SYNTHESIS AND PROPERTIES OF NON SYMMETRICALLY SUBSTITUTED PERYLENE DYES

M.S. THESIS

by

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Approval of the Graduate Institute

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We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master Arts and Sciences in Chemistry.

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To my family

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ABSTRACT

In this study, we have aimed to synthesize symmetrical and unsymmetrical diimides. We have succeeded to synthesize the N,N′-dioctadecyl-3,4,9,10-perylene bis(dicarboximide) and N-octadecyl-3,4,9,10-perylene tetracarboxylic diimide from perylene dianhydride and determine their structure and purity by spectral analysis.

We have calculated their fluorescence quantum yields from the UV absorption and emission spectra. The fluorescence quantum yield is reduced from 0.80 to 0.37. We know the differences are coming from higher tendency to aggregate in unsymmetrical perylene diimides.

Solid state analysis by IR, elemental analysis and MS gave consistent results for purities and structural characteristics.

ÖZET

Bu çalışmada simetrik ve antisimetrik diimidlerin sentezleri amaçlanmıştır. Bu amaçla N,N'- dioktadesil-3,4,9,10-perilen bis(dikarboksimid) ve N-oktadesil-3,4,9,10-perilen tetrakarboksilik diimidler perilen dianhidritten sentezlenip yapıları ve saflıkları spektral yöntemlerle kanıtlanmıştır.

UV Absorpsiyon ve emisyon spektrumlarından faydalanılarak fluoresans kunatum verimleri hesaplanmıştır. Fluoresans kuantum veriminin 0.80'den 0.37'ye düştüğü gözlemlendi. Bu düşüşün antisimetrik perilen diimidlerdeki aggregrasyon eğiliminden geldiği düşünülmektedir.

IR, elementel analiz ve MS spektroskopik yöntemlerle sentezlenen diimidlerin saflıkları ve yapıları kanıtlanmıştır.

ABBREVIATIONS

NMR : Nuclear Magnetic Resonance

UV : Ultra Violet

IR : Infra Red

MS : Mass Spectra

S_n : Singlet State

T_n : Triplet State

E_T : Triplet Energy

A : Acceptor

^3A : Triplet State of Acceptor

D : Donor

^1D : Singlet State of Donor

^3D : Triplet State of Donor

Q : Quencher

K_q : Quenching Rate Constant

T : Transmission

A : Absorbance

ε : Excitation Coefficient

max : Maximum

l : Path length

c : Concentration

λ : Wavelength

ϕ : Quantum Yield

ϕ_F : Fluorescence Quantum yield

nm : Nanometer

$\bar{\nu}$: Wavenumber

eV : Electron Volt

m.p : Melting Point

log : Logarithm

Hz : Hertz

Ph : Phenyl

NaOH : Sodium Hydroxide

HCl : Hydrochloric Acid

H_2SO_4 : Sulphuric Acid

Conc. : Concentration

NH_3 : Ammonia

H_3PO_4 : Phosphoric Acid

KOH : Pottasium Hydroxide

H_2O : Water

K_2CO_3 : Pottasium Carbonate

DMF : N,N′- Dimethyl Formamide

DOD : Dodecyl Diimide

Rhd101: Rhodamine 101

$BaSO_4$: Barium Sulphate

C_9H_7N : Isoquinoline

C_7H_8O : m-Cresol

$CHCl_3$: Chloroform

KBr : Pottasium Bromide

S_1 : First Excited Singlet State

RNH_2 : Primary Amine

ν : Frequency

E : Photon Energy

h : Planck Constant

fig. : Figure

I : Emergent Radiation

I_0 : Incident Radiation

m : Meter

Å : Angstrom

kcal : Kilo Calorie

kJ : Kilo Joule

NO_2 : Nitro Group

Me : Methyl Group

K_a : Acid Dissociation Constant

sec. : Second

S_0 : Ground State

S_2 : Second Excited Singlet State

T_1 : First Excited Triplet State

K_n : Equilibrium Constant

R_0 : Molecule at Ground State

R^* : Molecule at Excited State

D_T : Triplet State Donor

D_S : Singlet State Donor

A_S : Singlet State Acceptor

E_S : Siglet Energy

τ : Lifetime

Co : Cobalt

ml : Millilitre

mg : Milligram

g : Gram

CH_4 : Methane

M : Molarity

M.W. : Molecular Weight

S : Integrated Emission Area

u : Unknown

s : Standard

per : Perylene

Rh : Rhodamine 101

N_D : Refractive Index

P1 : Monopotassium Carboxylate of 3,4,9,10-Perylene Tetracarboxylicacid

P2 : 3,4,9,10-Perylene Tetracarboxylic-3,4-Anhydride-9,10-Imide

P3 : N-Octadecyl-3,4,9,10-Perylene Tetracarboxylic Diimide

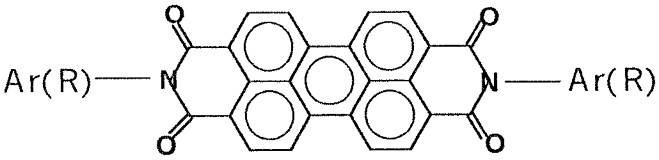
P4 : N,N′-dioctadecyl-3,4,9,10-Perylene bis(dicarboximide)

M+1 : Base Peak

$CH_3(CH_2)_{17}NH_2$: Octadecyl Amine

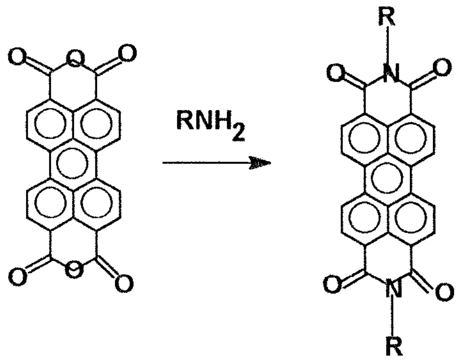
I. INTRODUCTION

Perylene 3,4,9,10-bis (dicarboximides) (1), perylene dyes have been known since 1913 as highly photostable pigments or vat dyes [18,26]. Geisser and Remy firstly described the fluorescence of perylene in solution in 1559. However the high fluorescence potential of the dyes could not be realized and applied because of the low solubility of these substances. More recent development has led to soluble derivatives which are highly fluorescent and which form one of the most stable classes of fluorescent dyes. [29, 47].



(1)

The synthesis of symmetrