	λ_{max}[a]	$10^{-4}\epsilon$[b]	solvent	ref(s)
38	Ni	$n = 0$, $X_1 = X_2 = NH$, $R = H$	790	5.49	DMSO	116a
38	Pd[c]	$n = 0$, $X_1 = X_2 = NH$, $R = H$	780	4.82	DMSO	116a
38	Ni	$n = -1$, $X_1 = X_2 = S$, $R = H$	881	1.34	CH_2Cl_2	117
38	Ni	$n = -1$, $X_1 = X_2 = S$, $R = 3,4,6\text{-}Cl_3$	870	1.40	CH_2Cl_2	108c, 118b
38	Ni	$n = -1$, $X_1 = X_2 = S$, $R = 4\text{-}NH_2$	1053	1.53	CH_2Cl_2	118a
38	Ni	$n = -1$, $X_1 = NH$, $X_2 = S$, $R = H$	894	1.20	DMF	119
38	Ni	$n = -1$, $X_1 = S$, $X_2 = O$, $R = H$	1025	1.27	DMF	118b
39	Ni	$R_{1,1} = 4\text{-}MeC_6H_3$, $R_2 = Me$, $R_3 = Ph$	720	0.72	$CHCl_3$	120
39	Pt	$R_{1,1} = 4\text{-}MeC_6H_3$, $R_2 = Me$, $R_3 = Ph$	704	1.48	$CHCl_3$	120
39	Pd	$R_{1,1} = 4\text{-}MeC_6H_3$, $R_2 = Me$, $R_3 = Ph$	741	0.5	$CHCl_3$	120
40	Ni	$R_1 = Me$, $R_2 = R_3 = C_6H_5$	780	0.92	benzene	121
40	Ni	$R_1 = R_2 = C_6H_5$, $R_3 = 4\text{-}MeC_6H_4$	786	1.04	THF	122
40	Pd	$R_1 = R_2 = R_3 = 4\text{-}(OMe)C_6H_4$	720	1.23	$CHCl_3$	123

[a] In nm. [b] In M^{-1} cm^{-1}. [c] Cobalt complex ($n = 0$, $R = H$, $X_1 = X_2 = NH$): $\lambda_{max} = 1135$ ($\log \epsilon = 3.58$), 763 nm ($\log \epsilon = 4.07$) in DMSO.[116a]

SCHEME IX



tution in the 4-position of the phenyl groups of **36a** (R_1,R_2 = Ph). The nickel complex with the julolidinyl group absorbs at about 1300 nm. Substituent effects are similarly reflected in the S(2p) and Ni(2p) binding energies of ESCA spectra of **36a**[124c] and in the Ni–S vibrations of resonance Raman spectra.[124d] Although the central NiS_4 unit in the nickel complex is approximately square planar (D_{4h} symmetry), the plane of phenyl ring is twisted 33° and 66° out of the plane defined by the five-membered nickel chelate rings, and its symmetry is reduced from D_{4h} to D_{2h} symmetry.[125] A pronounced hypsochromic shift is caused by steric hindrance between the 2-halogen atom in the phenyl group of **36** and the chelate ring, and the λ_{max} is shifted to about 780 nm.[108b,c] The near-IR absorption band changes from 780 nm to 1300 nm through substitution in the phenyl group of **36a**. Introduction of alkyl or alkoxy groups with long chains, which improve solubility, has little effect on the absorption spectra of **36a**. Reduction of the neutral complex to the mono anion complex causes a red shift of about 60–80 nm and lowering of the intensity of the absorption band (cf. Tables II and III). In the neutral dithiolene complex **36**, the absorption band shifts to longer wavelengths in the order Pt < Ni < Pd. A similar spectral effect when substituted by transition metals has been observed in the series **37** and **39** (Tables II and III). There is, however, no effect in series **38**. The near-IR band of the metal complex **38** is also dependent on the heteroatom X and various complexes have been reported which intensively absorb between 780 and 1100 nm.[116,119,118a–c] Oligomeric bis-aryldithiolene nickel complexes absorb as large as 2000 nm.[118d] Complexes of the structure **39** mostly absorb below 800 nm, except for some annelated compounds.

Although the dithiolene metal complexes show an absorption band in the near-IR region they are not useful, in general, as colorants in the recording layer of the optical DRAW disk[4d,124b] due to their low reflectivity at the oscillation wavelength of the GaAlAs diode lasers. Instead the dithiolene nickel complex has been applied to the optical DRAW disk as an inhibitor of laser-induced fading[126] and sunlight-induced fading[127] of the cyanine dye lasers. This is possible because they exhibit significant singlet oxygen quenching ability.[124e,f] Oxidation processes account for the fading of cyanine dyes. Practically, dithiolene Ni complexes (e.g. **38**, n = 1, X = S, R = halogen) are used as a counteranion of cyanine dyes or added as antioxidants (10–15 wt %) in the DRAW disk.[126]

Dithiolene metal complexes have also attracted much interest as Q-switching near-IR dyes. In this connection Mueller-Westerhoff et al. have recently reviewed dithiolene complexes substituted by strong donor groups.[128] They predict that dyes that absorb at wavelengths as large as 1500 nm might be accessible. Freyer et al. studied both the solvatochromism[128b] and deactivation[128c] of dithiolene Ni complexes.

Despite significant deviations of the ring atoms and the metal from the least-squares chelate planes in formazyl metal complexes (**40**) the electron system is delocalized over the chelate rings. This results in intense absorption bands observed at about 780 nm ($\log \epsilon \sim 4$) (Table III).

Because of their intense absorption band at about 800 nm ($\log \epsilon \sim 5$) metal complexes of the type **41** (X = $N\text{-}C_6H_4R_1$) are lightfast and useful as absorbers in optical disks.[29a–c,130] Spectral data of the longest wavelength absorptions of metal complexes of the series **41** to **43** are summarized in Table IV. The absorption band is shifted to longer wavelengths with the increasing electron-donating capacity of the substituent groups R, its intensity increases with the number of ligands.

Table IV. Spectral Data of Metal Complexes 41–43

no.	M	*n*	R	X	λ_{max}[a]	$10^{-4}\epsilon$[b]	solvent	ref
41	Cu	2	4-$(NEt_2)C_6H_4$	O	769	5.86	EtOH	129c
41	Cu	2	H	[4-$(NMe_2)C_6H_4$]N	772	14.4	EtOH	129a,b
41	Cu	1	H	[4-$(NMe_2)C_6H_4$]N	722	6.9	EtOH	129b
41	Ni	2	4-$(NMe_2)C_6H_4$	O	728	4.24	EtOH	129c
41	Ni	2	H	[4-$(NMe_2)C_6N_4$]N	745	8.5	EtOH	129a,b
41	Ni	2	H	[2-Me-4-$(NBu_2)C_6H_3$]N	801	15.7	$CHCl_3$	130
41	Ni	1	H	[4-$(NMe_2)C_6H_4$]N	728	6.0	EtOH	129b
41	Co	2	4-$(NMe_2)C_6H_4$	O	713	3.75	EtOH	129c
42	Cu	1	4-$(NEt_2)C_6H_4$	O	779	2.35	EtOH	129e
42	Ni	1	4-$(NEt_2)C_6H_4$	O	817	2.42	EtOH	129e
42	Co	1	4-$(NEt_2)C_6H_4$	O	803	1.85	EtOH	129e
43	Cu	2	[4-$(NMe_2)C_6H_4$]N	S	794	4.38	EtOH	129g
43	Ni	2	[4-$(NMe_2)C_6H_4$]N	S	782	4.36	EtOH	129f,g
43	Ni	1	[4-$(NMe_2)C_6H_4$]N	S	783	1.94	EtOH	122g

[a] In nm. [b] In M^{-1} cm^{-1}.

For example, in the case of the complex **42** the value of ϵ observed in the 1:2 complexes is twice that of the 1:1 complexes.[129f,g] In the metal complexes **41–43** the transition metal ion only slightly affects the position of the absorption band in the near-IR region.

Other metal complexes which exhibit an intense absorption band in the near-IR region are the 1:2 Cr-azo dyes **44**.[131a] They are in charge control agents used in electrophotographic processes (e.g. **44**, R = Bu: λ_{max} 760 nm in DMF, log ϵ = 4.45). Copper-containing triazo dyes likewise absorb at more than 700 nm.[132] Azo dye metal complexes absorb at 705–780 nm in H_2SO_4.[133] Bipyridine alkali metal complexes exhibit a relative weak intensive absorption band between 752 and 952 nm (log ϵ ~ 3). This absorption is due to a π–π^* transition of the bipyridine anion.[134] The *o*-benzosemiquinonato complexes Zn and Ni complexes are another series displaying weak near-IR absorptions beyond 700 nm.[134b] Deeply colored radical anions are discussed in section IV.H, and metal complexes of phthalocyanines, naphthalocyanines, porphyrins, isoporphyrins, and corrolates in section IV.A.

C. Polymethine Dyes

Well known since the early 1920s, polymethine dyes cover a large wavelength region[2,7c] due to the fact that the vinylene shift amounts to about 100 nm.[135] Many symmetric near-IR cyanine dyes with heterocyclic end groups have been described during the last decade. Some absorption data examples have been selected from refs 136–152 to be presented in Table V (dyes **45–59**, Scheme X). Because of their long wave absorptions dyes with chalcogenopyrylium (e.g. **47–49**) and benzo[*c,d*]indenylium (naphtholactam) nuclei (e.g. **51a**) have attracted particular attention in more recent research.

Few symmetric monomethines (*n* = 0) show absorption maxima above 700 nm[49,139,153] (e.g. **47**, X = Te). The majority of the near-IR dyes are trimethines (monocarbocyanines, *n* = 1) or pentamethines (dicarbocyanines, *n* = 2) but many higher vinylogs are also known (cf. Table V). The streptopolymethine parent chromophore **16** absorbs at more than 700 nm with *n* = 5.[2b] Annelation at the heterocyclic end groups results, in general, in a bathochromic shift.[154–156]

The longest chain polymethines known (the pentadecamethine in series **45**[136] and undecamethines in series **49**[141]) are less stable than dyes of shorter chain lengths. The most bathochromic dye of the previously mentioned series is **49b** (X = S), which has not yet been isolated as a pure compound (λ_{max} = 1610 nm).[142]

The origin of the first absorption band is theoretically well understood.[2b,c] The spectral effect of the different end groups can be estimated by Dyadyusha and Kachkovskii's topological approach.[157a] This concept has been used in predicting deeply colored cyanine dyes.[72]

Cationic dyes display solvent effects in nucleophilic solvents, but the spectral shift of the λ_{max} values is generally low for symmetric dyes.[158,159] Generally, the intensity of polymethine dyes (molar absorption coefficients, ϵ, and oscillator strength, *f*) increases as the chain length is extended.[158,160,161] Irregularities do occur in some vinylogous series. These results have been discussed in terms of both isomerization[162] and solvent effects.[158]

Polymethine cyanines are weakly fluorescent. The fluorescence quantum yield of cyanine dyes passes through a maximum value on going from short to long chain lengths.[163] Fluorescence enables application of near-IR cyanine dyes to the ultratrace detection of labeled organic compounds using laser fluorimetry.[164a] The fluorescence efficiency of some near-IR absorbing polymethines is enhanced if dye molecules are bound to proteins.[164b] By using a diode laser for excitation, the detection of labeled albumines was 1–2 orders of magnitude greater than by conventional methods. Another application is the ultrasensitive detection of surfactants.[164c]

There are numerous nonsymmetric near-IR cyanine dyes with two different heterocyclic end groups, one heterocyclic and one carbocyclic end group, or one heterocyclic and one noncyclic end group that likewise absorb in the near-IR region.[49,139a,165] In general, their maxima are more or less displaced to shorter wavelengths compared to the average values of λ_{max} in the corresponding symmetric dyes. Absorption maxima above 700 nm have also been found for some monomethines.[153,166] Many of the nonsymmetric and symmetric near-IR dyes are trimethines.[167]

Trinuclear cyanine dyes (e.g. **53**) absorb at similar wavelengths to the dinuclear ones but splitting of the absorption band occurs if the end groups are different.[147] Another type of trinuclear near-IR dye consists of two polymethine chains which have a common nucleus,[148] e.g. **54**.[148a]

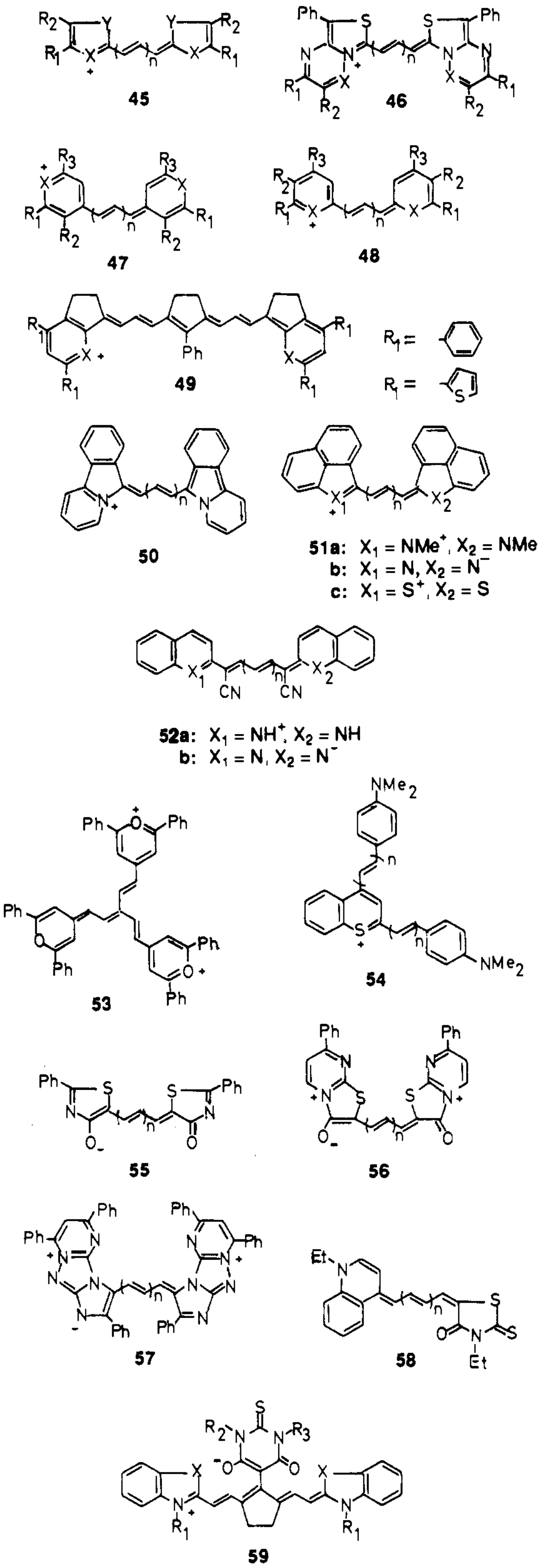
Less is known about deeply colored oxonol dyes[149] (e.g. **55**[149a]). Comparison of iso-π-electronic cationic

Table V. Spectral Data of Symmetric Polymethine Dyes

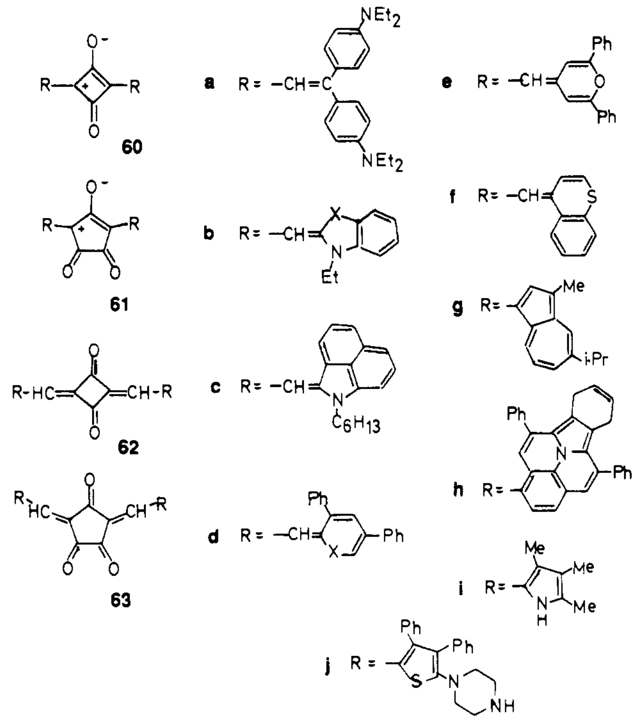
no.	X	Y	R_1	R_2	R_3	n	λ_{max}[a]	$10^{-4}\epsilon$[b]	solvent	ref
45	NMe	CMe_2	CH=CH—CH=CH			3	742.8	28.1	MeOH	4a
	NEt	S	CH=CH—CH=CH			3	760		EtOH	2b
	NEt	S	CH=CH—CH=CH			4	870		EtOH	2b
	NEt	S	CH=CH—CH=CH			5	995		EtOH	2b
	NEt	S	CH=CH—CH=CH			6	1130		CH_2Cl_2	136
	NEt	S	CH=CH—CH=CH			7	1250		CH_2Cl_2	136
	NMe	Se	CH=CH—CH=CH			3	769.2	24.1	MeOH	4a
	NMe	HC=CH	CH=CH—CH=CH			2	706.8	25.4	MeOH	4a
	NMe	HC=CH	CH=CH—CH=CH			3	816.4	23.4	MeOH	4a
46	CMe		Me	H	Me	1	805	57.5	MeCN	137
	CMe		Me	H	Me	2	895	83.2	MeCN	137
	N		Ph	Ph	H	1	790	83.2	MeCN	137
	N		Ph	Ph	H	2	870	44.7	MeCN	137
47	NEt		CH=CH—CH=CH		H	1	706.4	24.4	MeOH	4a
	NEt		CH=CH—CH=CH		H	2	812.9	23.9	MeOH	4a
	NEt		CH=CH—CH=CH		H	3	928	14.9	MeOH	4a
	NMe	NMe	Ph	H	Ph	2	758		CH_2Cl_2	138a
	O	O	Ph	H	Ph	2	806	31.6	CH_2Cl_2	138a
	S	S	Ph	H	Ph	1	755		$MeNO_2$	138c
	S	S	Ph	H	Ph	2	879		$MeNO_2$	138c
	S	S	Ph	H	Ph	3	1000		$MeNO_2$	138c
	Se	Se	Ph	H	Ph	1	795		$MeNO_2$	138c
	Se	Se	Ph	H	Ph	2	910		$MeNO_2$	138c
	Se	Se	Ph	H	Ph	3	1035		$MeNO_2$	138c
47	Te	Te	Ph	H	Ph	0	759	15.8	CH_2Cl_2	139a
	Te	Te	Ph	H	Ph	1	885	28.2	CH_2Cl_2	139a
	Te	Te	Ph	H	Ph	2	1010	15.1	CH_2Cl_2	139a
	Te	Te	*t*-Bu	H	*t*-Bu	1	810	16.6	H_2O	140a
48	O		Ph	H	Ph	1	800	8.5	CH_2Cl_2	138a
	O		Ph	H	Ph	2	910	12.0	CH_2Cl_2	138a
	S		Ph	H	Ph	1	865	7.1	CH_2Cl_2	138a
	S		Ph	H	Ph	2	1000	10.7	CH_2Cl_2	138a
	NMe		Ph	H	Ph	2	728		CH_2Cl_2	138a
	NMe		CH=CH—CH=CH		H	2	706.8	25.4	MeOH	4a
	NMe		CH=CH—CH=CH		H	3	816.4	23.4	MeOH	4a
49a	O		Ph				1408		o-$C_6H_4Cl_2$	141a
49b	O		2-thienyl				1510		o-$C_6H_4Cl_2$	142
49a	S		Ph				1495	8.5	o-$C_6H_4Cl_2$	141a
49b	S		2-thienyl				1610		o-$C_6H_4Cl_2$	142
50						1	716	19.6	MeOH	143
						2	826		MeOH	143
51a						1	760	13.20	$MeNO_2$	144a
						2	860	19.96	$MeNO_2$	144a
						3	972	21.20	$MeNO_2$	144a
51b						1	698	8.25	THF/Li^+	145a
						2	855		THF/Li^+	145a
						3	950		THF/Li^+	145a
51c						1	850		$MeNO_2$	145b
						2	930		$MeNO_2$	145b
52a						2	778	20.0	DMF	146
						3	881		DMF	146
						4	1000		DMF	146
52b						2	686	15.8	DMF	146
						3	780		DMF	146
						4	915		DMF	146
53							775	12.4	MeCN	147c
							820	11.7		
54						1	640	4.6	$(CH_2Cl_2)_2$	148a,b
							836	10.3		
						2	715	3.9	$(CH_2Cl_2)_2$	148a,b
							954	9.1		
55						2	781		MeOH	149a
56						1	714	5.4	MeCN	150c
							764	5.4		
						2	815	8.1	MeCN	150c
							886	9.5		
57						1	738	6.4	CH_2Cl_2	150b
						2	830	8.0	CH_2Cl_2	150b
58						2	584.5		CH	151a
						2	716		MeOH	151a
						3	606.5		CH	151a
						3	820		MeOH	151a
59	CMe_2		*n*-$C_{12}H_{25}$	*n*-C_6H_{13}	C_2H_4OH		785	30.1	EtOH	152

[a] In nm. [b] In M^{-1} cm^{-1}.

SCHEME X



SCHEME XI



and anionic polymethine dyes, such as **51a**/**51b** and **52a**/**52b** reveals that near-IR absorption occurs independent to the molecular charge provided that the chain length is sufficiently long (see Table V). The λ_{max} values of **52** are, however, shifted from the near-IR to the visible region on passing from the ions to the nonsymmetric neutral compounds (X_1 = NH,X_2 = N).[146] An interesting series of polymethine dyes with relatively long wavelength absorptions is that containing mesoionic end groups such as **56** and **57**. Dyes of the vinylogous series **56** consist formally of a polymethine oxonol chain and two terminal pyridinium fragments.

Uncharged dyes of the type **58** with $n \geq 2$ are examples of merocyanine (neutrocyanine) dyes which absorbs in the near-IR if dissolved in polar solvents (see Table V). The absorption maxima of this class of dyes are more or less sensitive to solvent effects (cf. section IV.G.1). Branched conjugated dyes such as **59** also belong to the neutrocyanines. They have been tested in optical recording materials.[152]

In order to increase the thermal and photochemical stability of near-IR cyanine dyes, the polymethine chain has been partially fixed by incorporating part of the chain into one[168] or more alicyclic rings[169] (e.g. **10**). The cycloaliphatic bridge can contain either heteroatoms or heteroatomic groups (O, S, NMe, etc.).[170] This structural modification results in small spectral shifts. Marked spectral effects occur with strongly electron donating or strongly electron withdrawing substituents on the chain.[171]

Some near-IR absorbing cyanine dyes have polymethine chains that are incorporated into carbo- or heterocyclic ring systems.[172] Formation of an antiaromatic ring structure through cyclization of the polymethine chain leads to deeply colored compounds.[173]

An interesting class of neutrocyanines are the squarylium and croconium dyes **60** and **61**[174-177] (Scheme XI). Some relevant spectral data are collected in Table VI. In general, squarylium dyes are close in wavelength to the cationic dinuclear cyanine dyes. They differ formally from them by substitution of H by O^- in the meso position of the chain and symmetrical bridging of the neighboring carbon atoms by the carbonyl group.[178] However, their structure appears to be more complex and cannot be represented by a single formula.[179] A comparison of croconium and squarylium dyes show the former to be more bathochromic[180] (cf. Table VI). A considerable bathochromic shift has also

Table VI. Spectral Data of Squarylium (60) and Croconium Dyes (61)

compd	X	λ_{max}[a]	$10^{-5}\epsilon$[b]	solvent	ref
60a		813	0.84	EtOH	174b
60b	S	667	1.6	$CHCl_3$	4a
60b	Se	683	1.0	$CHCl_3$	175
60b	CH=CH	706.6	2.63	MeOH	4a
60c		865		EtOH	174c
60d	O	815, 910	0.62, 0.66	DMF	174a
60d	S	885, 975	0.53, 0.51	DMF	174a
60f		842		$CHCl_3$	174d
60g		765.5	1.32	CH_2Cl_2	4a
60h		996	1.51	$CHCl_3$	176
60i		704	2.19	$CHCl_3$	174e
61b	S	771.3	2.23	MeCN	4a
61b	Se	789.5	2.00	MeCN	4a
61b	CH=CH	831.4	2.22	MeCN	4a
61e		954.2	2.75	$CHCl_3$	4a
61j		715	0.58	$CHCl_3$	177
62h		935	0.81	$CHCl_3$	176
63h		956	0.97	$CHCl_3$	176

[a] In nm. [b] In M^{-1} cm^{-1}.

been observed if the O^- in **60** is replaced by OMe.[175] Some diaminophenyl-substituted squarylium dyes, which show absorption maxima at about 650 nm only in solution, absorb in the near-IR in the solid state.[29,181]

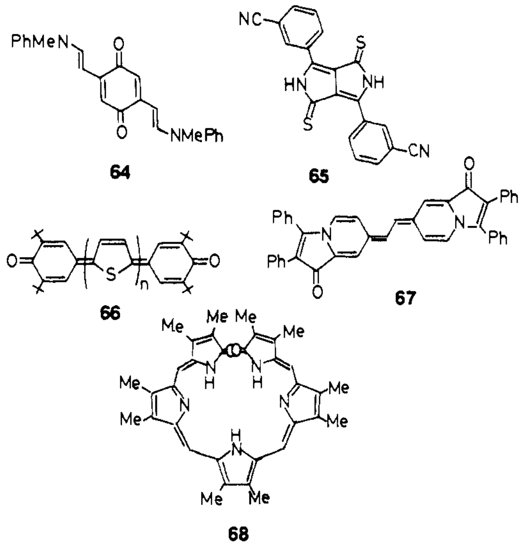
The methinologs of **62** and **63** of the betainic dyes **60** and **61** are, in principle, cross-conjugated merocyanines, which are related to ketomerocyanines. They absorb at shorter wavelengths than the betainic dyes even if they have a more extended conjugated system. Derivatives of the ullazine of these series, however, absorb in the near-IR.[176] Ketomerocyanines display a strong bathochromic shift if protonated, and near-IR absorption bands have been recorded in acids.[182]

Cyanine dyes are used as laser dyes[183] (emission wavelength up to 1800 nm[184a]). Near-IR absorbing cyanines have large nonlinear susceptibilities and fast response and decay times and are therefore strong candidates as materials for all-optical signal processing devices between 1000 and 1600 nm.[184b] Applications in photoreprography and optical data storage devices have been already mentioned in section II. Straight chain tricarbo- and pentacarbocyanines as well as squarylium and croconium dyes have proven to be of particular interest in this field. As already mentioned in section IV.B, the photostability of the dyes is increased if Ni dithiolene complexes or other metal complexes are added. Experiments in photochemotherapy dealt with derivatives of cryptocyanine (**47**, $n = 1$, X = NR, R_1,R_2 = CH=CH—CH=CH)[185] and tellurocarbocyanine (e.g. **11**, cf. section II.F).

The dyes previously mentioned are principally capable of forming dimers and aggregates which, in contrast to monomers, may exhibit absorption bands in the near-IR. J-type aggregates absorb more strongly at longer wavelengths than the corresponding monomers. Likewise, a bathochromic shift into the near-IR region has been observed for bichromophoric dyes[186] (cf. section IV.G.1).

Finally some dyes of a more complex structure are considered (**64**–**68**, Scheme XII). Compound **64** (λ_{max} = 725 nm, log ϵ = 3.67)[187] and **65** (718 nm, log ϵ = 3.77),[188] which absorb relatively weakly, may be seen as being composed of two conjugatively linked meropolymethinic chains whereas, **66** ($n = 3$, 785 nm, log ϵ = 4.77, $n = 4$ 830 nm, log ϵ = 4.45),[189] **67** (800 nm, log ϵ = 4.66),[190] and **68** (720 nm, log ϵ = 3.93)[191] are cross-conjugated merocyanines. The latter compound is deeply colored although the porphyrin ring structure is broken. Isoporpyrines such as **34** are another series with this structure. Compounds **64** and **66** may be alternatively assigned to the quinoid and **67** to the indigoid chromophores.

SCHEME XII



D. Diphenylmethane, Triphenylmethane, and Related Dyes

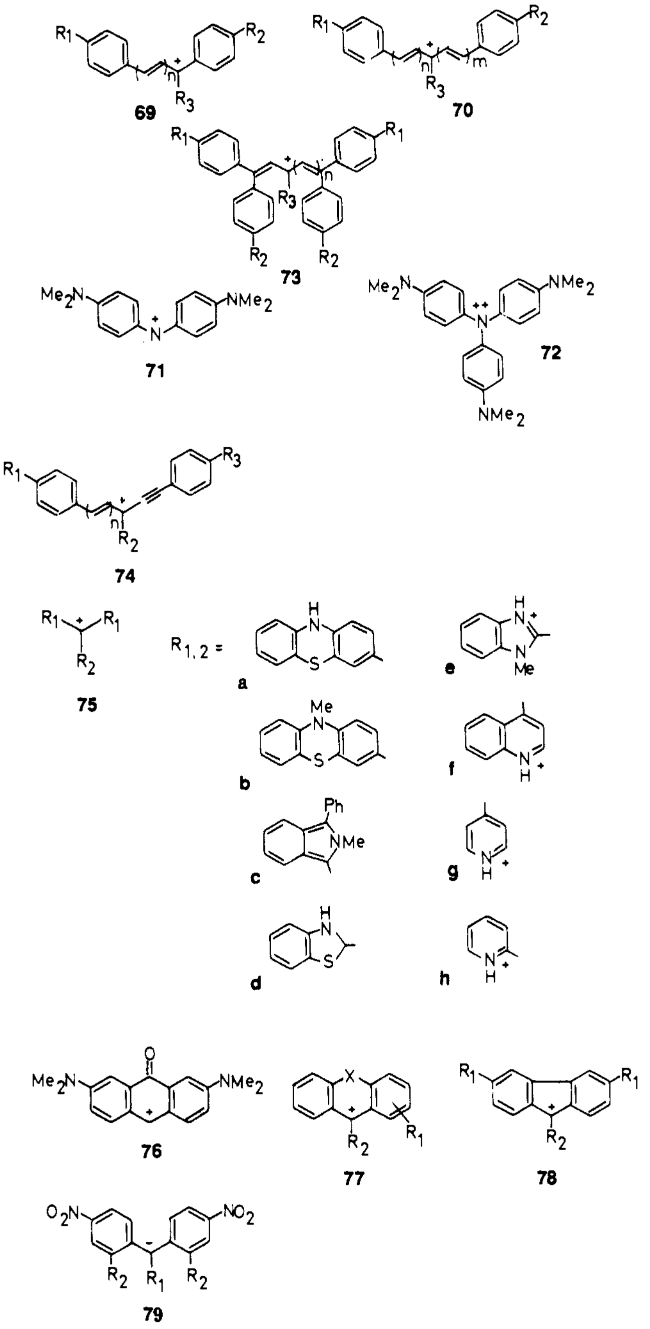
Introduction of conjugated HC=CH and —C≡C— units into the classical diphenylmethane and triphenylmethane dyes results in dyes **69** and **70** (Scheme XIII) which absorb in the near-IR[192-196] (Table VII). The vinylene shift which depends on the terminal donor substituents of the diphenylmethane and triphenylmethane dyes is about 70–100 nm. In the diphenylmethane dye series, introduction of an acceptor substituent CN at the central carbon and replacement of the central carbon atom by the more electronegative nitrogen give rise to a significant red shift. This is in agreement with Dewar's color rules. The dyes **69** ($n = 0$, $R_1 = R_2 = NMe_2$, R_3 = CN) and **71** absorb at 716 nm and 725 nm,[2b] respectively. For the same reason a strong bathochromic effect occurs when CH^+ of crystal violet is replaced by N^{2+} (**72**: 920 nm, log ϵ = 4.29 in MeOH[197]).

Dyes in the **73** series are of particular interest in the optical data storage field[198] because they exhibit a very intense absorption band at about 800 nm (log ϵ ~ 5). When substituted with the 2-carboxylatophenyl group (R_3) in the meso position they can form a lactone ring. They are therefore useful as near-IR absorbing color formers.[198c] The absorption bands of the dyes **73** have the x-band in the near-IR region and the y-band in the visible region.[194] Dyes with electron-withdrawing substituents R_2 absorb at longer wavelengths.

Expansion of the conjugated π-electron system achieved through insertion of the acetylene bond results in a bathochromic shift.[200-204] Near-IR dyes with this structure (**74**, Scheme XIII) are presented in Table VIII. The experimental data have been reproduced using PPP calculations.[202]

Replacement of the phenyl ring of the triphenylmethane dyes by heteroatomic fragments results in a

SCHEME XIII



red shift of the x-band[205,206] (Table IX). Only dyes of the structure **75** with protonated heterocyclic residues R_2 absorb in the near-IR region.

Whereas insertion of a heteroatomic bridge in Michlers Hydrolblue (**69**, $n = 0$, $R_1 = R_2 = NMe$, $R_3 = H$) produces a blue shift, the opposite effect occurs with insertion of an acceptor group such as CO. The compound **76** absorbs in the near-IR (850 nm, log ϵ = 4.18 in $MeNO_2$[207]). However, in spite of the heteroatomic bridge dyes of the structure **77** absorb in the near-IR if $R_2 = H$ is replaced by $C{\equiv}C{-}C_6H_4NMe_2$[202,204] (Table X). A decrease in the electronegativity of *X* results in a bathochromic shift.

In agreement with perturbational considerations and PPP calculations a strong red shift occurs on ring closure to the fluorenyl cations **78**[208-210] (Table X). An absorption band with a relatively small intensity is observed between 900 and 1000 nm. A hypsochromic shift of the long wavelength absorption is observed with donor substituents R_2. The double peak observed in the near-IR region may be due to components of a vibrational fine structure of a single electronic transition. Dyes such as **78** substituted by the 2-carboxylatophenyl group are in turn of interest for use as color formers since they absorb in the 700–900-nm region.[211]

Finally carbanions such as **79** should be mentioned. If these compounds are substituted by more than one nitro group, they absorb at more than 700 nm[212,213] (Table XI).

E. Quinone Dyes

Dyes based on the quinone chromophore are widely used in the modern dyestuff industry, and a wide range of colorants have been commercialized. The chemistry of quinone dyes has been thoroughly reviewed by Venkataraman[214] in 1971. Gordon and Gregory[84c] also reviewed recent advances in the anthraquinone dye chemistry in 1983, although they did not describe the infrared absorbing quinone dyes.

Quinone molecules are well known as electron acceptors. Introduction of donors and/or acceptors into the quinone nucleus produces visible to infrared absorption with intramolecular charge-transfer character. 1,4-Naphthoquinone and 9,10-anthraquinone are the main chromophores for the colorants. The chromophoric system has been quantitatively evaluated using the PPP method.[215]

The first synthesis of a near-IR absorbing 1,4-naphthoquinone was reported by Griffiths et al.[216] in 1978. They obtained 5-amino-8-anilino-2,3-dicyano-1,4-naphthoquinone (**80**, Scheme XIV) by the reaction of 5-amino-2,3-dicyano-1,4-naphthoquinone with aniline in ethanol. In acetone this compound has a λ_{max} at 759 nm. This novel direct 8-arylamination was reexamined by Kasai et al.[217] and Matsuoka et al.[218] 5,8-Bis(arylamino- and 5-amino-8-hydroxy-2,3-dicyano-1,4-naphthoquinones, which also absorb light in the near infrared region, were isolated as byproducts.

Matsuoka et al.[219] reported on the reaction of 2,3-dichloronaphthazarin with potassium 2-aminobenzenethiolate to give a new type of deeply colored bis-ring-closure product **81** which was obtained in the quinone form. It absorbs light at 725 nm. Similar ring closure reactions of quinizarins with 2-aminothiophenol have been reported by Peters et al.[220] They obtained the mono-ring-closure products which absorb light in the visible region. This type of novel ring-closure reaction produced many infrared absorbing quinone dyes. Zinc 2-aminobenzeneselenate reacts similarly to give the selena analog of **81**. This compound absorbs light at 727 nm, i.e. at slightly longer wavelength than **81** (λ_{max} = 725 nm).[221] A similar reaction of tetrabromonaphthazarin with potassium 2-aminobenzenethiolate gives the corresponding 1,5-bis-ring-closure product **82** which absorbs at 780 nm. This compound is more bathochromic than **81**.[222] Nishi et al.[223] obtained a similar phenothiazinequinone dye **83** (723 nm) through the reaction of chloroaniline with aniline followed by reaction with zinc 2-aminobenzenethiolate in dimethylformamide.

The anthraquinone analogs **84** (Scheme XIV) were also synthesized from 2,3-dihalogenoquinazarin.[224] They absorb between 712 and 720 nm and thus at somewhat

Table VII. Spectral Data of Di- and Triphenylmethane Dyes

no.	*n*	*m*	R_1	R_2	R_3	$\lambda_{max}{}^a$	$10^{-4}\epsilon^b$	solvent	ref
69	0		NMe_2	NMe_2	CN	716	5.37	$MeNO_2$	171g
69	1		NMe_2	NMe_2	H	710	21.5	CH_2Cl_2	161
	2		NMe_2	NMe_2	H	800	32.0	CH_2Cl_2	161
	3		NMe_2	NMe_2	H	880	34.0	CH_2Cl_2	161
	4		NMe_2	NMe_2	H	980	38.0	CH_2Cl_2	161
69	5		H	H	H	714	2.9	H_2SO_4	2b
	6		H	H	H	758	3.3	H_2SO_4	2b
70	1	0	NMe_2	NMe_2	Ph	713		AcOH	192
	2	0	NMe_2	NMe_2	Ph	810		AcOH	192
70	1	0	NMe_2	NMe_2	PhCH=CH	765		AcOH	192
70	1	1	NMe_2	NMe_2	Ph	815		AcOH	192
70	1	1	NMe_2	NMe_2	PhCH=CH	830		AcOH	192
73	0		NMe_2	H^c	H	755	10.4	$CHCl_3$	194
	1		NMe_2	H	H	833	20.8	$CHCl_3$	194
	2		NMe_2	H	H	935	19.5	$CHCl_3$	194
73	2		NMe_2	Cl	H	942	15.1	$CHCl_3$	194
73	1		OMe	OMe	Cl	723	3.63	AcOH	196

[a] In nm. [b] In M^{-1} cm^{-1}. [c] For derivatives of **73** with various R_2 and *n* = 0–2 (λ_{max} 740–911 nm), see refs 193–196.

Table VIII. Spectral Data of Ethynologs of Di- and Triphenylmethane Dyes (74)

n	R_1	R_2	R_3	$\lambda_{max}{}^a$	$10^{-4}\epsilon^b$	solvent	ref(s)
0	NMe_2	$4\text{-}(NMe_2)C_6H_4$	NO_2	713	8.14	CH_2Cl_2	200
0	NMe_2	$4\text{-}(NMe_2)C_6H_4$	NMe_2	727	8.51	CH_2Cl_2	201, 202
0	H	Ph	NMe_2	705	3.89	CH_2Cl_2	203, 202
1	NMe_2	Ph	NMe_2	814	7.24	CH_2Cl_2	201

[a] In nm. [b] In M^{-1} cm^{-1}.

Table IX. Spectral Data of Heterocyclic Compounds Related to Triphenylmethane Dyes (75)

$R_1{}^d$	$R_2{}^d$	$\lambda_{max}{}^a$	$10^{-4}\epsilon^b$	solvent	ref
a	C_6H_5	865	3.98	AcOH	205
b	C_6H_5	815	3.55	AcOH	205
c	d	777	2.34	$MeOH/H_2O^c$	206
c	e	721	4.37	$MeOH/H_2O^c$	206
c	f	730	3.24	$MeOH/H_2O^c$	206
c	g	732	1.91	$MeOH/H_2O^c$	206
c	h	722	4.79	$MeOH/H_2O^c$	206

[a] In nm. [b] In M^{-1} cm^{-1}. [c] Containing H_2SO_4. [d] See Scheme 13 for structures.

Table X. Spectral Data of Dyes 77 and 78

no.	X	R_1	R_2	$\lambda_{max}{}^a$	$10^{-4}\epsilon^b$	solvent	ref(s)
77	O	H	$[4\text{-}(NMe_2)C_6H_4]C{\equiv}C$	737	7.24	CH_2Cl_2	202, 204
77	S	H	$[4\text{-}(NMe_2)C_6H_4]C{\equiv}C$	775	8.71	CH_2Cl_2	202, 204
77	Se	H	$[4\text{-}(NMe_2)C_6H_4]C{\equiv}C$	802	8.51	CH_2Cl_2	202, 204
78		NMe_2	Ph^c	955 850	2.0 1.7	AcOH	193, 208
78		NMe_2	$4\text{-}(NMe_2)C_6H_4$	850	1.7	AcOH	193, 208
78		NMe_2	$PhC{\equiv}C$	1052 927	1.94 1.29	CH_2Cl_2	209
78		NMe_2	$[4\text{-}(NMe_2)C_6H_4]C{\equiv}C$	956 718	1.53 8.02	CH_2Cl_2	209

[a] In nm. [b] In M^{-1} cm^{-1}. [c] Dye 78 with the heterocyclic residue (R_2 = 2-(2-OHC_6H_4)-3-indonyl) absorbs at 879 nm (log ϵ = 3.98 in $MeOH/H^+$).[210]

shorter wavelengths than the corresponding naphthoquinone products **81**. The introduction of additional acceptor groups (Y) into ring A of dye **84** is possible. Consequently many types of infrared absorbing anthraquinone dyes of structure **84** can be synthesized.[225]

Indonaphthol dyes are well known for their cyan color in photography. They have been widely studied by Weissberger et al.[226] According to the results of molecular design using the PPP method, introduction of an acceptor group into the quinone moiety and/or of donor groups into the aniline moiety is expected to produce a bathochromic shift of λ_{max}.[227] Introduction of 2-carboxamide brings about a bathochromic shift of about 120–150 nm, and the resulting dyes **85** (X = CONHR, Y = H) absorb light at 690–730 nm. The 2,3-dicyano derivative of **85** (X,Y = CN)[228] absorbs light at 795 nm. A 212-nm bathochromic shift of λ_{max} is associated with the introduction of a dicyano group into the quinone moiety. The latter is very unstable and gradually reduces to the corresponding leuco compound.

Table XI. Spectral Data of 79

R_1	R_2	$\lambda_{max}{}^a$	$10^{-4}\epsilon^b$	solvent	ref
H	H	704	4.06	ETOH/DMSO	212a
$4\text{-}NO_2\text{-}C_6H_4$	H	775	4.43	HMP^c/NaOMe	212b
H	H	787	5.83	HMP^c/NaOMe	212b
		782	9.7	DMSO/NaOMe	213
H	NO_2	712	3.0	EtOH/KOH	212c
		708	5.4	DMSO/NaOMe	213
$2,4\text{-}(NO_2)_2C_6H_3$	NO_2	715		EtOH/KOH	212c

[a] In nm. [b] In M^{-1} cm^{-1}. [c] HMP = hexamethylphosphoramide.

Yoshida et al.[229a,230,231a] synthesized cyanomethine derivatives of indonaphthol **86** through the reaction of 1-naphthylmalonitrile or 1-naphthylcyanoacetamide with *p*-(*N*,*N*-dialkylamino)aniline in the presence of an oxidizing agent under alkaline conditions. These compounds absorb light between 720 and 760 nm in chloroform. PPP calculations confirm a strong intramolecular charge-transfer character for the first excited state of the chromophores. The cyanoimino derivatives of indonaphthol are related to these near-IR dyes.[231b]

The synthesis of a series of quinoid ligands has led to infrared absorbing metal complex dyes. These are the 5,8-quinolinediones (**87**),[129c] 1,2-naphthoquinones (**88**),[129d] 1-aza-9,10-anthraquinones (**89**),[232] azaindonaphthols (**90**),[129a,b] and dihydro-3-(phenylimino)pyrido[2,3-*a*]phenothiazines (**91**).[129f,233] All of these absorb light in the visible region as free ligands but after the formation of 1:1 or 2:1 (metal:ligand) metal complex with Ni^{2+} or Cu^{2+} ions they absorb in the IR region. The bathochromic shifts range from 30 up to 250 nm. The ϵ-values attained after metal complex formation are 1–10 times those of the free ligands. Since these are new classes of near-IR dyes some data are also

SCHEME XIV

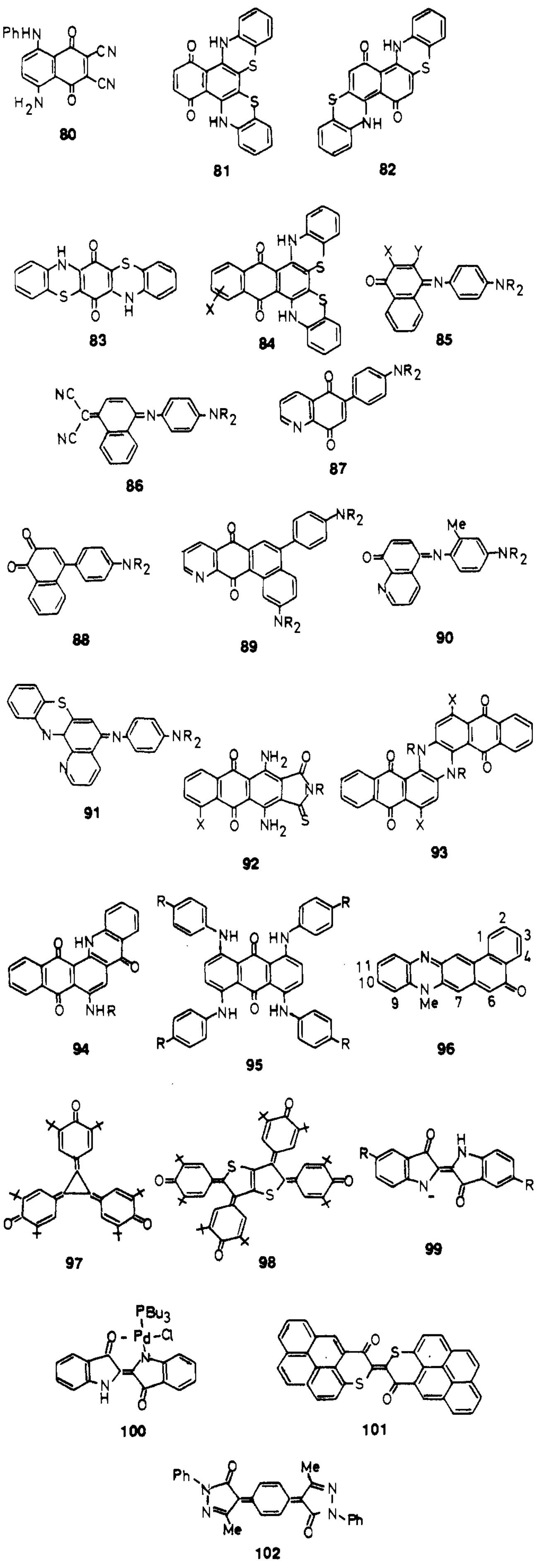


Table XII. Spectral Data of Quinoid Dyes

no.	substituent	λ_{max}[a]	$10^{-4}\epsilon$[b]	solvent	ref
80a		774	1.67	$CHCl_3$	218
81a		725	1.50	$CHCl_3$	219
82		750	3.24	$CHCl_3$	219
84	X = H	712	1.50	$CHCl_3$	224
86	R = Me	722	2.55	$CHCl_3$	229a
87	R = Et, Cu complex	769	5.89	EtOH	129c
88	R = Et, Cu complex	779	2.34	EtOH	129d
90	R = Et, Cu complex	776	14.45	EtOH	129a
92	X = H, R = *n*-C_6H_{13}	763		*c*	235
93	X = H, R = NHPh	790	5.50	$PhNO_2$	236
94	Ar = Ph	721	1.29	*d*	237a
95	R = alkyl	741	3.31	EtOH	238
96	6,10,11-Cl_3	710	1.60	DMF	239
97		769	5.13	benzene	240
98		782	3.47	benzene	241

[a] In nm. [b] In M^{-1} mol^{-1}. [c] In liquid crystal. [d] In trichlorobenzene.

presented in Table IV. Yoshida et al. have recently reported a series of dyes incorporating a redox system **90**.[233] The leuco dyes **90** easily produce intense absorption bands in the near-IR region on metal chelate complexation–oxidation and will form a new class of color formers.

Some anthraquinone derivatives absorb light over 700 nm. These include the *N*-alkyl-12,12a-dihydro-1,4-diaminoanthraquinone-3′-thio-2,3-dicarboximides (**92**) which are employed as deeply colored dichroic dyes for guest-host liquid crystal displays and optical recording media.[234,235] The well-known indanthrene pigments **93**[236] are also employed as optical recording media, and 2-(arylamino)-3,4-phthaloylacridones (**94**)[237] are used as deeply colored disperse dyes or pigments. Tetrakis(arylamino)anthraquinones (**95**) absorb light at 740 nm and are useful as organic filters in diode lasers.[238] 8-Methylnaphtho[1,2-*b*]phenazin-5(8*H*)-one (**96**)[239] absorb at about 700 nm. The novel branched conjugated quinoid dyes **97**[240] and **98**[241] absorb strongly at 770 and 782 nm, respectively.

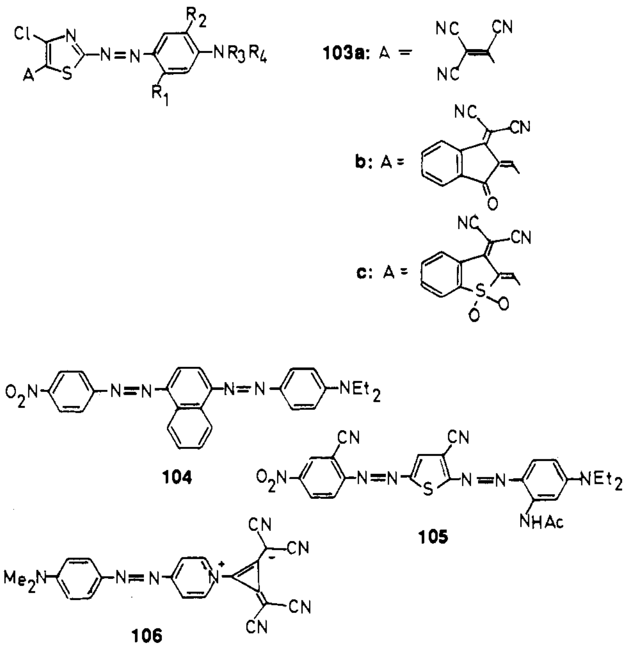
Indigo absorbs light at 605 nm but its monoanions **99** (R = H, R = SO_3K) and the metal complex **100** absorb at considerably longer wavelengths (773 nm[242] and 748 nm,[243] respectively). According to ref 244a *trans*-pyrenothioindigo **101** exhibits an absorption band at 728 nm, whereas the cis isomer absorbs in the visible region only. A significant red shift has recently been observed when the ethylenic bond of indigo dyes is replaced by a quinoid one such as in **102**[244b] (705 nm, log ϵ = 3.76, in $CHCl_3$) and related indigoids. Spectral data of some typical quinoid near-IR dyes are presented in Table XII.

F. Azo Dyes

Because of their usefulness as dispersion dyes[245–247] and in guest–host liquid crystals[248] much research into deeply colored azo dyes was stimulated. Absorptions at long wavelengths are produced if azo dyes bear electron-donor groups and electron-withdrawing groups in different parts of the molecule. The benzenoid fragments may be replaced by heterocyclic units. In the case of cationic compounds the dyes are diazacyanine dyes.

Only few azo dyes display absorption maxima at more than 700 nm. Griffiths and co-workers[249] were the first to synthesize near-IR monoazo dyes such as **103**

SCHEME XV



(Scheme XV) (**103a**, 725 nm, log ε = 4.88; **103b**, 700 nm, 4.83, $R_{1,2}$ = H, $R_{3,4}$ = Et in both cases; **103c**, 778 nm, 4.92, R_1 = NHAc, R_2 = OMe, R_3 = H, R_4 = $CHMeBu^n$, in CH_2Cl_2). These dyes show positive solvatochromism. The λ_{max} values are displaced to longer wavelengths by around 25 nm on going from CH_2Cl_2 to the more polar DMSO.

Another series of near-IR dyes are the polykisazo dyes.[248,250] Two typical bisazo dyes are **104** (710 nm, log ε = 4.33 in $CHCl_3$) and **105** (706 nm in AcOEt).[248b,250] Less is known about the structure of polykisazobenzenes in concentrated sulfuric acid where λ_{max} values of up to about 800 nm have been recorded for long-chain compounds.[251] Some metal complex bis- and trisazo dyes show good light sensitivity in the visible, near-IR, and IR regions[252] (cf. section IV.B). They are resistent to heat and light[253] and are used for printing and in plate making for near-IR lasers.[253,254a] For applications in lasography see section II.C. They are also found in near-IR readable inks.[254b]

The intense absorption of the above previously mentioned dyes are due to π–π* excitations.[248,255] Many of them have intramolecular charge transfer character.[255] The large absorption intensity, however, indicates marked electron delocalization in the ground and lowest energy π–π* excited states. This increases on going from the neutral azobenzene to the cationic diazacyanine dyes.

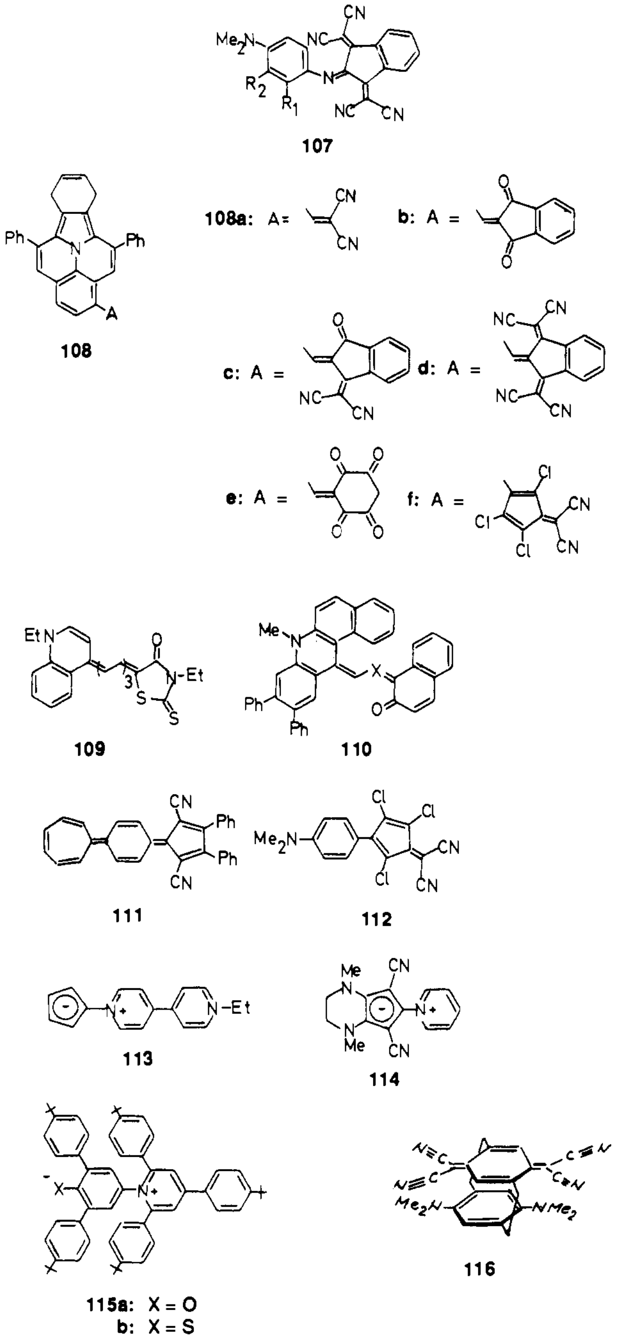
In structure **106** the [(dimethylamino)phenyl]azo group obviously increases the acceptor strength of the CT chromophore giving rise to an absorption at more than 700 nm (λ_{max} = 708 nm, log ε = 4.96, in MeCN[256]). Such as these chromophores are discussed in the following section.

G. Miscellaneous Chromophoric Systems

1. CT-type ππ Chromophores*

Dyes of low symmetry composed of two or more loosely joined fragments may display intramolecular charge transfer (ICT) bands. In such cases, one fragment is a donor and the other an acceptor, and partial electron transfer occurs on π–π* excitation. The donor and acceptor strengths determine the absorption wavelength. The λ_{max} values of the azamonomethines for example, increase on going from **107** ($R_{1,2}$ = H) to **107** (R_1,R_2 = HC=CHCH=CH) (Scheme XVI) from 755 nm (log ε = 4.41) to 850 nm in CH_2Cl_2[257a] due to the increased donor strength of the aryl substituent. The bathochromicity is increased if N is replaced by CCN.[257b] As shown by Balli and Kleiner[176], substituents of different acceptor strength bring about a strong shift in the λ_{max} (log ε) values in the ullazine (indolizino-[6,5,4,3-*ija*]quinoline) derivative series **108** in $CHCl_3$: **a**, 608 (4.58); b, 662 (4.68); **c**, 763 (4.82); **d**, 836 (4.74) **e**, 1007 (3.08); **f**, 1040 (4.00).

SCHEME XVI



The charge migration on excitation is connected to a change in the dipole moment which, in turn, results in appreciable solvent effects.[258] Absorption in the near-

IR occurs if the donor and acceptor strength are sufficiently strong and the bonding between the fragments is weak. Otherwise the π-electron system will be delocalized and the ICT character of the excitation is low.

In spite of strong delocalization of the π-electron system in composite donor–acceptor compounds such as in many meropolymethines (merocyanines) as well as quinone and azo dyes, the lowest energy excitation retains some ICT character. In **109**, the dipole moment increases on excitation and a positive solvatochromism has been observed on going from apolar to protic solvents[151a] (CH, 606.5 nm; MeOH, 820 nm). The opposite behavior has been found for **110** (X = N: $CHCl_3$, 773 nm; EtOH, 703 nm).[259] The latter shows negative solvatochromism. Because of some interfragmental overlap the absorption coefficients of the ICT bands of these dyes are relatively high (log $\epsilon \sim 3$). The quinarene 111 (C_6H_5Br: 934 nm) exemplifies another series of compounds which display negative solvatochromism.[260]

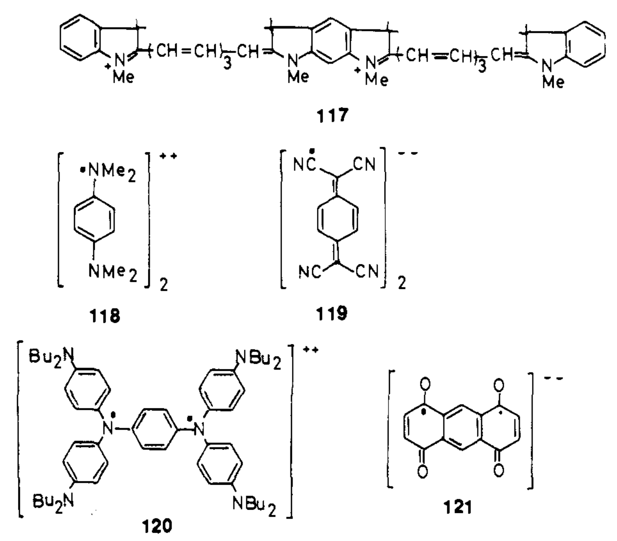
Junek and co-workers synthesized some carbodinitriles which absorb above 700 nm[261,262] (e.g. 112: 755 nm, log $\epsilon = 3.90$ in CH_2Cl_2[261]). At this point, some more or less solvatochromic cationic zeromethine dyes should be mentioned.[263] In these dyes heterocyclic or carbocyclic donor groups are immediately linked to the heterocyclic acceptor groups such as pyrylium or thiopyrylium.[263] They also absorb at more than 700 nm.

Another series of near-IR chromophores are zwitterionic compounds,[258,264,265] e.g. 113,[265] 114,[265] and 115[264i] (λ_{max} values more than 700 nm in nonpolar solvents). As shown by Reichardt and co-workers *N*-pyridinium phenolates such as 115 display very strong solvatochromic effects and are therefore used as solvent indicators.[258] The absorption band of 115 is shifted from the near-infrared into the visible region if the polarity of the solvent is increased (**115a** cyclohexane, 924 nm; MeOH, 524.8 nm;[264i] **115b** chlorocyclohexane, 828 nm; MeOH, 488 nm[264j]).

Staab and co-workers[266,267] described donor–acceptor cyclophanes with broad bands in the near-IR. The compounds show positive solvatochromism, e.g. **116** (in *n*-C_6H_{14}, 827 nm; in DMSO, 1094 nm). Cyclophanes such as **116** are related to electron donor–acceptor (EDA) complexes which are formed between donor and acceptor compounds in less polar solvents. They may also be deeply colored due to a broad weak intermolecular charge transfer band.

The spectral data of EDA complexes have been reported elsewhere.[268] They have been extensively studied, with hydrocarbons and their donor-substituted derivatives[268,269] and heterocycles[270] serving as donors and TCNE and TCNQ as acceptors. A bathochromic shift occurs if TCNE and TCNQ are replaced by 2,3-dichloro-5,6-dicyano-*p*-quinone.[271] Near-IR absorbing EDA complexes have been described with additional nitriles[272] as well as with carbo- and heterocyclic cations.[273] Intermolecular EDA complexes between carbazoles and naphtho- and anthraquinones absorbing in the near-IR have been studied in search of optical recording media for diode lasers.[274] Complexes between organic compounds in different oxidation states such as aromatic amines and diiminium cations[275] have also been discussed. However, radicals or dimeric structures generated through electron transfer may account for the observed near-IR absorption (see vide infra).

SCHEME XVII



In general, absorption maxima in solution are very similar to those measured either in the solid state or in KBr pellets.[276] This is not necessarily the case if the donor and/or acceptor strength of the component is large. Long wavelength absorptions may be either due to pure ionic radical salts (cf. section IV.G) or mixed-valence complexes (absorbing up to the middle IR).[277] The mixed valence complexes may exhibit electrical conductivity (organic metals). Their optical properties are similar to those of conducting polymers i.e. they are due to metallic free carrier interband absorptions.[278] The electronic transitions of doped polymers have been discussed in terms of both soliton and bipolaron defects.[278d-f]

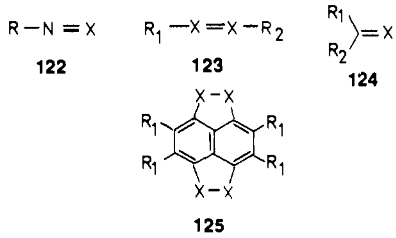
2. CR- and MX-type $\pi\pi^*$ Chromophores

If two identical chromophoric fragments are weakly joined in a single molecule or if molecules dimerize through a "two-way charge transfer" this can also be considered as charge resonance (CR). CR configurations will more or less generally mix with molecular exciton (MX) type configurations of chromophoric substructures. The excited state is, however, essentially of the MX-type if the interaction is weak and negligible.

An MX-type interaction in composite molecules results in a splitting of the longest wavelength absorption band. The longest wavelength component, therefore, is more strongly shifted to the near-IR relative to the absorption band of the subchromophores or the monomeric chromophores. The intensity of the first absorption band is very large if the chromophores are laterally shifted rather than arranged in a stacklike fashion. Near-absorbing MX/CR chromophores are contained in various bichromophoric dyes[279,180] and dye aggregates.[281] The bichromophoric cyanine dye 117 (Scheme XVII) absorbs at both 688 nm (log $\epsilon = 4.97$) and 827 nm (5.49) in $MeNO_2$, whereas the dye containing the subchromophore absorbs at about 740 nm.[279]

Such interactions may also account for bathochromic shifts observed on going from solution to the crystalline state. There are dyes of practical importance which absorb in the near-IR in the solid state only, e.g. squaraines,[29,181] triphenodioxazines,[282] and 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dithione.[35]

SCHEME XVIII



Mutual charge transfer has also been used to explain the near-IR absorption bands ("CT band") of dimer radicals that are diamagnetic in contrast to the monomers.[283,284] The dimer radicals of phenylenediamine **118** and TCNQ **119** absorb at longer wavelengths than the respective monomers (about 800 nm[285] and 1200 nm,[286] respectively). Dimeric substructures are also found in various radical salts in the solid state if the radical molecules are arranged in segregated stacks.[277a,287]

Very long wavelength absorption are observed if two radicals are joined by a chemical bond. The color of some dications (e.g. **120**, λ_{max} = 1090 nm, log ϵ = 5.02 in CH_2Cl_2)[4a] and dianions (e.g. **121**, λ_{max} = 866 nm, log ϵ = 4.15 in DMF)[288] might be understood in terms of such an interaction between two radical fragments such as indicated by the formulae **120** and **121**. With respect to the MO's involved in the lowest energy excitation, the near-IR absorption can also be discussed in terms of a π–π excitation in the case of **114** and as π^*–π^* excitation in the case of **121**.

Dications related to **120** have been studied in relation to the optical recording media.[289] For additional dications and dianions absorbing at more than 700 nm see refs 290 and 291, respectively. The dianion of a triquinoid compound absorbs strongly at 1900 nm in DMF (log ϵ = 4.87).[291a] In a study of hexaazaoctadecahydrocoronene cations its tetracation has also been identified. It absorbs at about 1000 nm.[292]

3. Non $\pi\pi^*$ Chromophores

$\sigma\pi^*$ and $\pi\sigma^*$ near-IR chromophores generally display low absorption intensities. Most nitroso compounds absorb at more than 700 nm,[293] but azo,[294] thiocarbonyl,[295] and selenocarbonyl compounds[296] absorb only in this region with substituents that strongly increase the electron affinity. Less is known about thionitroso compounds absorbing in the near-IR.[297] Spectral data for **122**–**125** (Scheme XVIII) are given in Table XIII. Absorption bands of these compounds show negative solvatochromism and are well described in terms of n–π^* transitions. Tertiary nitrosoalkanes in solid polymer matrices have been used for holographic recordings using diode lasers.[298]

Cyclic conjugated disulfides display weak absorption at long wavelengths which have been interpreted as π–σ^* excitations.[299] Some 1,2-dithioles and hetero analogs absorb at more than 700 nm.[300] As shown for 1,4,5,8-tetrachalcogenonaphthalenes (**125**, R_1 = Me) the absorption wavelengths of the first maxima increases on passing from X = S via Se to Te (cf. Table XIII). These compounds form semiconductive complexes with TCNQ.

Table XIII. Spectral Data of $\sigma\pi^*$- and $\pi\sigma^*$-Chromophoric Compounds

no.	X	R_1	R_2	λ_{max}[b]	ϵ[c]	solvent	ref
122	O	Ph		750	45.0	MeCN	293b
	S	NMe_2		705	1.5	CH	297
123	N	$SiMe_3$	$SiMe_3$	785	5	hexane	294a
	N	$OC(CEt_2)CO$		724	37	CH_2Cl_2	294b
124	S	$SiMe_3$	$SiMe_3$	(756)[d]			295a
	S	H_4C_6–C_6H_4[e]		759	8	3-methylpentane	295c
	Se	t-Bu	t-Bu	710	21	CH	296a
	Se	H	Mes[f]	758	39	hexane	296b
125	S	Me		700	56	$CHCl_3$	300a
	Se	Me		855	167	$CHCl_3$	300a
	Te	Me		1028	148	$CHCl_3$	300a

[a] First absorption maximum in the case of vibrational fine structure. [b] In nm. [c] In M^{-1} cm^{-1}. [d] Estimated from ^{13}C chemical shifts. [e] o,o′-Biphenyl. [f] Mes = mesityl.

H. Radical Dyes

A large number of radical organic compounds with conjugated bond systems are known to be deeply colored. Many of them are transient cations or anions formed through the oxidation or reduction of organic compounds. They are also generated by exposing organic compounds to ionizing radiation (electrons and γ and x-rays) in appropriate matrices. Shida and coworkers have performed systematic spectroscopic studies in γ-irradiated gamma frozen solutions of Me–THF (formation of anions) and in BuCl (formation of cations).[301]

Near-IR absorbing cation and anion radicals have been obtained through the ionization of various conjugated hydrocarbons and heterocycles.[301–303] The spectra of radical ions of polyenes[278f,302,303] including carotinoides,[304] acenes up to hexacene,[302,305] perylene and derivatives,[306] pyrroles,[307] and porphyrins[308] have been more extensively studied. In agreement with the pairing theorem, the spectra of cation and anion radicals of alternant hydrocarbons closely correspond to each other. Acceptor-substituted benzenes favor formation of anion radicals (e.g. near-IR absorbing ketyls[301,302]) and donor substituted benzenes favor those of cation radicals (e.g. near-IR absorbing tri- up to hexa-substituted benzenes[309]).

The above mentioned radicals are in general less stable and sensitive to air. Moreover, the first absorption band may be of low intensity, e.g. in the case of aromatic hydrocarbons.[305,310] The resulting detection of these absorptions is more difficult using absorption measurements although its position has been indirectly estimated in many cases using photoelectron spectroscopy.[310,311] In the case of Koopmans-type transitions, the difference in the first ionization energies of the neutral compound corresponds approximately to the lowest energy electronic transition of the radical cation. The same holds for the difference of the lowest energy electron affinities as determined by electron transmission spectroscopy of the neutral molecule. This difference corresponds approximately to the lowest energy transition energy of the radical anion.[312]

As shown and reviewed by Zahradnı̆k and Čarský[313] the absorption features of such radicals are well reproduced semiempirically by means of the LHP method. There is a regular shift of the first absorption band to longer wavelengths if the chain length is extended.

The derivatives of substituted benzenes, heterocyclic compounds, and quinones are more stable radical ions.[314–325] They contain branched conjugated polymethine structures, such as in **126**–**135** (Scheme XIX). Relevant data are collected in Table XIV. Most of these radicals absorb intensively in the near-IR region (log $\epsilon \sim 4$). As demonstrated for **135** (R = 2,5-*tert*-butylphenyl) λ_{max} values as large as 1700 nm have been found.

The near-IR absorptions of di- and triaryl aminiumyl cations **126**[314] have been studied in solution. These are mostly compounds of green color. The anionic counterparts are borenate radical anions that absorb intensively at about 800 nm.[326]

Deeply colored Wurster-type salts obtained by oxidation of *p*-phenylenediamines or benzidines (**127**, n = 0,1, X = NR_2) are relatively stable compounds.[315] Examples are the various salts of anionic radicals derived from strong electron acceptors, such as quinones (e.g. **128**, n = 0, X = O)[316] and tetracyanoquinodimethanes (e.g. **128**, n = 0, X = $C(CN)_2$).[317,327] Many compounds containing radical anions have been synthesized in the search for organic conductors.[325] For the same reason, radical cations of tetrathiofulvalenes and their hetero analogs and vinylogs of the general structure **129** have received much attention.[318] The related dendralenes should also be mentioned.[290e] Radicals such as **129** and **130** are known as Weitz-type radicals.

The radicals **131**–**135** are derived from heterocyclic 6-membered rings (phenodiazines,[320] phenothiazines,[321] and thianthrenes[322]), from heterocyclic azines,[323] from dithioles,[62a,324] or from di- and triquinone and derivatives.[325] Spectroelectrochemical studies have furnished a great variety of spectral data. The practical application of radical dyes has been studied in ECD displays sensitive to near-IR light.[328] Near-IR absorbing Weitz-type radicals are also generated in redox photochromic systems.[329]

Dimerization ("pimerization") of Wurster-type radicals such as **127**[285] and Weitz-type radicals such as **130**[319] in solution or in the solid state lead to absorption at longer wavelengths than the corresponding monomers.

The diazatetramethine radical **136** is a derivative of a short chain polymethine dye. It absorbs in the near-IR (λ_{max} = 1150 nm).[330] The absorption maxima of radical dyes undergo a regular shift to longer wavelengths in vinylogous series such as **137**–**141**[331] (Table XV). Vinylogous dyes have been extensively studied by Hünig and co-workers. These radicals are "semiquinones" (SEM), i.e. intermediates of a two-step redox reaction (OX $\rightleftharpoons$ SEM $\rightleftharpoons$ RED).[332] The first absorption band of the polymethine structures **137**–**141** display a regular shift in wavelength of around 100 nm. MO theory predicts two absorption bands at long wavelengths. Experimentally structured absorption bands are observed. An additional electronic transition not yet identified may also be involved.

The previously mentioned vinylogous radicals are counterparts of the nonradical polymethine cyanines. They are also known as polymethine violenes. The Wurster- and Weitz-type radicals mentioned earlier are branched conjugated representatives of this series.

Finally some neutral radicals which are well characterized in solution should be mentioned. Some which are less sensitve to air were obtained as liquids and crystals. Spectral data of a few neutral **142**–**149** radicals

SCHEME XIX

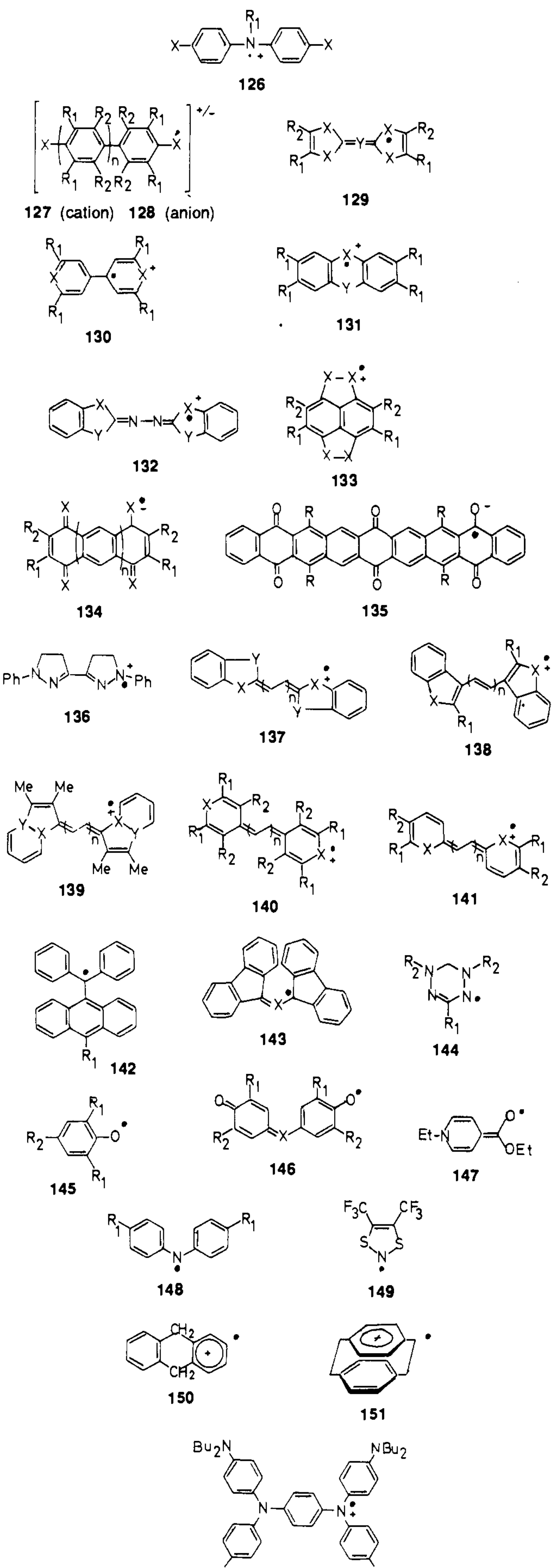


Table XIV. Spectral Data of Wurster- and Weitz-type Radicals

no.	X	Y	R_1	R_2	*n*	λ_{max}[a]	$10^{-3}\epsilon$[b]	solvent	ref
126	Me		H			714		CF_3COOH	307a
	OMe		H			~780		KBr	314b
	Me		C_6H_4Me			720		KBr	314d
	OMe		C_6H_4OMe			723	24.4	CH_2Cl_2	314g
	Br		C_6H_4Br			727	20.9	CH_2Cl_2	314f
127	NPh_2		H	H	0	820		MeCOMe	6c
	SMe		H	H	0	725, 787		H_2SO_4	315d
	NMe_2		H	H	1	1075		*s*-BuCl	301
	NPh_2		H	H	1	1240		MeCOMe	6c
	OMe		H	H	1	~800	~15.8	$MeNO_2$, $AlCl_3$	315e
128	O		CH=CH—CH=CH		0	890, 1010		Me–THF	301
	O		H	H	1	800	7.5	MeCN	316
	O		Br	H	1	775	2.3	MeCN	316
	$C(CN)_2$		H	H	0	842	40.5	MeCN	317b
	NO_2		H	H	0	926		Me–THF	301
	NO_2		H	H	1	1480		Me–THF	301
129	S	CH=CH	CH=CH—CH=CH			782	11.7	PhCN	318g
	S	1,4-C_6H_4	CH=C(Me)—CH=CH			762		MeCN	318e
	S	CSMe=CSMe	SMe	SMe		980			318d
	Se		H	H		700	5.1	MeCN	318f
	S	CH=CH	H	H		760			290e
	S	2,6-$C_{10}H_6$	Me	Me		785		MeCN	318g
130	NME		Ph			770	8.3	MeCN	319
	O		Ph			785	22.4	MeCN	319
	S		Ph			868	20.9	MeCN	319
131	NMe	NMe	H			719	1.63	MeCN	320c
	NMe	S	H			784, 880	4.5, 4.5	CH_2Cl_2	321f
	S	S	H			920, 1050		H_2SO_4	322c
	S	S	OMe			840	10.0	$MeNO_2$	322d
	Se	Se	OMe			820	11.0	$MeNO_2$	322d
132	NMe	NMe				686	10.47	MeCN	323a
	NMe	O				793	9.12	MeCN	323a
	NMe	S				814	11.7	MeCN	323a
	NMe	Se				860	11.5	MeCN	323a
	NMe	CMe_2				955	9.3	MeCN	323a
133	S		CH=CH—CH=CH			1267	5.0	MeOH	324a
134	O		H	H	0	900	4.5	DMF	325c
	O		H	H	1	1560	16.2	DMF	325c
	O		CH=CH—CH=CH		1	1335	4.5	DMF	325c
	NCN		CH=CH—CH=CH		1	1520	15.0	DMF	325d
135[c]						1730	26.9	DMF	325e,f

[a] In nm. [b] In M^{-1} cm^{-1}. [c] R = 2,5-di-*tert*-butylphenyl.

are collected in Table XVI. Whereas near-IR absorbing triarylmethyl radicals are only known in solution,[333] some allyl type radicals are more stable.[334,335] Verdazyls (e.g. **144**) are green crystalline compounds and were extensively studied by Kuhn and Neugebauer.[335] The long wavelength absorption band is due to a π–π^* transition.[336a] Because of their fluorescence they have been tested as dye lasers.[336b] another interesting series is the phenoxide radicals.[337] The relatively stable blue **145** (*R* = *t*-Bu) absorbs most strongly in the visible region[337a] but the λ_{max} is shifted to the near-IR if *t*-Bu is replaced by Ph[337b] (cf. Table XVI). Many galvanoxyls **146** (X = CH) and their aza analogs (X = N) absorb in the near-infrared.[338] Both the galvanoxyl[338a] and verdazyl chromophore[338b] have also been incorporated into polymeric chains.[339]

Diradicals and triradicals of verdazyl[340] and galvanoxyl[337d] behave spectroscopically as mono radicals but spin pairing has been found using ESR spectroscopy. The λ_{max} values of the bi(or tri-)chromphoric dyes corresponds closely to that of the monomer but their intensity is twice (threefold) that of the monomer. The interaction between the chromophoric substructures is obviously very weak. This is due to the node properties of the singly occupied MO's of the radical fragments.

Weak and broad absorption bands tailing into the near-IR region have also been observed for the rather stable pyridinyl[341a] (e.g. **147**) and oxoindolizinyl radicals.[190] Both series of radicals may be considered as branched-conjugated polymethines or, according to Viehe and co-workers,[342] as radicals stabilized by the captodative effect. Some vat dyes absorb in the near-IR absorption because they contain radical species.[343]

Near-IR absorption maxima have also been reported for some aminyl[344] (e.g. **148**) and hydrazinyl radicals.[345] 4,5-Bistrifluoromethyl)-1,3,2-dithiazolyl (**149**) is an example of a thermally stable heterocyclic radical which undergoes in part pimerization on passing from the gas to the liquid state.[346] The near-absorption at about 740 nm is only weak.

Two near-IR chromophores of radicals may be weakly joined in a single molecule displaying the absorption features of the radical components. Compounds like that are formed, for example, if the ethano-bridged viologene pyromellitimide accepts an electron resulting in a zwitterionic biradical structure.[347]

Extremely long wavelength absorptions are expected if the unpaired electron is distributed over two weakly joint molecular fragments of the same structure. Shida and co-workers actually found absorption maxima as large as 2000 nm by converting hydrocarbons bridged

Table XV. Spectral Data of Polymethine Violenes

no.	X	Y	R_1	R_2	n	λ_{max}[a]	solvent	ref
136						1150	MeCN	330
137	NMe	CMe_2			1	774	MeCN	331a
					2	884	MeCN	
					3	996	MeCN	
					4	1135	MeCN	
					5	1290	MeCN	
	NMe	S			2	814	MeCN	331b
					3	959	MeCN	
138	NMe		H		0	720	MeCN	331c
					1	845	MeCN	
					2	930	MeCN	
	NMe		Me		1	834	MeCN	331c
					2	930	MeCN	
					3	1063	MeCN	
139	N	CH			1	982	MeCN	331d
					2	1112	MeCN	
					3	1258	MeCN	
					4	1420	MeCN	
	CH	N			1	1010	MeCN	331d
					2	1118	MeCN	
					3	1240	MeCN	
					4	1350	MeCN	
140	NMe		H	H	1	783	MeCN	331g
					2	926	MeCN	
					3	1073	MeCN	
	NMe		CH═CH—CH═CH		1	935	MeCN	331g
					2	1093	MeCN	
					3	1264	MeCN	
	O		*t*-Bu	H	1	740	CH_2Cl_2	331e
	O		Ph	H	0	785	MeCN	319
					1	925	CH_2Cl_2	331e
141	NMe				2	724	MeCN	331g
					3	860	MeCN	
	NMe		CH═CH—CH═CH		1	882	MeCN	331g
					2	983	MeCN	
					3	1096	MeCN	

[a] In nm. [b] In M^{-1} mol^{-1}.

Table XVI. Spectral Data of Neutral Radicals

no.	X	R_1	R_2	λ_{max}[a]	$10^{-3}\epsilon$[b]	solvent	ref
142		H		780	11.7	SO_2	333a
		Ph		820	12.0	SO_2	333a
143	CPh			860	1.6	dioxan	334a
	N			787	~2.0	dioxan	334a
144		*t*-Bu	$C_6H_4NO_2$	704	8.5	dioxan	335d
		Ph	Ph	720	4.3	C_6H_6	335a
145		Ph	Ph	750	3.0	propanol	337b
146	CH	*t*-Bu	*t*-Bu	770	2.9	CCl_4	338b
	CH	*t*-Bu	Ph	815	1.9	CCl_4	338b
	N	Ph	Ph	840	3.0	CCl_4	338b
147				632.6[c]	0.08	MeCN	341a
148		Me		~735		benzene	344
		OMe		740		benzene	344
		NMe_2		784	8.7	benzene	344
149				738	0.26	hexane	346

[a] In nm. [b] In M^{-1} cm^{-1}. [c] Broad absorption band up to more than 900 nm.

via methylene groups or linked to paracyclophanes into ions (e.g. **150**, 1960 nm and **151**, 805 nm, in Me–THF.[301] Near-IR absorptions are also observed for ions which consist of two weakly linked aryl[301] or heteroaryl residues.[132,301,348]

Further examples are cations derived from phenylenediamine and related compounds. According to Matsuoka[4a] **152** absorbs at 950 nm (log ϵ = 4.38) and 1470 nm (log ϵ = 4.31) in CH_2Cl_2. Compounds such as these proved of interest due to their usefulness as near-IR absorbing dyes in heat and pressure recording materials.[289,349]

The long wavelength absorptions mentioned above are reminescent of those observed with the bisferrocene TCNQ complex (1550 nm, log ϵ = 3.28).[350a] In that case the near-IR absorption is due to the bisferrocene cation which is of a mixed valence structure (intervalence transfer bands).[350b]

V. Summary and Outlook

There are a great number of organic compounds that absorb intensively above 700 nm and up to about 1300 nm due to electronic excitation. The basic acyclic near-IR chromophores (polymethine dyes) as well as the basic cyclic near-IR chromophores (annulenes, porphyrines, and tetraazaporphins) are well known. They can be widely modified through substitution, annelation, complex formation, etc. Empirical knowledge and semiempirical quantum chemical approaches such as the π methods HMO, PPP, or LHP permit the prediction of designer dyes that absorb at definite wavelengths within this absorption region. Structurally more complex near-IR dyes with some meropolymethinic, quinonoid, and/or indigoid character will eventually be found. Color–structure–relationships are at present better known and more reliably predictable for closed shell than for open shell systems. Absorption in the mid-infrared is observed for organic metals but so far has been less well studied.

After the search for photographic materials capable of sensitizing up about 1300 nm and dyes lasing up to about 1800 nm, the more recent interest in near-IR dyes has been directed to developing photoreceptors of diode lasers that emit tunable light at about 800 nm. Applications to optical memory devices have strongly revived research. Naphthalocyanine and quinone dyes are relatively stable dyes, whereas cyanine dyes have to be to stabilized by additives. In some interesting new applications near-IR dyes are produced in photochromic processes, or near-IR absorbing radical dyes are generated through chemical or electrochemical redox processes.

If diode lasers that emit tunable light in the UV/vis region become available near-IR dyes on optical disks may be replaced by conventional dyes. However, near-IR dyes will continue to attract increasing interest in photodynamic therapy due to the fact that tissue penetration using near-IR dyes is optimal in the near-IR spectral region (~760 nm).

There is no reliable information available concerning the upper limits of absorption wavelengths of molecular species on going to longer wavelengths. Theoretical predictions must be considered with caution as long as the molecular geometry of large π-systems is unreliably predicted and electron correlation not treated better. Singlet molecules of very low electronic excitation energy are biradicaloid and may undergo molecular distortion because of vibronic interactions. The conventional semiempirical quantum chemical methods mentioned above do not take electron correlation sufficiently into consideration. Here is a definite need for better methods, and MCSCF-CI and RPA look promising in this account.

Abbreviations, Conventions, and Dimensions

near-IR	near infrared
λ_{max}	wavelength at maximum absorption, in nm
ϵ	molar decadic absorption coefficient, in cm^{-1} M^{-1} (= L mol^{-1} cm^{-1} = cm^2 $mmol^{-1}$)
CH	cyclohexane
DMF	dimethylformamide
DMS	dimethyl sulfoxide
THF	tetrahydrofuran
TCNE	tetracyanoethylene
TCNQ	tetracyanodiquinomethane

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VI. References

(1) (a) Jones, F. *Rev. Prog. Color. Relat. Top.* **1989**, *19*, 20. (b) Matsuoka, M. *J. Soc. Dyers Colour.* **1989**, *105*, 167. (c) Griffiths, J. *J. Soc. Dyers Colour.* **1988**, *104*, 416. (d) Yoshida, Z., Kitao, T., Eds. *Chemistry of Functional Dyes*; Mita Press: Tokyo, 1989.

(2) (a) Zollinger, M. *Colour Chemistry. Synthesis, Properties and Applications of Organic Dyes and Pigments*; VCH: Weinheim, 1987. (b) Fabian, J.; Hartmann, H. *Light Absorption of Organic Colorants. Theoretical Treatment and Empirical Rules*; Springer Verlag: Berlin, 1980. (c) Griffiths, J. *Colour and Constitution of Organic Molecules*; Acad. Press: London, 1976. (d) Hünig, S.; Quast, H. In *Optische Anregung organischer Systeme*; Verlag Chemie: Weinheim, 1966; pp 184 ff.

(3) (a) Matsuoka, M., Ed. *Infrared Absorbing Dyes*; Plenum: New York, 1990. (b) Artamonova, T. V.; Zakhs, E. R.; Khromenkov, O. V.; Shaburov, V. V. *Izv. Vys. Ucheb. Zaved., Khim. Techn.* **1989**, *32*, 2.

(4) (a) Matsuoka, M. *Absorption Spectra of Dyes for Diode Lasers*; Bunshin Publ. Co.: Tokyo, 1990. (b) Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem.* **1989**, *101*, 1475; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1445. (c) Ishchenko, A. A.; Slominskii, Yu. L.; Tolmachev, A. I. *Ukrain. Khim. Zh.* **1989**, *55*, 979. (d) Nakazumi, H. *J. Soc. Dyers Colour.* **1988**, *104*, 121. (e) Fujimoto, M.; Sato, G. *Shikizai Kyokaishi* **1988**, *61*, 215; *Chem. Abstr.* **1988**, *109*, 14450c.

(5) Piccard, J. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 1843; *J. Am. Chem. Soc.* **1926**, *48*, 2352.

(6) (a) Alt, W. Doctoral Dissertation, Technical University of Dresden, 1933. (b) Ertaman, M. Doctoral Dissertation, University of Basel, 1952. (c) Zenhäusern, U. Doctoral Dissertation, University of Basel, 1965.

(7) (a) Kõnig, W. *Z. Wiss. Photogr. Photophys. Photochem.* **1935**, *34*, 15. (b) Dieterle, W.; Zeh, W. *Wiss. Photogr. Photophys. Photochem.* **1935**, *34*, 245. (c) Hamer, F. M. In *Chemistry of Heterocyclic Compounds*; Interscience: New York, 1964; Vol. 18, and references given therein.

(8) Jones, O. T. G. *Chlorophyll in Photochemistry*; Reinhold Comp.: Van Norstrand, 1973; p 75.

(9) Luk'yanets, E. A. *Electronic Spectra of Phthalocyanines and Related Compounds*; Cherkassi, 1989; Catalogue (in Russian).

(10) (a) Umehara, M.; Abe, M.; Oba, H. *J. Syn. Org. Chem. Jpn.* **1985**, *43*, 334. (b) Abe, M. *Organic Recording Materials for Optical Disc*; Bunshin Pub.: Tokyo, 1989.

(11) (a) Case Western Res. Univ. Jpn. Kokai Tokkyo JP 61 1772871, 1986; *Chem. Abstr.* **1987**, *107*, 106491d. (b) Nikles, D. E.; Jones, R.; Sidney, J.; Kuder, J. E. Jpn. Kokai Tokkyo JP 61 235188, 1986; *Chem. Abstr.* **1987**, *106*, 224572h; U.S. Pat. 4605607, 1986; *Chem. Abstr.* **1986**, *105*, 200633g. (c) Hayashida, S.; Tai, S. Eur. Pat. Appl. EP 254553, 1988; *Chem. Abstr.* **1989**, *110*, 48533t; Eur. Pat. Appl. EP 296876, 1988, *Chem. Abstr.* **1989**, *111*, 105880a.

(12) (a) Hirose, S.; Ozawa, H.; Abe, K.; Hosono, Y. Jpn. Kokai Tokkyo JP 61 268487, 1986; *Chem. Abstr.* **1987**, *107*, 124687b; Jpn. Kokai Tokkyo JP 62 90291, 1987; *Chem. Abstr.* **1987**, *107*, 246772w; (b) Eda, T. Jpn. Kokai Tokkyo JP 61 25886, 1986; *Chem. Abstr.* **1986**, *105*, 200579u. (c) Law, K. Y.; Johnson, G. E.; Lin, J. W. P. U.S. Pat. 4492750, 1985; *Chem. Abstr.* **1985**, *102*, 158202b.

(13) Itoh, M.; Esho, S.; Nakagawa, K. Proc. *SPIE-Int. Soc. Opt. Eng.* **1983**, *420*, 332.

(14) Arakawa, S.; Kondo, H.; Seto, J. *Chem. Lett.* **1985**, 1805.

(15) (a) Darcy, P. J.; Heller, H. G.; Strydom, J. P.; Whithall, J. *J. Chem. Soc., Perkin Trans. 1*, **1981**, 202. (b) Heller, H. G. see ref 1d; p 267. (c) Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803.

(16) Nagae, Y. see ref 3a; p 141. (b) Sasaki, A.; Kurahashi, K.; Takagi, T. *Conf. Rec. IEEE Conf. Display Devices* **1972**, 161. (c) Maydan, D.; Melchior, H.; Kahn, F. J. *Conf. Rec. IEEE Conf. Display Devices* **1972**, 66. (d) Nagae, Y.; Kaneko, E.; Mori, Y.; Kawakami, H. *Proc. SIF* **1987**, *28-1*, 55.

(17) Urabe, T.; Usui, H.; Arai, K.; Ohnishi, A. Proceedings of the 3rd International Research Conference (Japan Display) 1983, 486.

(18) Nagae, Y.; Takasaka, M.; Kitajima, M.; Kawakami, H. Technical Report, Japan TV Engineering Association, ED892, 45, 1985.

(19) Lu, S.; Davies, D. H.; Albert, R.; Chung, D.; Hochbaum, A.; Chung, C. *SID 82 Digest* **1982**, 238.

(20) Kakuta, A. see ref 3a; p 155.

(21) Schaffert, R. M. *IBM J. Res. Develop.* **1971**, *15*, 75.

(22) Kakuta, A.; Mori, Y.; Morishita, H. *IEEE Trans. Ind. Appl.* **1981**, IA-*17*, 382.

(23) Umeda, M. *Electrophotography* **1988**, *27*, 539 (in Japanese).

(24) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.

(25) Hackett, C. F. *J. Chem. Phys.* **1971**, *53*, 3178.

(26) Yagishita, T.; Ikegami, K.; Narusawa, T.; Okuyama, H. *IEEE Trans. Ind. Appl.* **1984**, *IA-20*, 1642.

(27) Takano, S.; Enokida, T.; Kakuta, A.; Mori, Y. *Chem. Lett.* **1984**, 2037.

(28) Bluhm, T. L.; Wagner, H. J.; Loutfy, R. O. *J. Mater. Sci. Lett.* **1983**, *2*, 85.

(29) Loutfy, R. O.; Hor, A. M.; DiPaola-Baranyi, G.; Hsiao, C. K. *J. Imaging Sci.* **1985**, *29*, 116.

(30) Kobayashi, T.; Uyeda, N.; Suito, E. *J. Phys. Chem.* **1968**, *72*, 2446.

(31) Borsenberger, P. M.; Weiss, D. S. *J. Imaging Technol.* **1989**, *15*, 6.

(32) Tanaka, T.; Hirohashi, R. *Electrophotography* **1986**, *25*, 284 (in Japanese).

(33) Ohta, K. *Electrophotography* **1986**, *25*, 303 (in Japanese).

(34) DiPaola-Baranyi, G.; Hsiao, C. K.; Kazmaier, P. M.; Burt, R.; Loutfy, R. O.; Martin, T. I. *J. Imaging Sci.* **1988**, *32*, 60.

(35) Mizuguchi, J.; Rochat, A. C. *J. Imaging Sci.* **1988**, *32*, 135.

(36) Katagiri, K.; Oguchi, Y.; Takasu, Y. *Nippon Kagaku Kaishi* **1986**, *387* (in Japanese).

(37) Suzuki, Y. see ref 3a; p 173.

(38) Hamilton, J. F. In *The Theory of the Photographic Process*, 4th ed.; James, T. H., Ed.; Macmillan: New York, 1977; Chapter 5.

(39) West, W.; Gilman, P. B. see ref 38; Chapter 10.

(40) Tani, T.; Kikuchi, S. *Photogr. Sci. Eng.* **1967**, *11*, 129.

(41) Tani, T.; Mihara, Y. see ref 3a; p 183.

(42) Sternberg, E.; Dolphin, D. see ref 3a; p 193.

(43) Auler, H.; Banzer, G. *Z. Krebsforsch.* **1942**, *53*, 65.

(44) (a) Lipson, R. L.; Blader, E. J.; Olsen, E. M. *J. Natl. Cancer Inst.* **1961**, *26*, 1. (b) Dougherty, T. J. *Cancer Res.* **1988**, *32*, 2628.

(45) Photofrin II is marketed by Quadra Logic Technologies, Vancouver, British Columbia.

(46) Dougherty, T. J. *Photochem. Photobiol.* **1987**, *46*, 569.

(47) Seis, H. *Angew. Chem.* **1986**, *98*, 1061; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1058.

(48) Dorion, D. R. Porphyrin Localization and Treatment of Tumors. In *Progress in Clinical and Biological Research*; (Dorion, D. R., Gomer, C. J., Eds.) Alan R. Liss: New York, 1984; Vol. 170, p 46.

(49) Detty, M. R.; McKelvey, J. M.; Luss, H. R. *Organometallics* **1986**, *5*, 2250.

(50) Wohrle, D.; Isakandar, N.; Wendt, A. Lasers in Medical Science, 3, Abstract 1988, 60.

(51) Rodgers, M. J. A. Private communication, 1988.

(52) (a) Irie, K.; Shirosuki, M.; Ando, T.; Nakajima, S.; Samejima, N.; Kakiuchi, Y.; Sakata, I.; Kashimizu, K. Lasers in Medical Science, 3, Abstract 1988, 61. (b) Beems, E. M.; Dubbelman, T. M. A. R.; Lugtenburg, J.; Van Best, J. A.; Smeets, M. F. M. A.; Boegheim, J. P. T. *Photochem. Photobiol.* **1987**, *46*, 639.

(53) Fincher, C. R.; Ozaki, M.; Tanaka, M.; Peebles, D.; Lauchlan, L.; Heeger, A. J.; MacDiarmid, A. G. *Phys. Rev. B, Condens. Matter* **1979**, *20*, 1589.

(54) (a) Blanchard-Desce, M.; Ledoux, I.; Lehn, J.-M.; Malthete, J.; Zyss, J. *J. Chem. Soc., Chem. Commun.* **1988**, 737. (b) Slama-Schwok, A.; Blanchard-Desce, M.; Lehn, J.-M. *J. Phys. Chem.* **1990**, *94*, 3894. (c) Scheibe, P.; Schneider, S.; Dõrr, F.; Daltrozzo, E. *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 630.

(55) Dähne, S. *Science* **1978**, *199*, 1163, and references given therein.

(56) (a) Eierman, M.; Stowasser, B.; Hafner, K.; Bierwirth, K.; Frank, A.; Lerch, A.; Reusswig, J. *Chem. Ber.* **1990**, *123*, 1421. (b) Ott, N.; Rewicki, D. *Angew. Chem.* **1982**, *94*, 80; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 68.

(57) (a) Blattman, H.-R.; Heilbronner, E.; Wagniere, G. *J. Am. Chem. Soc.* **1968**, *90*, 4786. (b) Woo, E. P.; Sondheimer, F. *Tetrahedron* **1970**, *26*, 3933. (c) Calder, I. C.; Garrat, P. J.; Longuet-Higgins, H. C.; Sondheimer, F.; Wolovsky, R. *J. Chem. Soc. C* **1967**, 1041. (d) Gilb, W.; Schröder, G. *Chem. Ber.* **1982**, *115*, 240.

(58) (a) Katakami, T.; Fukui, K.; Okamoto, T.; Nakagawa, M. *Bull. Soc. Chem. Jpn.* **1976**, *49*, 297. (b) Nomoto, T.; Fukui, K.; Nakagawa, M. *Bull. Soc. Chem. Jpn.* **1976**, *49*, 305. (c) Tomita, S.; Nakagawa, M. *Bull. Soc. Chem. Jpn.* **1976**, *49*, 302. (d) Ojima, J.; Katakami, T.; Nakaminami, G.; Nakagawa, M. *Bull. Soc. Chem. Jpn.* **1976**, *49*, 292. (e) Akiyama, S.; Iyoda, M.; Yoshitsugu, K.; Furuoka, M.; Nakagawa, M. *Bull. Soc. Chem. Jpn.* **1978**, *51*, 3351. (f) Iyoda, M.; Akiyama, S.; Nakagawa, M. *Bull. Soc. Chem. Jpn.* **1978**, *51*, 3359. (g) Akiyama, S.; Nomoto, T.; Iyoda, M.; Nakagawa, M. *Bull. Soc. Chem. Jpn.* **1976**, *49*, 2579. (h) Iyoda, M.; Miyazaki, H.; Nakagawa,

M. *Bull. Soc. Chem. Jpn.* **1976**, *49*, 2306. (i) Iyoda, M.; Nakagawa, M. *Bull. Soc. Chem. Jpn.* **1978**, *51*, 3363. (j) Morigaki, M.; Iyoda, M.; Nakagawa, M. *Tetrahedron Lett.* **1975**, 2311, 2315. (k) Akiyama, S.; Iyoda, M.; Nakagawa, M. *J. Am. Chem. Soc.* **1976**, *98*, 6410. (l) Nakatsuji, S.; Akiyama, S.; Nakagawa, M. *Tetrahedron Lett.* **1978**, 1483. (m) Tanaka, J.; Tanaka, M.; Morita, M.; Nakagawa, M.; Iyoda, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3458.

(59) Mitchell, R. H.; Williams, R. V.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2560.

(60) Clar, E. *Ber. Dtsch. Chem. Ges. B.* **1942**, *75*, 1330.

(61) Bohnen, A.; Koch, K.-M.; Lüttke, W.; Müllen, K. *Angew. Chem.* **1990**, *102*, 548; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 525. Müllen, K. Private communication 1990.

(62) (a) Perez-Albuerne, E. A.; Johnson, H.; Trevoy, D. J. *J. Chem. Phys.* 1971, *55*, 1547. (b) Balodis, K. A.; Livdane, A. D.; Medne, P. S.; Neiland, O. Ya. *Zh. Org. Khim.* **1979**, *15*, 391. (c) Sandmann, D. J.; Stark, J. C.; Foxman, B. M. *Organometallics* **1982**, *1*, 739.

(63) (a) Eisner, U. *J. Chem. Soc.* **1957**, 3461. (b) Gosmann, M.; Vogt, A.; Franck, B. *Liebigs Ann. Chem.* **1990**, 163. (c) Knübel, G.; Frank, B. *Angew. Chem.* 1988, *100*, 1203; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1170. (d) Le Goff, E.; Weaver, O. G. *J. Org. Chem.* **1987**, *52*, 710. (e) Jux, N.; Koch, P.; Schmickler, H.; Lex, J.; Vogel, E. *Angew. Chem.* **1990**, *102*, 1429; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1385.

(64) Dolphin, D. *The Porphyrins*; Acad. Press: New York, 1978; Vol. 3, Part A.

(65) (a) Hafner, K.; Schneider, G. *Liebigs Ann. Chem.* **1964**, *672*, 194. (b) Hafner, K.; Fleischer, R.; Fritz, K. *Angew. Chem.* **1965**, *77*, 42, *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 69. (c) Jutz, C.; Kirchlechner, R. *Angew. Chem.* **1966**, 78, 493; *Angew. Chem., Int. Ed. Engl.* **1966**, 516. (d) Hafner, K.; Hafner-Schneider, G.; Bauer, F. *Angew. Chem.* **1968**, *80*, 801; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 808. (e) Jutz, C.; Kirchlechner, R.; Seidel, H.-J. *Chem. Ber.* **1969**, *102*, 2301. (f) Anderson, A. G.; Montana, A. F.; MacDonald, A. A.; Masada, G. M. *J. Org. Chem.* **1973**, *38*, 1445. (g) Murata, I.; Nakasuji, K.; Yamamoto, K.; Nakazawa, T.; Kayane, Y.; Kimura, A.; Hara, O. *Angew. Chem.* **1975**, 87, 170; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 170. (h) Nakasuji, K.; Toda, E.; Murata, I. *Angew. Chem.* **1977**, *89*, 821; *Angew. Chem., Int. Ed. Engl.* **1977**, *17*, 784. (i) Tajiro, A.; Hatano, M.; Murata, I.; Nakasuji, K. *Chem. Lett.* **1976**, 543. (j) Todo, E.; Shímazaki, N.; Mukai, T.; Kabuto, C. *Tetrahedron Lett.* **1980**, 4001. (k) Yoshida, Z.; Shibata, M.; Ogino, E.; Sugimoto, T. *Tetrahedron Lett.* **1984**, *25*, 3343. (l) Ito, S. *Pure Appl. Chem.* **1982**, *54*, 957. (m) Hafner, K.; Thiele, G. F.; Mink, C. *Angew. Chem.* 1988, *100*, 1213; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1191. (n) Sugimoto, T.; Shibata, T.; Sakai, A.; Ando, H.; Arai, Y.; Sakaguchi, M.; Yoshida, Z.; Kai, Y.; Kanehisa, N.; Kasai, N. *Angew. Chem.* 1991, *103*, 454.

(66) (a) El'tsov, A. V.; Ginesina, A. A.; Kivokurtseva, L. N. *Zh. Org. Khim.* **1969**, *5*, 2072. (b) El'tsov, A. V.; Ginesina, A. A. *Zh. Org. Khim.* **1967**, *3*, 191. (c) Conner, M. K.; LeGoff, E. *Tetrahedron Lett.* **1970**, 2687.

(67) (a) Ammon, H. L.; Replogle, L. L.; Watts, P. H., Jr.; Katsumot, K.; Stewart, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2196. (b) Boyd, G. V. *J. Chem. Soc.* **1959**, 55. (c) Hayashi, S.; Kurokawa, S.; Matsuura, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1404. (d) Replogle, L. L.; Katsumoto, K.; Morrill, T. C.; Minor, C. A. *J. Org. Chem.* **1968**, *33*, 823. (e) Morril, T. C.; Opitz, R.; Replogle, L. L.; Katsumoto, K.; Schroeder, W.; Hess, B. A. *Tetrahedron Lett.* **1975**, 2077. (f) Nozoe, T.; Asao, T.; Kobayashi, M. *Bull. Soc. Chem. Jpn.* **1973**, *46*, 3161. (g) Porshnev, Yu. N.; Tereshchenko, E. M. *Zh. Org. Khim.* **1974**, *10*, 1315. (h) Hafner, K.; Lindner, H. J.; Wassem, W. *Heterocycles* **1978**, *11*, 387.

(68) Hünig, S. *Pure Appl. Chem.* **1967**, *15*, 109.

(69) Fabian, J.; Hartmann, H. *Theor. Chim. Acta* **1975**, *36*, 351; *J. Mole. Struct.* **1975**, *27*, 67.

(70) (a) Bachilo, S. M.; Bondarev, S. L. *Zh. Prikl. Spektrosk.* **1988**, *49*, 959. (b) Shevedova, L. A.; Boresevich, Yu. E.; Tatikolov, A. S. *Izv. Akad. Nauk, Ser. Khim.* **1983**, 1421. (c) Razi Naqvi, K. *Spectrosc. Lett.* **1987**, *20*, 319. (d) Grajcar, L.; Baudet, J. *J. Mol. Struct.* **1988**, *168*, 205. (e) Kikuchi, K.; Kurabayashi, Y.; Kokubun, H.; Kaizu, Y.; Kobayashi, H. *J. Photochem. Photobiol. A* **1988**, *45*, 261.

(71) Sturmer, D. M.; Gaugh, W. S. *Photogr. Sci. Eng.* **1973**, *17*, 146.

(72) (a) Dyadyusha, G. G.; Kachkovskii, A. D.; Dekhtyar', M. L. *J. Mol. Struct.* **1990**, *217*, 195. (b) Kornilov, M. Yu.; Dyadyusha, G. G.; Zamkovoi, V. I.; Dekhtyar', M. L.; Kachkovskii, A. D. *Khim. Geterots. Soed.* **1984**, 217.

(73) Michl, J.; Thulstrup, E. W. *Tetrahedron* **1976**, *32*, 205.

(74) (a) Zahradník, R. *Fortschr. Chem. Forsch.* **1968**, *10*, 1. (b) Čársky, P.; Zahradník, R. *Top. Curr. Chem.* **1973**, *43*, 1.

(75) (a) Fabian, J.; Zahradník, R. *Wiss. Z. Techn. Univ. Dresden* **1977**, *26*, 315; *Chem. Abstr.* **1977**, 87, 167301g. (b) Kachkovskii, A. D.; Kudinova, M. A.; Shapiro, B.; Derevyanko, N. A.; Kurkina, L. G.; Tolmachev, A. I. *Dyes Pigm.* 1984, 5, 295. (c) Yasui, S.; Matsuoka, M.; Kitao, T. *Dyes Pigm.* **1989**, *10*, 13. (d) Grif, V. Kh.; Nikitchenko, V. M.; Lavrushin, V. F. *Zh. Org. Khim.* **1978**, *14*, 1293.

(76) Grajcar, L.; Baudet, J. *J. Mol. Struct.* (*THEOCHEM*) **1988**, *168*, 205.

(77) Fabian, J.; Zahradník, R. *Angew. Chem.* **1988**, *101*, 693; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 677.

(78) (a) Leupin, W.; Wirz, J. *J. Am. Chem. Soc.* **1980**, *102*, 6068. (b) Cunningham, R. P.; Farquhar, D.; Gibson, W. K.; Leaver, D. *J. Chem. Soc. C* **1969**, 239.

(79) Potts, K. T.; McKeough, D. *J. Am. Chem. Soc.* **1974**, *96*, 4276.

(80) (a) Calder, I. C.; Gaoni, Y.; Sondheimer, F. *J. Am. Chem. Soc.* **1968**, *90*, 4946. (b) Nakatsuji, S.; Morigaki, M.; Akiyama, S.; Nakagawa, M. *Tetrahedron Lett.* **1975**, 1233. (c) Aso, Y.; Iyoda, M.; Nakagawa, M. *Tetrahedron Lett.* **1979**, *43*, 4217.

(81) Zilm, K. W.; Merrill, R. A.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1567.

(82) (a) Linstead, R. P. *J. Chem. Soc.* **1934**, 1016. (b) Byrne, G. T.; Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1017. (c) Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1022. (d) Dent, C. E.; Linstead, R. P. *J. Chem. Soc.* **1934**, 2027. (e) Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1031. (f) Dent, C. E.; Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1033.

(83) (a) Robertson, J. M. *J. Chem. Soc.* **1935**, 615; **1936**, 1195. (b) Linstead, R. P.; Robertson, J. M. *J. Chem. Soc.* **1936**, 1736. (c) Robertson, J. M.; Woodward, I. *J. Chem. Soc.* **1937**, 219; **1940**, 36.

(84) (a) Moser, F. H.; Thomas, A. L. *Phthalocyanine Compounds*; Reinhold: New York, 1963. (b) Booth, G. *The Chemistry of Synthetic Dyes*; Venkataraman, K., Ed.; Academic Press: New York, 1971; Vol. 5, p 241. (c) Gordon, P. F.; Gregory, P. *Organic Chemistry in Colour*; Springer-Verlag: London, 1983; p 219.

(85) Edwards, L.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *33*, 292.

(86) (a) Cook, M. J.; Dunn, A. J.; Howe, S. D.; Thomson, A. J.; Harrison, K. J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2453. (b) Freyer, W.; Minh, L. Q. *J. Prakt. Chem.* **1987**, *329*, 365. (c) Freyer, W. *Z. Chem.* **1986**, *26*, 263. (d) Freyer, W.; Fink, F. *Z. Chem.* **1988**, *28*, 67. (e) Kobayashi, N.; Kondo, R.; Nakajima, S.; Osa, T. *J. Am. Chem. Soc.* **1990**, *112*, 9640. (f) Freyer, W.; Minh, L. Q. *Monatsh. Chem.* **1986**, *117*, 475. (g) Freyer, W. *Z. Chem.* **1988**, *28*, 216, 217. (h) Freyer, W.; Minh, L. Q.; Teuchner, K. *Z. Chem.* **1988**, *28*, 25. (i) Freyer, W.; Teuchner, K. *J. Photochem. Photobiol. A, Chem.* **1988**, *45*, 117.

(87) Tsunehito, E. Eur. Pat. Appl. EP 134 518, 1985; *Chem. Abstr.* **1985**, *103*, 38703q.

(88) Harrison, K. J.; Cook, M. J.; Howe, S. D.; Thomson, A. J. Brit. UK Pat. Appl., GB 2 168 372, 1986; *Chem. Abstr.* **1986**, *105*, 228518.

(89) Firey, P. A.; Ford, W. E.; Sounik, J. R.; Kenney, M. E.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1988**, *110*, 7626.

(90) Iwakabe, Y.; Numata, S.; Kaneshiro, T.; Tai, S.; Hayashida, S.; Hayashi, N. Jpn. Kokai Tokkyo Koho JP 63 72761; *Chem. Abstr.* **1988**, *109*, 112067c.

(91) (a) Nakamura, K.; Shibano, H.; Morikawa, K.; Yamazaki, H. Jpn. Kokai Tokkyo Koho JP 63 95269, 1988; *Chem. Abstr.* **1989**, *110*, 77512r. (b) Nakamura, K.; Shibano, H. M.; Yamazaki, H. Jpn. Kokai Tokkyo Koho JP 63 275584, 1988; *Chem. Abstr.* **1989**, *111*, 79903p.

(92) (a) Era, S.; Kobayashi, S.; Mukoh, A. Eur. Pat. Appl. EP 279 501, 1988; *Chem. Abstr.* **1989**, *110*, 77514t. (b) Tai, S.; Hayashida, S.; Hayashi, N.; Iwakabe, Y.; Numata, S.; Kinjo, N.; Era, S.; Kobayashi, S.; Mukoh, A.; Sato, Y. Eur. Pat. Appl. EP 284 370, 1986; *Chem. Abstr.* **1989**, *110*, 97172h.

(93) Numa, T. Jpn. Kokai Tokkyo Koho JP 63 154767, 1988; *Chem. Abstr.* **1989**, *110*, 116679x.

(94) (a) Kovshev, E. I.; Puchnova, V. A.; Luk'yanets, E. A. *Zh. Org. Khim.* **1971**, *7*, 369. (b) Yamamoto Chemicals Co., Ltd., Jpn. Kokai Tokkyo Koho JP 60 2345, 1985; *Chem. Abstr.* **1985**, *103*, 106304n. (c) Wheeler, B. L.; Nagasubramanian, G.; Bard, A. J.; Schechtman, L. A.; Dininny, D. R.; Kenney, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7404.

(95) Bradbrook, E. F.; Linstead, R. P. *J. Chem. Soc.* **1936**, 1744.

(96) Tamura, S. *Shikizai Kyokaishi* **1985**, *58*, 528.

(97) Rihter, B. D.; Kenney, M. E.; Ford, W. E.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1990**, *112*, 8064.

(98) (a) Dieng, M.; Contamin, O.; Savy, M. *Electrochim. Acta* **1988**, *33*, 121. (b) Riga, J.; Savy, M.; Verbist, J. J.; Guerchais, J. E.; Sala-Pala, J. *J. Chem. Soc., Faraday Trans. 1* **1982**, 78, 2773.

(99) (a) Grigg, R.; Johnson, A. W.; Richardson, K.; Smith, M. J. *J. Chem. Soc. C* **1970**, 1289. (b) Grigg, R.; Johnson, A. W.; Shelton, G. *J. Chem. Soc. C* **1971**, 2287. (c) Grigg, R.; Johnson, A. W.; Shelton, G. *Liebigs Ann. Chem.* 1971, *746*, 32.

(100) Takeda, Y.; Takahara, S.; Kobayashi, Y.; Misawa, H.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1990**, 2103.

(101) Rein, M.; Hanack, M. *Chem. Ber.* **1988**, *121*, 1601.

(102) (a) Barrett, P. A.; Linstead, R. P.; Rundall, F. G.; Tuey, G. A. P. *J. Chem. Soc.* **1940**, 1079. (b) Anderson, J. S.; Bradbrook, A. H.; Cook, A. H.; Linstead, R. P. *J. Chem. Soc.* **1938**, 1151.

(103) (a) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, 87, 1483; **1965**, 87, 3585. (b) Schrauzer, G. N. *Acc. Chem. Res.* **1969**, *2*, 72.

(104) (a) Herman, Z. S.; Kirchner, R. F.; Loew, G. H.; Mueller-Westerhoff, U. T.; Nazzal, A.; Zerner, M. C. *Inorg. Chem.* **1982**, *21*, 46. (b) Lelj, F.; Rosa, A.; Ricciardi, G. P.; Caserin, M.; Christinziano, P. L.; Morelli, G. *Chem. Phys. Lett.* **1989**, *160*, 39.

(105) Bloom, S. M.; Buzzell, H. O. U.S.Pat. 3588216, 1971.

(106) (a) Suzuki, Y.; Hayashi, K. Jpn. Kokai Tokkyo Koho JP 01 69686, 1989; *Chem. Abstr.* **1990**, *112*, 66875b. (b) Suzuki, Y.; Hayashi, K. Jpn. Kokai Tokkyo Koho JP 61 26686; *Chem. Abstr.* **1986**, *105*,

200221w. (c) Suzuki, Y.; Hayashi, G. Jpn. Kokai Tokkyo Koho JP 63 139303; *Chem. Abstr.* **1988**, *109*, 111522k.

(107) Freyer, W. *J. Prakt. Chem.* **1986**, *328*, 253.

(108) (a) Nakazumi, H.; Takamura, R.; Kitao, T.; Kashiwagi, K.; Harada, H.; Shiozaki, H. *J. Soc. Dyers Colour.* **1990**, *106*, 363. (b) Shiozaki, H.; Nakazumi, H.; Nakado, Y.; Kitao, T.; Ohizumi, M. *Chem. Express* **1988**, *3*, 61. (c) Shiozaki, H.; Nakazumi, H.; Nakado, Y.; Kitao, T. *Chem. Lett.* **1987**, 2393.

(109) Gordon, P. F.; Thompson, D. J.; McDonnel, D. G.; Hughes, A. J. Eur. Pat. Appl. EP 135 995, 1986; *Chem. Abstr.* **1986**, *104*, 7837c.

(110) Kajitani, M.; Yoshida, Y.; Akiyama, T.; Sugimori, A. *Nippon Kagakukaishi* **1985**, 433.

(111) Schrott, W.; Neumann, P.; Albert, B.; Thomas, M.; Barzynski, H.; Schomann, K. D.; Kuppelmaier, H. Ger. Offen DE 350 751, 1986; *Chem. Abstr.* **1987**, *106*, 224563f.

(112) Kusters, W.; Mayo, P. D. *J. Am. Chem. Soc.* **1974**, *96*, 3502.

(113) Hoyer, E.; Dietzsch, W.; Henning, H.; Schroth, W. *Chem. Ber.* **1969**, *102*, 603.

(114) Shupack, S. I.; Billig, E.; Clark, R. J. H.; Williams, R.; Cray, H. B. *J. Am. Chem. Soc.* **1964**, *86*, 4594.

(115) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1963**, *2*, 1227.

(116) (a) Balch, A. L.; Holm, R. H. *J. Am. Chem. Soc.* **1966**, *88*, 5201. (b) Tom Dieck, H.; Svoboda, M.; Greiser, T. *Z. Naturforsch. B* **1981**, *36*, 823.

(117) Baker-Hawkes, M. J.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 4870.

(118) (a) Suzuki, Y.; Hayashi, K. Jpn. Kokai Tokkyo Koho JP 61 32003, 1986; *Chem. Abstr.* **1986**, *105*, 116134n. (b) Hirose, S.; Ozawa, H.; Hosono, Y.; Sasagawa, K.; Imai, M. Jpn. Kokai Tokkyo Koho JP 60 157739, 1985; *Chem. Abstr.* **1986**, *104*, 139370e. (c) Tabushi, I.; Yamamura, K.; Nonoguchi, H. *Chem. Lett.* **1987**, 1373. (d) Campbell, J.; Jackson, D. A.; Stark, W. M.; Watson, A. A. *Dyes Pigm.* **1991**, *15*, 15.

(119) Kim, S. H.; Matsuoka, M.; Yomoto, M.; Tsuchiya, Y.; Kitao, T. *Dyes Pigm.* **1987**, 8, 381.

(120) Vogler, A.; Kunkely, H.; Hlavatsch, J.; Merz, A. *Inorg. Chem.* **1984**, *23*, 506.

(121) Irving, H.; Gill, J. B.; Cross, W. R. *J. Chem. Soc.* **1960**, 2087.

(122) Schiele, C.; Halfar, K.; Arnold, G. *Tetrahedron* **1967**, *23*, 2693.

(123) Siedle, A. R.; Pignolet, L. H. *Inorg. Chem.* **1980**, *19*, 2052.

(124) (a) Shiozaki, H.; Nakazumi, H.; Kitao, T. *Shikizai Kyokaishi* **1987**, *60*, 415. (b) *J. Soc. Dyers Colour.* **1988**, *104*, 173. (c) Shiozaki, H.; Nakazumi, H.; Morikawa, T.; Sato, Y.; Kitao, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 646. (d) Nakazumi, H.; Shiozaki, H.; Kitao, T. *Spectrochim. Acta A* **1988**, *44*, 209. (e) Shiozaki, H.; Nakazumi, H.; Takamura, Y.; Kitao, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2653. (f) Kuramoto, N. J. *J. Soc. Dyers Colour.* **1990**, *106*, 181.

(125) Sartain, D.; Truter, M. R. *J. Chem. Soc. A* **1967**, 1264.

(126) (a) Namba, K. In ref 1d; p 349. (b) Namba, K. Jpn. Kokai Tokkyo Koho JP 60 73891, 1985; *Chem. Abstr.* **1985**, *103*, 132471j; Eur. Pat. Appl. EP 147083, 1985; *Chem. Abstr.* **1985**, *103*, 216911v.

(127) Nakazumi, H.; Hamada, E.; Ishiguro, T.; Kitao, T. *J. Soc. Dyers Colour.* **1989**, *105*, 26.

(128) (a) Mueller-Westerhoff, U. T.; Vance, B.; Yoon, D. I. *Tetrahedron* **1991**, *47*, 909. (b) Freyer, W. *Z. Chem.* **1984**, *24*, 32; **1985**, *25*, 104. (c) Freyer, W.; Fink, F.; Poleschner, H.; Fanghänel, E. *Z. Chem.* **1989**, *29*, 149.

(129) (a) Kubo, Y.; Sasaki, K.; Yoshida, K. *Chem. Lett.* **1987**, 1563. (b) Kubo, Y.; Sasaki, K.; Kataoka, H.; Yoshida, K. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1469. (c) Yoshida, K.; Ishiguro, M.; Kubo, Y. *Chem. Lett.* **1987**, 2057. (d) Yoshida, K.; Koujiri, T.; Oga, N.; Ishiguro, M.; Kubo, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 708. (e) Yoshida, K.; Oga, N.; Koujiri, T.; Ishiguro, M.; Kubo, Y. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1891. (f) Kubo, Y.; Kataoka, H.; Yoshida, K. *J. Chem. Soc., Chem. Commun.* **1988**, 1457. (g) Kubo, Y.; Kataoka, H.; Ikezawa, M.; Yoshida, K. *J. Chem. Soc., Perkin Trans. 1* **1990**, 585.

(130) Maeda, S.; Yoshida, H.; Kurose, Y.; Uchino, K.; Inaba, S.; Kubo, Y.; Yoshida, K. in ref 1d; p 393.

(131) See ref 4a; p 160.

(132) Sato, G.; Shindo, S.; Sumiya, M. Jpn. Kokai Tokkyo Koho JP 61 064761, 1986; *Chem. Abstr.* **1987**, *106*, 51682p.

(133) (a) Dziomoko, V. M.; Tomsons, U.; Ryabokobylko, Yu. S. *Khim. Geterots. Soed.* **1976**, 968. (b) Dziomoko, V. A.; Stopnikova, M. N.; Shmelev, L. V.; Ryabokobylko, Yu.; Adamova, G. M.; Gurevich, M. Z.; Poponova, R. V. *Khim. Geterots. Soed.* **1981**, 546. (c) Barinov, I. V.; Voyevodsakaya, T. I.; Ustynyuk, Yu. A. *J. Organometal. Chem.* **1971**, *30*, C28.

(134) (a) Torii, Y.; Yazaki, T.; Kaizu, Y.; Murasoto, S.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2264. (b) Bodini, M. E.; Copia, G.; Robinson, R.; Sawyer, D. T. *Inorg. Chem.* **1983**, *22*, 126.

(135) Kōnig, W. *Z. Angew. Chem.* **1925**, 743.

(136) Monich, N. V.; Vompe, A. F.; Makin, S. M.; Shavrygina, O. A.; Levkoev, I. I. *Zh. Org. Khim.* **1985**, *21*, 1093.

(137) Kovtun, Yu. P.; Kachkovskii, A. D.; Romanov, N. N. *Khim. Geterots. Soed.* **1988**, 418.

(138) (a) Kudinova, M. A.; Derevyanko, N. A.; Dyadyusha, G. G.; Ishchenko, A. A.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1980**, 898. (b) Dyadyusha, G. G.; Ishchenko, A. A.; Derevyanko, N. A.; Kudinova, M. A.; Tolmachev, A. I. *Teor. Eksp. Khim.* **1979**, *15*, 412. (c) Tolmachev, A. I.; Kudinova, M. A. *Khim. Geterots. Soed.* **1974**, 49. (d) Kudinova, M. A.; Kurdyukov, V. V.; Ishchenko, A. A.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1990**, 902. (e) Kurdyukov, V. V.; Ishchenko, A. A.; Kudinova, M. A.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1987**, 760.

(139) (a) Detty, M. R.; Murray, B. J. *J. Org. Chem.* **1982**, *47*, 5235. (b) Detty, M. R.; Merkel, P. B.; Powers, S. K. *J. Am. Chem. Soc.* **1988**, *110*, 5920.

(140) (a) Detty, M. R.; Merkel, P. E. *J. Am. Chem. Soc.* **1990**, *112*, 3845. (b) Detty, M. R.; Gibson, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 4086.

(141) (a) Drexhage, K.-H.; Kussler, M.; Sens, B.; Marx, N.-J. Ger. Offen DE 3 316 666, 1984; *Chem. Abstr.* **1985**, *102*, 80288n. (b) Sens, B. Doctoral Dissertation, University of Siegen 1984. (c) Kudinova, M. A.; Slominskii, Yu. L.; Shokod'ko, I. V.; Tolmachev, A. I. *Ukrain. Khim. Zh.* **1985**, *51*, 95.

(142) Kussler, M. Private communication, 1990.

(143) Romanov, N. N. *Ukrain. Khim. Zh.* **1981**, *47*, 1280.

(144) (a) Mikhailenko, F. A.; Vasilenko, N. P.; Kachkovskii, A. D.; Rozhinskii, Yu. I. *Zh. Org. Khim.* **1982**, *18*, 435. (b) Ishchenko, A. A.; Vasilenko, M. P.; Maidannik, A. G.; Balina, L. V. *Zh. Org. Khim.* **1989**, *25*, 1086. (c) Sliteinberg, Ya. B. *Khim. Geterots. Soed.* **1973**, 340.

(145) (a) Vasilenko, N. P.; Maidannik, A. G.; Mikhailenko, F. A. *Ukrain. Khim. Zh.* **1989**, *55*, 742. (b) Vasilenko, N. P.; Mikhailenko, F. A.; Maidannik, A. G. *Khim. Geterots. Soed.* **1987**, 418.

(146) (a) Daltrozzo, E.; Sulger, W. Ger. Offen DE 1987, 3 533 772; *Chem. Abstr.* **1987**, *107*, 135892r. (b) Daltrozzo, E. University of Konstanz. Private communication, 1991.

(147) (a) Reichardt, C.; Knecht, J.; Mrosek, W.; Plaas, D.; Allman, R.; Kucharczyk, D. *Chem. Ber.* **1983**, *116*, 1982. (b) Reynolds, G. A.; VanAllan, J. A.; Daniel, D. *J. Heterocycl. Chem.* **1970**, *7*, 1395. (c) Bricks, Yu. L.; Ishchenko, A. A.; Kachkovskii, A. D.; Tolmachev, A. I. *Dyes Pigm.* **1987**, 8, 353. (d) Briks, Yu. L.; Kachkovskii, A. D.; Tolmachev, A. I. *Ukrain. Khim. Zh.* **1985**, *51*, 1198.

(148) (a) Nakazumi, H.; Watanabe, S.; Kado, S.; Kitao, T. *Chem. Lett.* **1989**, 1039. (b) Watanabe, S.; Nakazumi, H.; Kado, S.; Maeda, K.; Kitao, T. *J. Chem. Res. (S)* **1990**, 50; *J. Chem. Res. (M)* **1990**, 537. (c) Watanabe, S.; Nakazumi, H.; Maeda, K.; Kitao, T. *J. Chem. Soc., Chem. Commun.* **1990**, 421. (d) Gorb, L. T.; Romanov, H. H.; Fedotov, K. V.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1981**, 481.

(149) (a) Förster, E. Doctoral Dissertation, Technical University of Dresden, 1971. (b) Ford, J. A.; Wilson, C. V.; Young, W. R. *J. Org. Chem.* **1967**, *32*, 173.

(150) (a) Maidannik, A. G.; Chuiguk, A. A.; Mikhailenko, F. A. *Ukrain. Khim. Zh.* **1986**, *52*, 519. (b) Fedotov, K. V.; Romanov, N. N. *Ukrain. Khim. Zh.* **1986**, *52*, 519. (c) Fedotov, K. V.; Kachkovskii, A. D.; Romanov, N. N.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1989**, 114.

(151) (a) Hofer, L. J. E.; Grabenstetter, R. J.; Wiig, E. O. *J. Am. Chem. Soc.* **1950**, *72*, 203. (b) Hünig, S.; Rosenthal, O. *Liebigs Ann. Chem.* **1955**, *592*, 161. (c) Brooker, L. G. S.; Craig, A. C.; Heseltine, D. W.; Jenkins, P. W.; Lincoln, L. L. *J. Am. Chem. Soc.* **1965**, 87, 2443. (d) Bell, N. A.; Broughton, R. A.; Brooks, J. S.; Jones, T. A.; Thorpe, S. T.; Ashwell, G. J. *J. Chem. Soc., Chem. Commun.* **1990**, 325. (e) Schelz, D. *Helv. Chim. Acta* **1975**, 58, 1207.

(152) Acker, M.; Dust, M.; Neumann, P.; Brosius, S.; Schomann, K. D.; Kuppelmaier, H. Eur. Pat. Appl. EP 335 236, 1990; *Chem. Abstr.* **1990**, *112*, 141245b.

(153) (a) Tilak, B. D.; Jain, S. K. *Indian J. Chem.* **1969**, *7*, 17. (b) VanAllan, J. A.; Reynolds, G. A. *J. Heterocycl. Chem.* **1972**, *9*, 669.

(154) (a) Makin, S. M.; Kruglikova, R. I.; Popova, T. P.; Monich, N. P.; Vompe, A. V. *Zh. Org. Khim.* **1984**, *20*, 439. (b) Slominskii, Yu. L.; Zubarovskii, V. M.; Khodot, G. P.; Efimenko, N. I. *Ukrain. Khim. Zh.* **1979**, *45*, 43. (c) Slominskii, Yu. L.; Shulezko, L. M. *Ukrain. Khim. Zh.* **1974**, *40*, 625.

(155) (a) Opanasenko, E. P.; Skalkina, V. I.; Kozhyshko, G. I. *Zh. Obshch. Khim.* **1970**, *40*, 2722. (b) Kozlov, N. S.; Zhikhareva, O. D.; Mostovnikov, V. A.; Batishche, S. A. *Khim. Geterots. Soed.* **1982**, 1523.

(156) (a) Gavrilyuk, I. M.; Ishchenko, A. A.; Kudinova, M. A.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1984**, 1486. (b) Kamel, M.; Shoeb, H. *Liebigs Ann. Chem.* **1966**, *699*, 168. (c) Tolmachev, A. I.; Shulezko, L. M. *Khim. Geterots. Soed.* **1980**, 777. (d) Tolmachev, A. I.; Derevyanko, N. A.; Ishchenko, A. A. *Khim. Geterots. Soed.* **1982**, 1173. (e) Tolmachev, A. I.; Derevyanko, N. A.; Kudinova, M. A. *Khim. Geterots. Soed.* **1975**, 617. (f) VanAllan, J. A.; Reynolds, G. A.; Petropoulos, C. C. *J. Heterocycl. Chem.* **1978**, *15*, 365. (g) Vasserman, A. I.; Mezheritskii, V. V.; Dorofeenko, G. N. *Khim. Geterots. Soed.* 1974, 892.

(157) Dyadyusha, G. G.; Kachkovskii, A. D. *Ukrain. Khim. Zh.* **1975**, *41*, 1176.

(158) Ishchenko, A. A.; Derevyanko, N. A.; Zubarovskii, V. M.; Tolmachev, A. I. *Theor. Eksp. Khim.* **1984**, *20*, 443.

(159) (a) Derevyanko, N. A.; Dyadyusha, G. G.; Ishchenko, A. A.; Tolmachev, A. I. *Theor. Eksp. Khim.* **1983**, *19*, 169. (b) Dyadyusha, G. G.; Popov, S. V.; Slominskii, Yu. L. *Teor. Eksp. Khim.* **1989**, *25*, 47. (c) Avdeeva, V. I.; Al'perovich, M. A. *Dokl. Akad. Nauk SSSR* **1984**, *277*, 104.

(160) Försterling, H. D.; Huber, W.; Kuhn, H.; Martin, H. H.; Schweig, A.; Seelig, F. F.; Stratmann, W. In *Optische Anregung organischer Systeme*; Verlag Chemie: Weinheim, 1966; p 55.
(161) Grif, V. Kh.; Lavrushin, V. F. *Ukrain. Khim. Zh.* **1987**, *53*, 866.
(162) Brooker, L. G. S. In *Recent Progress in the Chemistry Natural and Synthetic Coloring Matters and Related Fields*; Acad. Press: New York, 1963; p 573.
(163) Mostovnikov, V. A.; Rubinov, A. N.; Al'perovich, M. A.; Avdeeva, V. I.; Levkoev, I. I.; Loiko, M. M. *Zh. Prikl. Spektrosk.* **1974**, *20*, 42.
(164) (a) Sauda, K.; Imasaki, T.; Ishibashi, N. *Anal. Chim. Acta* **1986**, *187*, 353. (b) Sauda, K.; Imasaki, T.; Ishibashi, N. *Anal. Chem.* **1986**, *58*, 2649. (c) Imasaka, T.; Yoshitake, A.; Ishibashi, N. *Anal. Chem.* **1984**, *56*, 1077.
(165) (a) Dyadyusha, G. G.; Ishchenko, A. A.; Derevyanko, N. A.; Karaban, E. F.; Tolmachev, A. I. *Ukrain. Khim. Zh.* **1980**, *46*, 1186. (b) Kudinova, M. A.; Derevyanko, N. A.; Dyadyusha, G. G.; Ishchenko, A. A.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1980**, 903. (c) Kudinova, M. A.; Derevyanko, N. A.; Ishchenko, A. A.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1981**, 1327. (d) Tolmachev, A. I.; Derevyanko, N. A.; Ishchenko, A. A. *Khim. Geterots. Soed.* **1982**, 1178. (e) Mikitenko, E. K.; Romanov, N. N. *Ukrain. Khim. Zh.* **1982**, *48*, 1071. (f) Mikhailenko, F. A.; Shevchuk, L. I.; Kiprianov, A. I. *Khim. Geterots. Soed.* **1973**, 923. (g) Mezheritskii, V. V.; Vasserman, A. L.; Dorofeenko, G. N. *Khim. Geterots. Soed.* **1976**, 739. (h) Dorofeenko, G. N.; Mezheritskii, V. V.; Vasserman, A. L. *Khim. Geterots. Soed.* **1974**, 37. (i) Vompe, A. F.; Meshki, L. M.; Tyurin, V. S.; Yagupol'skii, L. M.; Troitskaya, V. I. *Dokl. Akad. Nauk* **1983**, *272*, 615. (j) Gadjev, N. I.; Deligeorgiev, T. G. *Dyes Pigm.* **1990**, *14*, 73.
(166) (a) Rudenko, V. N.; Il'chenko, A. Ya. *Khim. Geterots. Soed.* **1973**, 1552. (b) Il'chenko, A. Ya.; Rudenko, V. N. *Khim. Geterots. Soed.* **1972**, 1425.
(167) (a) Deligeorgiev, T. G.; Gadjev, N. I. *Dyes Pigm.* **1990**, *12*, 157. (b) Boiko, I. I.; Derevyanko, A. A.; Ishchenko, A. A.; Markina, T. A.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1986**, 1607. (c) Pulst, M.; Hantschmann, A.; Müller, M.; Weissenfels, M. *Z. Chem.* **1984**, *24*, 146. (d) Weissenfels, M.; Pulst, M.; Greif, D.; Hollborn, B. *J. Prakt. Chem.* **1989**, *331*, 763. (e) Tolmachev, A. I.; Kudinova, M. A. *Dokl. Akad. Nauk Ukrain. SSR B* **1977**, 50.
(168) (a) Slominskii, Yu. L.; Dyadyusha, G. G.; Ushchenko, I. K.; Radchenko, I. D.; Tolmachev, A. I. *Ukrain. Khim. Zh.* **1974**, *40*, 1163. (b) Slominskii, Yu. L.; Smirnova, A. L.; Popov, S. V. *Ukrain. Khim. Zh.* **1984**, *50*, 638. (c) Slominskii, Yu. L.; Gromova, G. A.; Zubarovskii, V. M. *Ukrain. Khim. Zh.* **1987**, *53*, 93. (d) Slominskii, Yu. L.; Smirnova, A. L.; Kudinova, M. A.; Efimenko, N. I.; Tolmachev, A. I. *Ukrain. Khim. Zh.* **1978**, *44*, 838. (e) Slominskii, Yu. L.; Shapiro, B. I.; Kachkovskii, A. D.; Kurkina, L. G.; Radchenko, I. D.; Chizhova, M. A.; Tolmachev, A. I. *J. Inf. Rec. Mater.* **1988**, *16*, 23. (f) Slominskii, Yu. L.; Radchenko, I. D.; Popov, S. V.; Tolmachev, A. I. *Zh. Org. Khim.* **1983**, *19*, 2134. (g) Makin, S. M.; Shavrygina, O. A.; Boiko, T. N.; Monich, N. V.; Pomogaev, A. I. *Zh. Org. Khim.* **1988**, *24*, 835. (h) Makin, S. M.; Pomogaev, A. I. *Zh. Org. Khim.* **1982**, *18*, 2176. (i) Boiko, I. I.; Shinkorenko, S. V.; Opanasenko, E. P.; Lizin, V. V. *Zh. Org. Khim.* **1985**, *21*, 859. (j) Slominskii, Yu. L.; Radchenko, I. D.; Tolmachev, A. I. *Zh. Org. Khim.* **1978**, *10*, 2214.
(169) (a) Ishchenko, A. A.; Kudinova, M. A.; Slominskii, Yu. L.; Tolmachev, A. I. *Zh. Org. Khim.* **1986**, *22*, 170. (b) Slominskii, Yu. L.; Skul'bidenko, A. L.; Tolmachev, A. I. *Zh. Org. Khim.* **1975**, *11*, 392. (c) Kudinova, M. A.; Slominskii, Yu. L.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1983**, 1559. (d) Kudinova, M. A.; Derevyanko, N. A.; Dyadyusha, G. G.; Ishchenko, A. A.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1981**, 1195. (e) Kudinova, M. A.; Kurdyukov, V. V.; Ishchenko, A. A.; Tolmachev, A. I. *Khim. Geterots. Soed.* **1984**, 451. (f) Tolmachev, A. I.; Slominskii, Yu. L.; Kiprianov, A. I. *Dokl.* Akad. *Nauk* **1967**, *177*, 869. (g) Heilig, G.; Lüttke, W. *Chem. Ber.* **1986**, *119*, 3102; **1988**, *121*, 407.
(170) (a) Tolmachev, A. I.; Slominkii, Yu. L.; Belaya, Zh. N.; Rodova, E. Z. *Khim. Geterots. Soed.* **1976**, 175. (b) Monich, N. V.; Krasnaya, Zh. A.; Levkoev, I. I.; Kucherov, V. F. *Khim. Geterots. Soed.* **1981**, 1631.
(171) (a) Reichardt, C. *Liebigs Ann. Chem.* **1968**, *715*, 74. (b) Reichardt, C.; Schlagerer, K. *Liebigs Ann. Chem.* **1982**, 530. (c) Reichardt, C.; Halbritter, K. *Chem. Ber.* **1971**, *104*, 822. (d) Reichardt, C.; Mormann, W. *Chem. Ber.* **1972**, *105*, 1815. (e) Grahn, W.; Mrosek, W.; Reichardt, C. *Chem. Ber.* **1977**, *110*, 1674. (f) Slominskii, Yu. L.; Radchenko, I. D.; Tolmachev, A. I. *Zh. Org. Khim.* **1979**, *15*, 400. (g) Il'chenko, A. Ya.; Koval'chuk, R. E.; Yagupol'skii, L. M. *Chem. Ber.* **1973**, *9*, 1744. (h) Pasanok, S. V.; Gerns, I. I.; Chaika, E. A.; Yagupol'skii, L. M. *Chem. Ber.* **1989**, *25*, 379. (i) Zubarovskii, V. M.; Briks, Y. L. *Khim. Geterots. Soed.* **1980**, 524. (j) Ischenko, A. A.; Kudinova, M. A.; Slominskii, Yu. L.; Tolmachev, A. I. *Ukrain. Khim. Zh.* **1986**, *52*, 175.
(172) (a) Shulezko, A. A. *Zh. Org. Khim.* **1968**, *4*, 2207. (b) Shulezko, A. A.; Rozhdestvenskaya, I. T.; Kiprianov, A. I. *Zh. Org. Khim.* **1970**, *6*, 2118. (c) Sosnovskii, G. M.; Lugovskii, A. P.; Tishchenko, I. G. *Zh. Org. Khim.* **1983**, *19*, 2143. (d) Hünig, S.; Wolff, E. *Chimia* **1968**, *22*, 33. (e) Ficken, G. E.; Kendall, J. D. *Zh. Org. Khim.* **1961**, *15*, 110. (f) Elwood, J. K. *J. Org. Chem.* **1973**, *38*, 2425. (g) Tolmachev, A. I.; Karaban, E. F.; Chudakov, V. I. *Ukrain. Khim. Zh.* **1980**, *46*, 965.
(173) (a) Gompper, R.; Gessner, T. *Angew. Chem.* **1985**, *97*, 996; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 982. (b) Fraser, M.; Malera, A.; Reid, D. H. *J. Chem. Soc. B* **1966**, 483.
(174) (a) Canon, K. K. Jpn. Kokai Tokkyo Koho JP 58 217558, 1983; *Chem. Abstr.* **1984**, *100*, 193532q. (b) Enomoto, K.; Akira, I. Jpn. Kokai Tokkyo Koho JP 62 187087, 1987; *Chem. Abstr.* **1988**, *108*, 66058e. (c) Dust, M.; Neumann, P.; Hauser, P.; Wagenblast, G.; Benthack-Thoms, H.; Barzynski, H.; Schomann, K. D.; Kuppelmaier, H. Ger. Offen DE 3 631 843, 1988; *Chem. Abstr.* **1988**, *109*, 75205y. (d) Miura, K.; Ozawa, T.; Iwanami, J. Jpn. Kokai Tokkyo Koho JP 61 167680, 1986; *Chem. Abstr.* **1987**, *106*, 50042t. (e) Keil, D.; Hartmann, H.; Moschny, T. *Dyes Pigm.* **1991**, *17*, 19.
(175) Kuramoto, N.; Natsukawa, K.; Asao, K. *Dyes Pigm.* **1989**, *11*, 21.
(176) Kleiner, C. Doctoral Dissertation, University of Basel 1990. Balli, H. Private communication, 1990.
(177) Treibs, A.; Schulze, L. Liebigs. *Ann. Chem.* **1973**, 201.
(178) Treibs, A.; Jacob, K. *Angew. Chem.* **1965**, *77*, 680; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 694.
(179) Budzelaar, P. M. M.; Dietrich, M.; Macheleid, J.; Weiss, R.; Schleyer, P. v. R. *Chem. Ber.* **1985**, *118*, 2118. (b) Bigelow, R. W.; Freund, H.-J. *Chem. Phys.* **1986**, *107*, 149. (c) Kazmeier, P. M.; Hamer, G. K.; Burt, R. A. *Canad. J. Chem.* **1990**, *68*, 530.
(180) Yasui, S.; Matsuoka, M.; Kitao, T. *Dyes Pigm.* **1988**, *10*, 13.
(181) (a) Loutfy, R. O.; Hsiao, C. K.; Kazmaier, P. M. *Photogr. Sci. Eng.* **1983**, *27*, 5. (b) Tristani-Kendra, M.; Eckhardt, C. J. *J. Chem. Phys.* **1984**, *81*, 1160.
(182) Slominskii, Yu. L.; Radchenko, I. D. *Ukrain. Khim. Zh.* **1977**, *43*, 263.
(183) (a) Tolmachev, A. I. *Teubner Texte zur Physik* **1987**, *13*, 115. (b) Ishchenko, A. A.; Slominskii, Yu. L.; Tolmachev, A. I. *Ukrain. Khim. Zh.* **1989**, *55*, 979. (c) Reynolds, G. A.; Drexhage, K. H. *J. Org. Chem.* **1977**, *42*, 885. (d) Babenko, V. A.; Sychev, A. A. *Kvantovaya Elektron.* (*Moscow*) **1987**, *14*, 2179; *Chem. Abstr.* **1988**, *108*, 65526u. (e) Freyer, W.; Fink, F. *Z. Chem.* **1989**, *29*, 105.
(184) (a) Polland, H. J.; Elsaesser, T.; Seilmeier, A.; Kaiser, W.; Kussler, M.; Marx, N. J.; Sens, B.; Drexhage, K. H. *Appl. Phys. B* **1982**, *32*, 53; *Chem. Abstr.* **1983**, *99*, 203181b. (b) Blau, W. *Phys. Technol.* **1987**, *18*, 250.
(185) Oseroff, A. R.; Ohuoka, D.; Ara, G.; McAuliffe, D.; Foley, J.; Cincotta, L. *Proc. Nat. Acad. Sci. U.S.A.* **1986**, *83*, 9729; *Chem. Abstr.* **1987**, *106*, 80947j.
(186) (a) Mushkalo, I. L.; Sogulyaev, Yu. A. *Zh. Org. Khim.* **1987**, *23*, 2212. (b) Kiprianov, A. I.; Fridman, S. G.; Dyadyusha, G. G.; Kotova, L. I. *Zh. Org. Khim.* **1975**, *11*, 891. (c) Mikhailenko, F. A.; Dyadyusha, G. G.; Boguslavskaya, A. N. *Khim. Geterots. Soed.* **1975**, 370.
(187) Cameron, D. W.; Feutrill, G. I.; Thiel, J. M. *Aust. J. Chem.* **1981**, *34*, 453.
(188) Closs, F.; Gompper, R. *Angew. Chem.* **1987**, *99*, 564; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 552.
(189) Takahashi, K.; Suzuki, T. *J. Am. Chem. Soc.* **1989**, *111*, 5483.
(190) Wadsworth, D. H.; Weidner, C. H.; Bender, S. L.; Nuttall, R. H.; Luss, H. R. *J. Org. Chem.* **1989**, *54*, 3652.
(191) Falk, H.; Flödl, H. *Monatsh. Chem.* **1985**, *116*, 1177.
(192) Schmidt, H.; Wizinger, R. *Liebigs Ann. Chem.* **1959**, *623*, 204.
(193) Griffiths, J.; Pender, K. J. *Dyes Pigm.* 1981, *2*, 37.
(194) Tuemmler, W. B.; Wildi, B. S. *J. Am. Chem. Soc.* **1958**, *80*, 3772.
(195) See ref 4a; p 27.
(196) Fischer, H.; Fischer, H. *Chem. Ber.* **1964**, *97*, 2959.
(197) Neunhoeffer, O.; Heitmann, P. *Chem. Ber.* **1959**, *92*, 245.
(198) (a) Canon Co., Jpn. Kokai Tokkyo Koho JP 58 219090, 1983; *Chem. Abstr.* **1984**, *101*, 81728x. (b) Sato, T.; Abe, M.; Oba, H.; Ueda, Y.; Umehara, M. Jpn. Kokai Tokkyo Koho JP 60 252344, 1985; *Chem. Abstr.* **1986**, *105*, 15349f.
(199) Kanda, N.; Yonese, N.; Kondo, M. Eur. Pat. Appl. EP 188377, 1986; *Chem. Abstr.* **1986**, *105*, 216755j.
(200) Nakatsuji, S.; Okamoto, N.; Nakashima, K.; Akiyama, S. *Chem. Lett.* **1986**, 329.
(201) Akiyama, S.; Nakatsuji, S.; Nakashima, K.; Yamasaki, S. *Dyes Pigm.* **1988**, *9*, 459.
(202) Akiyama, S.; Nakatsuji, S.; Nakashima, K.; Watanabe, M. *J. Chem. Soc., Chem. Commun.* **1987**, 710; **1987**, 1420.
(203) Akiyama, S.; Yoshida, K.; Hayashida, M.; Nakashima, K.; Nakatsuji, S.; Iyoda, M. *Chem. Lett.* **1981**, 311.
(204) Akiyama, S.; Nakatsuji, S.; Nakashima, K.; Watanabe, M.; Nakazumi, H. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3155.
(205) Wizinger, R.; Rembold, H. *Chimia* **1959**, *13*, 156.
(206) Naef, R. *Dyes Pigm.* **1985**, *6*, 233.
(207) Yamaguchi, T.; Murofushi, K.; Ohmori, K.; Nakazumi, H.; Kitao, T. 57th Ann. Meet. Japan Chem. Soc., Sendai 1988; Abstr. II, p 707.
(208) Barker, A.; Barker, C. C. *J. Chem. Soc.* **1954**, 1307.
(209) Nakatsuji, S.; Nakazumi, H.; Fukuma, H.; Yahiro, T.; Nakashima, K.; Iyoda, M.; Akiyama, S. *J. Chem. Soc., Chem. Commun.* **1990**, 489; *J. Chem. Soc., Perkin Trans. 1* **1991**, 1881.
(210) Gunzenhauser, S.; Balli, H. *Helv. Chim. Acta* **1980**, *63*, 1264.

(211) Ikegama, S.; Amako, T. Jpn. Kokai Tokkyo Koho JP 59 199757, 1984; *Chem. Abstr.* **1985**, *102*, 133556g; 60 226871, 1985; *Chem. Abstr.* **1986**, *105*, 143650j.

(212) (a) Bowden, K.; Stewart, R. *Tetrahedron* **1965**, *21*, 261. (b) Fyfe, C. A.; Albagli, A.; Stewart, R. *Can. J. Chem.* **1970**, *48*, 3721. (c) Margerum, J. D.; Miller, L. J.; Saito, E.; Brown, M. S.; Mosher, H. S.; Hardwick, R. *J. Phys. Chem.* **1962**, *66*, 2434.

(213) Simonnin, M.-P.; Xie, H.-Q.; Ferrier, F.; LeLievre, J.; Farrell, P. G. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1553.

(214) Venkataraman, K. In *The Chemistry of Synthetic Dyes*; Venkataraman, K., Ed.; Academic Press: London, 1971; Vol. V, p 132.

(215) (a) Kogo, Y.; Kikuchi, H.; Matsuoka, M.; Kitao, T. *J. Soc. Dyers Colour.* **1980**, *96*, 475. (b) Matsuoka, M.; Takagi, K.; Obayashi, H.; Wakasugi, K.; Kitao, T. *J. Soc. Dyers Colour.* **1983**, *99*, 257.

(216) Chu, K. Y.; Griffiths, J. *J. Chem. Res.* (*S*) **1978**, 180; (M) 2319.

(217) Nakamori, T.; Chiba, T.; Kasai, T. *Nippon Kagaku Kaishi* **1981**, 1916.

(218) Takagi, K.; Matsuoka, M.; Kubo, Y.; Kitao, T. *Dyes Pigm.* **1985**, *6*, 75.

(219) Takagi, K.; Kawabe, M.; Matsuoka, M.; Kitao, T. *Dyes Pigm.* **1985**, *6*, 177.

(220) Peters, A. T.; Tenny, B. A. *J. Soc. Dyers Colour.* **1977**, *93*, 373; *Dyes Pigm.* **1980**, *1*, 91.

(221) Kim, S. H.; Matsuoka, M.; Kitao, T. *Chem. Lett.* **1985**, 1351.

(222) Takagi, K.; Kanamoto, S.; Itoh, K.; Matsuoka, M.; Kim, S. H.; Kitao, T. *Dyes Pigm.* **1987**, 8, 71.

(223) Nishi, H.; Hatada, Y.; Kitahara, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1482.

(224) Kim, S. H.; Matsuoka, M.; Kubo, Y.; Yodoshi, T.; Kitao, T. *Dyes Pigm.* **1986**, *7*, 93.

(225) Kim, S. H.; Matsuoka, M.; Yodoshi, T.; Kitao, T. *Chem. Express* **1986**, *1*, 129.

(226) Barr, C. R.; Brown, G. H.; Thirtle, J. R.; Weissberger, A. *Photogr. Sci. Eng.* **1961**, *5*, 195.

(227) Matsuoka, M. In *Hikarikiroku Gijutsu to Zairyo*, CMC Inc.: Tokyo, 1985; p 176 (in Japanese).

(228) Kim, S. H.; Matsuoka, M.; Yodoshi, T.; Suga, K.; Kitao, T. *J. Soc. Dyers Color.* **1989**, *105*, 212.

(229) Kubo, Y.; Mori, F.; Yoshida, K. *Chem. Lett.* **1987**, 1761.

(230) Kubo, Y.; Mori, F.; Komatsu, K.; Yoshida, K. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2439.

(231) (a) Kubo, Y.; Kuwana, M.; Yoshida, K.; Tomotake, Y.; Matsuzaki, T.; Maeda, S. *J. Chem. Soc., Chem. Commun.* **1989**, 35. (b) Kubo, Y.; Kuwana, M.; Okamoto, K.; Yoshida, K. *J. Chem. Soc., Chem. Commun.* **1989**, 855.

(232) Yoshida, K.; Kaugiri, T.; Sakamoto, E.; Kubo, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1878.

(233) Kubo, Y.; Yasuoka, H.; Yoshida, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1253.

(234) Nippon Kayaku Co. Ltd., Jpn. Kokai Tokkyo Koho JP 58 219262, 1983; *Chem. Abstr.* **1984**, *100*, 193530.

(235) Matsunaga, D.; Morishita, Y.; Shoji, O. Jpn. Kokai Tokkyo Koho JP 62 54761, 1987; *Chem. Abstr.* **1987**, *107*, 135886s.

(236) Ricoh Co. Ltd., Jpn. Kokai Tokkyo Koho JP 58 169152, 1983; 58 22448, 1983.

(237) (a) Boguslavskaya, I. L.; Gudzenko, V. I. *Zh. Org. Khim.* **1968**, *4*, 101. (b) Hohmann, W.; Wunderlich, K. Eur. Pat. Appl. EP 57375, 1983; *Chem. Abstr.* **1983**, *98*, 55570q.

(238) Ohyamata, T.; Takuma, K.; Kuroda, S.; Aiga, H. Eur. Pat. Appl. EP 323184, 1989; *Chem. Abstr.* **1990**, *112*, 8710h.

(239) D. Schelz *Helv. Chim. Acta* **1974**, *57*, 1075.

(240) West, R.; Zecher, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 155.

(241) Sugimoto, T.; Nagatomi, T.; Ando, H.; Yoshida, Z. *Angew. Chem.* **1988**, *100*, 597; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 560.

(242) Bauer, H.; Pfeiffer, G. *Chem. Ztg.* **1976**, *100*, 373.

(243) Beck, W.; Schmidt, C.; Whienold, R.; Steimann, M.; Wagner, B. *Angew. Chem.* **1989**, *101*, 1532; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1529.

(244) (a) Paramonov, V. D.; Mostoslavskii, M. A.; Shevchuk, I. N. *Zh. Fiz. Khim.* **1978**, *52*, 2676. (b) Gompper, R.; Kellner, R., University of Munich. Private communication, 1991.

(245) Dawson, J. F. *Rev. Prog. Color Rel. Top.* **1984**, *14*, 90.

(246) Raue, R. *Rev. Prog. Color Rel. Top.* **1984**, *14*, 187.

(247) (a) Thiel, W.; Mayer, R.; Jauer, E.-A.; Modrow, H.; Dost, H. *J. Prakt. Chem.* **1986**, *328*, 497. (b) Gandel'sman, L. Z.; Il'chenko, A. Ya.; Yagupol'skii, L. M. *Zh. Org. Khim.* **1989**, *25*, 1257.

(248) (a) Yasui, S.; Matsuoka, M.; Kitao, T. *J. Jpn. Soc. Colour. Mat.* **1988**, *61*, 678. (b) Yasui, S.; Matsuoka, M.; Takao, M.; Kitao, T. *J. Soc. Dyers Colour.* **1988**, *104*, 284.

(249) Bello, K. A.; Griffiths, J. *J. Chem. Soc., Chem. Commun.* **1986**, 1639.

(250) Gregory, P. Eur. Pat. Appl. EP 280434, 1988; *Chem. Abstr.* **1989**, *110*, 116654k.

(251) Yabe, A.; Niino, M.; Moriyama, H.; Ouchi, A. In ref 1d; p 206.

(252) Takiguchi, T. Jpn. Kokai Tokkyo Koho JP 86 174046, 1986; *Chem. Abstr.* **1988**, *109*, 83367t.

(253) Sato, G.; Shindo, S.; Sumiya, M. Jpn. Kokai Tokkyo Koho JP 84 185450, 1984; *Chem. Abstr.* **1986**, *106*, 51682p.

(254) (a) Takimoto, H.; Sano, H. Jpn. Kokai Tokkyo Koho JP 01 040392, 1990; *Chem. Abstr.* **1990**, *112*, 66808g. (b) Takimoto, H. Jpn. Kokai Tokkyo Koho JP 63 309568, 1988; *Chem. Abstr.* **1989**, *110*, 214916s.

(255) Fabian, J. *Chimia* **1978**, *32*, 323.

(256) Gompper, R.; Lensky, S., University of Munich. Private communication, 1991.

(257) (a) Bello, K. A.; Cheng, L.; Griffiths, J. *J. Chem. Soc., Perkin Trans. 2* **1987**, 815. (b) Matsuda, Y.; Gotou, H.; Katou, K.; Matsumoto, H.; Yamashita, M.; Maeda, S. *Dyes Pigm.* **1990**, *14*, 225.

(258) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988.

(259) Kozlov, N. S.; Zikhareva, O. D.; Fedorova, L. N.; Butmerchuk, T. D.; Kuz'min, R. N. *Khim. Geterots. Soed.* **1977**, 1343.

(260) (a) Takahashi, K.; Ishikawa, F.; Takase, K. *Tetrahedron Lett.* **1976**, 4655. (b) Takahashi, K.; Takase, K. *Tetrahedron Lett.* **1975**, 245. (c) Takahashi, K.; Sakae, T.; Takase, K. *Chem. Lett.* **1978**, 237.

(261) Junek, H.; Uray, G.; Zuschnigg, G. *Dyes Pigm.* **1988**, *9*, 137.

(262) Zacharias, G.; Junek, H. *Z. Naturforsch. B* **1976**, *31*, 371.

(263) (a) VanAllan, J. A.; Reynolds, G. A. *J. Heterocycl. Chem.* **1976**, *13*, 73. (b) Reynolds, G. A.; VanAllan, J. A. *J. Org. Chem.* **1969**, *34*, 2736. (c) Neidlein, R.; Körber, I. *Arch. Pharm.* **1978**, *311*, 256.

(264) (a) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1. (b) Dimroth, K.; Reichardt, C. *Liebigs Ann. Chem.* **1969**, *727*, 93. (c) Reichardt, C.; Müller, R. *Liebigs Ann. Chem.* **1976**, 1937. (d) Reichardt, C.; Harbusch-Görnert, E. *Liebigs Ann. Chem.* **1983**, 721. (e) Reichardt, C.; Harbusch-Görnert, E.; Schäfer, G. *Liebigs Ann. Chem.* **1988**, 839. (f) Kreitsberga, Ya. N.; Neiland, O. Ya.; Kampar, V. E. *Zh. Org. Khim.* **1975**, *11*, 1941. (g) Paley, M. S.; Meehan, E. J.; Smith, C. D.; Rosenberger, F. E.; Howard, S. C.; Harris, J. M. *J. Org. Chem.* **1989**, 3432. (h) Dürr, H. *Angew. Chem.* **1989**, *101*, 427; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 413. (i) Laurence, C.; Nicolet, P.; Reichardt, C. *Bull. Chim. Soc. Fr.* **1987**, 125. (j) Reichhardt, C.; Eschner, M. *Liebigs Ann. Chem.* **1991**, *10*, 1003.

(265) Gessner, T. Doctoral Dissertation, University of München, 1986.

(266) Staab, H. A.; Hinz, R.; Knaus, G. H.; Krieger, C. *Chem. Ber.* **1983**, *116*, 2835.

(267) Staab, H. A.; Knaus, G. H.; Henke, H.-E.; Krieger, C. *Chem. Ber.* **1983**, *116*, 2785.

(268) Rao, C. N. R.; Bhat, S. N.; Dwivedi, P. C. *Appl. Spectrosc. Rev.* **1971**, *5*, 1.

(269) Beukers, R.; Szent-György, A. *Rec. Trav. Chim.* **1962**, *81*, 255.

(270) (a) Sandmann, D. J.; Ceasar, G. P.; Nielsen, P.; Epstein, A. J.; Holmes, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 202. (b) Ryzhikov, M. B.; Rodionov, A. N.; Serov, S. A.; Shigorin, D. N. *Khim. Geterots. Soed.* **1989**, 1676.

(271) Schofield, E.; Schulz, R. C. *Makromol. Chem., Rapid. Commun.* **1981**, *2*, 677.

(272) (a) Webster, O. W. *J. Am. Chem. Soc.* **1964**, *86*, 2898. (b) Mukherjee, T. K.; Levasseur, L. A. *J. Org. Chem.* **1965**, *30*, 644. (c) Junek, H.; Zuschnig, G.; Thierrichter, R.; Gfrerer, G.; Sterk, H. *Monatsh. Chem.* **1982**, *113*, 1045.

(273) Feldman, M.; Jackson, J. A. *Tetrahedron Lett.* **1966**, 797.

(274) (a) Matsuoka, M.; Han, L.; Kitao, T.; Mochizuki, S.; Nakatsu, K. *Chem. Lett.* **1988**, 905. (b) Matsuoka, M.; Yodoshi, T.; Han, L.; Kitao, T. *Dyes Pigm.* **1988**, *9*, 343.

(275) (a) Awano, H.; Ohigashi, M. *Synth. Met.* **1989**, *32*, 389; *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2101. (b) Awano, H.; Ogata, T.; Murakami, H.; Yamashita, T.; Ohigashi, H. *Synth. Met.* **1990**, *36*, 263. (c) Monkhorst, H. J.; Pott, G. T.; Kommandeur, J. *J. Chem. Phys.* **1967**, *47*, 401.

(276) Kuroda, H.; Kobayashi, M.; Kinoshita, M.; Takemoto, S. *J. Chem. Phys.* **1962**, *36*, 457.

(277) (a) Tanaka, J.; Tanaka, M.; Kawai, T.; Takabe, T.; Maki, O. *Bull. Soc. Chem. Jpn.* **1976**, *49*, 2358. (b) Mayerle, J. J.; Torrance, J. B. *Bull. Soc. Chem. Jpn.* **1981**, *54*, 3170.

(278) (a) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183. (b) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1989**, *32*, 268. (c) Hajiwara, T.; Yamaura, M.; Kato, K.; Hirasaka, M.; Iwata, K. *Synth. Met.* **1989**, *32*, 367. (d) Bertho, D.; Jouanin, C. *Phys. Rev. B* **1987**, *35*, 626. (e) Stafström, S.; Bredas, J. L. *J. Molec. Struct.* **1989**, *188*, 393. (f) Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.

(279) Mikhailenko, F. A.; Mushkalo, I. I.; Boguslavskaya, A. N. *Ukrain. Khim. Zh.* **1974**, *40*, 253.

(280) Kovalenko, S. N.; Chuev, V. P.; Nikitchenko, V. M.; Asimov, M. M. *Teor. Eks. Khim.* **1990**, *26*, 284.

(281) (a) Sano, N.; Tanaka, J. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 843. (b) Nakashima, N.; Ando, R.; Fukushima, H.; Kunitake, T. *J. Chem. Soc., Chem. Commun.* **1982**, 707.

(282) Renfrew, A. H. M. *J. Soc. Dyers Colour.* **1989**, *105*, 262.

(283) Hausser, K. H.; Murrell, J. N. *J. Chem. Phys.* **1957**, *27*, 500.

(284) Kimura, K.; Yamazaki, E.; Katsumata, S. *J. Phys. Chem.* **1971**, *75*, 1768.

(285) Kimura, K.; Yamada, H.; Tsubomura, H. *J. Chem. Phys.* **1968**, *48*, 440.

(286) Hiroma, S.; Kuroda, H.; Akamatu, H. *Bull. Soc. Chem. Jpn.* **1971**, *44*, 9.

(287) (a) Tanaka, J.; Mizuno, M. *Bull. Soc. Chem. Jpn.* **1969**, *42*, 1841. (b) Sato, Y.; Kinoshito, M.; Sano, M.; Akamatu, H. *Bull. Soc. Chem.*

Jpn. **1970**, *43*, 2370. (c) Oohashi, Y.; Sakata, T. *Bull. Soc. Chem. Jpn.* **1973**, *46*, 765.

(288) Almlöf, J. E.; Feyereisen, M. W.; Jozefiak, T. M.; Miller, L. L. *J. Am. Chem. Soc.* **1990**, *112*, 1206.

(289) Hioki, C.; Fukui, T. Jpn. Kokai Tokkyo Koho JP 01 113482, 1989; *Chem. Abstr.* **1990**, *112*, 45764z.

(290) (a) Chien, C. K.; Wang, H. C.; Szwarc, M.; Bard, A. J.; Itaya, K. *J. Am. Chem. Soc.* **1980**, *102*, 3100. (b) Moses, P. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1974**, *96*, 945. (c) Addison, A. W.; Li, T. H.; Weiler, L. *Can. J. Chem.* **1977**, *55*, 766. (d) Fanghänel, E.; Richter, A. M.; Kordts, B.; Beye, N. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1989**, *43*, 165. (e) Misaki, Y.; Matsumura, Y.; Sugimoto, T.; Yoshida, Z. *Tetrahedron Lett.* **1989**, *30*, 5289. (f) Gompper, R.; Wagner, H.-U. *Angew. Chem.* **1988**, *100*, 1492; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1437.

(291) (a) Kenny, P. W.; Jozefiak, T. H.; Miller, L. L. *J. Org. Chem.* **1988**, *53*, 5007. (b) Evans, A. G.; Evans, J. C.; Pomery, P. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1385.

(292) Miller, J. S.; Dixon, D. A.; Calabrese, J. C.; Vazquez, C.; Krusic, P. J.; Ward, M. D.; Wassermann, E.; Harlow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 381.

(293) (a) Rao, C. N. R.; Bhaskar, K. R. In *The Chemistry of the Nitro and Nitroso Groups*; Feuer, H., Ed.; Intersc. Publ.: New York; Part 1, pp 147 ff; (b) *DMS UV Atlas of Organic Compounds*; Verlag Chemie: Weinheim, 1967; D8/15.

(294) (a) Kroner, J.; Schneid, W.; Wiberg, N.; Wrackmeyer, B.; Ziegleder, G. *J. Chem. Soc., Faraday Trans. 2* **1978**, 1909. (b) Gillis, B. T.; Izydore, R. A. *J. Org. Chem.* **1969**, *34*, 3181.

(295) (a) Barbarella, G.; Bongini, A. *Tetrahedron* **1989**, *45*, 5137. (b) Fabian, J.; Mehlhorn, A. *Z. Chem.* **1967**, *7*, 192. (c) Serafimov, O.; Brühlmann, U.; Huber, J. R. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 202. (d) Reid, D. H.; Webster, R. G.; McKenzie, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2334.

(296) (a) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079. (b) Okazaki, R.; Kumon, N.; Inamoto, N. *J. Am. Chem. Soc.* **1989**, *111*, 5949. (c) Reid, D. H. *J. Chem. Soc. C* **1971**, 3187.

(297) Middleton, W. J. *J. Am. Chem. Soc.* **1966**, 88, 3842.

(298) Pinsl, J.; Gehrtz, M.; Reggel, A.; Bräuchle, C. *J. Am. Chem. Soc.* **1987**, *109*, 6479.

(299) (a) Zweig, A.; Hoffmann, A. K. *J. Org. Chem.* **1965**, *30*, 3997. (b) Cimiraglia, R.; Fabian, J.; Hess, B. A. *J. Mol. Struct.* (*THEOCHEM*) 1991, *230*, 287.

(300) (a) Otsubo, T.; Sukenobe, N.; Aso, Y.; Ogura, F. *Chem. Lett.* **1987**, 315. (b) Otsubo, T.; Miyamoto, H.; Aso, Y.; Ogura, F. *Synth. Met.* **1987**, *19*, 595. (c) Behringer. H.; Meinetsberger, E. *Tetrahedron Lett.* **1975**, 3473.

(301) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

(302) Rao, C. N. R.; Kalyanaraman, V.; George, M. V. *Appl. Spectr. Rev.* **1970**, *3*, 153 and references given therein.

(303) (a) Suzuki, H.; Koyano, K.; Shida, T.; Kira, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2794. (b) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 2268. (c) Hünig, S.; Scheutzow, D.; Friedrich, H. J. *Angew. Chem.* **1964**, *3*, 701. (d) Berneth, H.; Hagenbruch, B.; Hünig, S.; Burkhard, O. *Liebigs Ann. Chem.* **1984**, 354. (e) Hug, S.; Yee, W. A.; Kliger, D. S. *Chem. Phys. Lett.* **1990**, *168*, 385.

(304) Lafferty, J.; Roach, A. C.; Sinclair, R. S.; Truscott, T. G.; Land, E. J. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 416.

(305) (a) Angliker, H.; Gerson, F.; Lopez, J.; Wirz, J. *Chem. Phys. Lett.* **1981**, *81*, 242. (b) *DMS UV Atlas of Organic Compounds*; Verlag Chemie: Weinheim, 1967; E4/3–E4/4.

(306) (a) Jain, V. K.; Zaidi, Z. H. *Spectrochim. Acta A* **1987**, *43*, 1275. (b) Ford, W. E.; Hiratsuka, H.; Kamat, P. V. *J. Phys. Chem.* **1989**, *93*, 6629. (c) *DMS UV Atlas of Organic Compounds*; Verlag Chemie: Weinheim, 1967; E6/23–24. (d) Salbeck, J.; Kunkely, H.; Langhals, H.; Saalfrank, R. W.; Daub, J. *Chimia* **1989**, *43*, 6. (e) Penneau, J.-F.; Stallman, B. J.; Kasai, P. H.; Miller, L. L. *Chem. Mater.* **1991**, *3*, 791.

(307) (a) Neugebauer, F. A.; Fischer, H.; Bamberger, S.; Smith, H. O. *Chem. Ber.* **1972**, *105*, 2694. (b) Grimison, A.; Simpson, G. A. *J. Phys. Chem.* **1968**, *72*, 1776. (c) Hünig, S.; Steinmetzer, H.-C. *Liebigs Ann. Chem.* **1976**, 1090. (d) Washio, M.; Tagawa, S.; Tabato, Y. *J. Phys. Chem.* **1980**, *84*, 2876.

(308) Peychal-Heiling, G.; Wilson, G. S. *Anal. Chem.* **1971**, *43*, 545, 550.

(309) (a) Effenberger, F.; Stohrer, W.-D.; Mack, K.-E.; Reisinger, F.; Seufert, W.; Kramer, H. E. A.; Föll, R.; Vogelmann, E. *J. Am. Chem. Soc.* **1990**, *112*, 4849. (b) Gompper, R.; Wagner, H.-U. *Angew. Chem.* **1988**, *100*, 1492; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1437. (c) Breslow, R.; Maslak, P.; Thomaides, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 6453.

(310) Khan, Z. H. *Z. Naturforsch. A* **1984**, *39*, 668; **1987**, *42*, 91; *Spectrochim. Acta A* **1988**, *44*, 313, 1125.

(311) (a) Zahradník, R.; Čársky, P.; Slanina, Z. *Collect. Czechoslov. Chem. Commun.* **1973**, *38*, 1886. (b) Shida, T.; Nosaka, Y.; Kato, T. *J. Phys. Chem.* **1978**, *82*, 695. (c) Haselbach, E.; Bally, T.; Gschwind, R.; Klemm, U.; Lanyiova, Z. *Chimia* **1979**, *33*, 405. (d) Anklam, E.; Asmus, K.-D.; Robertson, L. W. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1569.

(312) Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, 87, 557.

(313) Zahradník, R.; Čársky, P. *Prog. Phys. Org. Chem.* **1973**, *10*, 327.

(314) (a) Neugebauer, F. A.; Fischer, H.; Bamberger, S.; Smith, H. O. *Chem. Ber.* **1972**, *105*, 2694. (b) Kainer, H.; Hausser, K. H. *Chem. Ber.* **1953**, *86*, 1563. (c) Neunhoeffer, O.; Heitmann, P. *Chem. Ber.* **1959**, *92*, 245. (d) Hausser, K. H.; Kainer, H. *Z. Naturforsch. A* **1954**, *9*, 783. (e) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. (f) Burrows, H. D.; Greatorex, D.; Kemp, T. J. *J. Phys. Chem.* **1972**, *76*, 20. (g) Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055.

(315) (a) Wizinger, R. *Palette (Basel)* **1966**, *24*, 24. (b) Katulin, V. A.; Petrov, A. L.; Freyer, W. *Kvantovaya Electron.* (*Moscow*) **1984**, *11*, 115. (c) Otto, M.; Stach, J.; Kirmse, R.; Werner, G. *Z. Chem.* **1981**, *21*, 297. (d) Zweig, A.; Hodgson, W. G.; Jura, W. H.; Maricle, D. L. *Tetrahedron Lett.* **1963**, *26*, 1821. (e) Buck, H. M.; Bloemhoff, W.; Oosterhoff, W. J. *Tetrahedron Lett.* **1960**, *9*, 5.

(316) Lantratova, O. B.; Prokof'ev, A. I.; Khurdyakov, I. V.; Kuzmin, V. A.; Pokrovskaya, I. E. *Nouv. J. Chim.* **1982**, *6*, 365.

(317) (a) Haller, I.; Kaufman, F. B. *J. Am. Chem. Soc.* **1976**, *98*, 1464. (b) *DMS UV Atlas of Organic Compounds*, Verlag Chemie: Weinheim, 1967; D9/52. (c) Melby, L. R.; *Can. J. Chem.* **1965**, *43*, 1448. (d) Frank, W.; Gompper, R. *Tetrahedron Lett.* **1987**, *28*, 3083. (e) Kossmehl, G.; Wallis, J. *Makromol. Chem.* **1982**, *183*, 347. (f) Schmidt, R. R.; Hensen, H. *Chem. Ber.* **1981**, *114*, 1723. (g) Motta, S.; Waragai, K. *Synth. Met.* **1989**, *32*, 395.

(318) (a) Schukat, G.; van Minh, L.; Fanghänel, E. *Z. Chem.* **1976**, *16*, 360. (b) Fanghänel, E.; Schukat, G.; Schützendübel, J. *Z. Chem.* **1981**, *21*, 447. (c) Franghänel, E.; von Minh, L.; Schukat, G. *J. Prakt. Chem.* **1989**, *321*, 479. (d) Fanghänel, E.; Richter, A. M.; Kordts, B.; Berge, N. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1989**, *43*, 165. (e) Ueno, Y.; Nakayama, A.; Okawara, M. *J. Chem. Soc., Chem. Commun.* **1978**, 74. (f) Zhilyaeva, E. I.; Zolotukhin, S. P.; Lyubovskaya, R. N.; Lyubovskii, P. B.; Khidekel', M. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 917. (g) Bryce, M. R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 675.

(319) Hünig, S.; Garner, B. J.; Ruider, G.; Schenk, W. *Liebigs Ann. Chem.* **1973**, 1036.

(320) (a) Neugebauer, F. A.; Fischer, H. *Chem. Ber.* **1971**, *104*, 886. (b) Clark-Lewis, J. W.; Moody, K. *Aust. J. Chem.* **1971**, *24*, 2593. (c) Bandlish, B. K.; Shine, H. J. *J. Org. Chem.* **1977**, *42*, 561.

(321) (a) Cauquis, G.; Deronzier, A.; Lepage, J.-L.; Serve, D. *Bull. Soc. Chim. Fr.* **1977**, 295. (b) Serve, D. *Bull. Soc. Chim. Fr.* **1976**, 1567. (c) Moutet, J.-C.; Reverdy, G. *Tetrahedron Lett.* **1979**, 2389. (d) Bidan, G.; Genies, M. *Nouv. J. Chem.* **1981**, *5*, 117. (e) Fujita, H.; Yamauchi, J. *J. Heterocycl. Chem.* **1980**, *17*, 1053.

(322) (a) Hinrichs, W.; Berges, P.; Klar, G. *Z. Naturforsch. B* **1987**, *42*, 169. (b) Schulz, P.; Mansel, V.; Klar, G. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1989**, *42*, 227. (c) Fava, A.; Sogo, P. B.; Calvin, H. *J. Am. Chem. Soc.* **1957**, *79*, 1078. (d) Addison, A. W.; Li, T. H.; Weiler, L. *Can. J. Chem.* **1977**, *55*, 766.

(323) (a) Hünig, S.; Kiesslich, G.; Linhart, F.; Schlaf, H. *Liebigs Ann. Chem.* **1971**, *752*, 196. (b) Hünig, S.; Sauer, G. *Liebigs Ann. Chem.* **1971**, *748*, 173. (c) Hünig, S.; Steinmetzer, H.-C. *Tetrahedron Lett.* **1972**, 643.

(324) Geiger, W. E. *J. Phys. Chem.* **1973**, *77*, 1862.

(325) (a) Jozefiak, T. H.; Miller, L. L. *J. Am. Chem. Soc.* **1987**, *109*, 6560. (b) Jozefiak, T. H.; Thomas, M.; Almlöf, J. F.; Feyereisen, M. W.; Miller, L. L. *J. Am. Chem. Soc.* **1989**, *111*, 4105. (c) Almlöf, J. E.; Feyereisen, M. W.; Jozefiak, T. H.; Miller, L. L. *J. Am. Chem. Soc.* **1990**, *112*, 1206. (d) Miller, L. L.; Liberko, C. A. *Chem. Mater.* **1990**, 339. (e) Kenny, P. W.; Jozefiak, T. H.; Miller, L. L. *J. Org. Chem.* **1988**, *53*, 5007. (f) Rak, S. F.; Jozefiak, T. H.; Miller, L. L. *J. Org. Chem.* **1990**, *55*, 4794.

(326) Chu, T. L.; Weismann, T. J. *J. Am. Chem. Soc.* **1956**, *78*, 3610.

(327) (a) Dieckman, J.; Hertler, W. R.; Benson, R. E. *J. Org. Chem.* **1963**, *28*, 2719. (b) Maxfield, M.; Bloch, A. N.; Cowan, D. O. *J. Org. Chem.* **1985**, *50*, 1789. (c) Le Goff, E.; Lacount, R. B. *J. Org. Chem.* **1968**, *33*, 2529. (d) Morinaga, M.; Nogami, T.; Mikawa, M. *Bull. Soc. Chem. Jpn.* **1979**, *52*, 3739.

(328) Yasuda, A.; Seto, J. *J. Electroanal. Chem.* **1988**, *247*, 193.

(329) Kamogawa, H.; Nanasawa, M. *Chem. Lett.* **1988**, 373.

(330) Pragst, F.; Schwertferger, I. *J. Prakt. Chem.* **1974**, *316*, 795.

(331) (a) Hünig, S.; Linhart, F. *Liebigs Ann. Chem.* **1975**, 2116. (b) Hünig, S.; Scheutzow, D.; Schlaf, H.; Pütter, H. *Liebigs Ann. Chem.* **1974**, 1436. (c) Hünig, S.; Steinmetzer, H.-C. *Liebigs Ann. Chem.* **1976**, 1060. (d) Hünig, S.; Linhart, F. *Liebigs Ann. Chem.* **1976**, 317. (e) Hesse, K.; Hünig, S. *Liebigs Ann. Chem.* **1985**, 708. (f) Hünig, S.; Garner, B. J.; Ruider, G.; Schenk, W. *Liebigs Ann. Chem.* **1973**, 1036. (g) Stemmler, I. Doctoral Dissertation, University of Würzburg 1976; p 116.

(332) (a) Deuchert, K.; Hünig, S. *Angew. Chem.* **1978**, *90*, 917; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 875. (b) Hünig, S.; Berneth, M. *Top. Curr. Chem.* **1980**, *92*, 3.

(333) (a) Nojima, M.; Takagi, M.; Morinaga, M.; Nagao, G.; Tokura, N. *J. Chem. Soc., Perkin Trans. 1* **1978**, 488. (b) Ballester, M.; Riera, J.; Castañer, J.; Rodriguez, A.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1982**, *47*, 4498.

(334) (a) Kuhn, R.; Neugebauer, F. A. *Monatsh. Chem.* **1963**, *94*, 17; **1964**, *95*, 3. (b) Watanabe, K.; Yamauchi, J.; Ohya-Nishiguchi, M.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 274.

(335) (a) Kuhn, R.; Trischmann, H. *Monatsh. Chem.* **1964**, *95*, 457. (b) Neugebauer, F. A. *Angew. Chem.* **1973**, 85, 485; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 455. (c) Neugebauer, F. A.; Bernhardt, R. *Chem. Ber.* **1974**, *107*, 529. (d) Neugebauer, F. A. *Tetrahedron* **1970**, *26*, 4853.

(336) (a) Polumbrik, O. M. *Usp. Khim.* **1978**, *47*, 1444. (b) Aslanidi, E. B.; Gandels'man, I. L.; Tikhonov, E. A.; Shpak, M. T. *Ukrain. Fiz. Zh.* **1970**, *15*, 1284.

(337) (a) Müller, E.; Ley, K. *Chem. Ber.* **1954**, 87, 922. (b) Khudyakov, I. V.; Levin, P. P.; Kuz'min, V. A.; deIonge, K. *Izv. Akad. Nauk, Ser. Khim.* **1977**, 1303.

(338) (a) Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2596. (b) Khudyakov, I. V.; Levin, P. P.; deIonge, K.; Bekman, K.-M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1977**, 1655. (c) Gierke, W.; Harrer, W.; Kirste, B.; Kurreck, H.; Reusch, J. *Z. Naturforsch. B* **1976**, *31*, 965. (d) Chandross, E. A. *J. Am. Chem. Soc.* **1964**, *86*, 1263.

(339) (a) Miura, Y.; Kinoshita, M. *Makromol. Chem.* **1974**, *175*, 23. (b) Breitenbücher, J. Doctoral Dissertation, University of Stuttgart, 1990.

(340) (a) Kuhn, R.; Neugebauer, F. A.; Trischmann, H. *Angew. Chem.* **1965**, *77*, 43. (b) Neugebauer, F. A.; Trischmann, H.; Jenne, H. *Angew. Chem.* **1967**, *79*, 317. (c) Neugebauer, F. A.; Bernhardt, R.; Fischer, H. *Chem. Ber.* **1977**, *110*, 2254. (c) Kuhn, R.; Neugebauer, F. A.; Trischmann, H. *Monatsh. Chem.* **1966**, *97*, 525.

(341) (a) Kosower, E. M.; Poziomek, F. J. *J. Am. Chem. Soc.* **1964**, *86*, 5515. (b) Hermolin, J.; Levin, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 4801, 4808.

(342) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148.

(343) Kelemen, J. *Chimia* **1991**, *45*, 15.

(344) Neugebauer, F. A.; Fischer, P. H. H. *Chem. Ber.* **1965**, *98*, 844.

(345) El'chinov, D. P.; Matevosyan, R. O. *Zh. Org. Khim.* **1967**, *3*, 422.

(346) Awere, E. G.; Burford, N.; Mailer, C.; Passmore, J.; Schriver, M. J.; White, P. S.; Banister, A. J.; Oberhammer, H.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1987**, 66.

(347) Buchwalter, S. L.; Iyenger, R.; Viehbeg, A.; O'Toole, T. R. *J. Am. Chem. Soc.* **1991**, *113*, 376.

(348) (a) Elliott, C. M.; Hershenhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7519. (b) Kaizu, Y.; Kobayashi, H. *Bull. Soc. Chem. Jpn.* **1970**, *43*, 2492.

(349) (a) Mihara, C.; Santo, T.; Sugata, H. Jpn. Kokkai Tokkyo Koho JP 02 243656, 1990; *Chem. Abstr.* **1991**, *114*, 19644j. (b) Sumiya, M.; Sato, G. Jpn. Kokai Tokkyo Koho JP 63 051462, 1988; *Chem. Abstr.* **1988**, *109*, 75215b.

(350) (a) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181. (b) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Rausch, M. D. *J. Am. Chem. Soc.* **1977**, *99*, 2964.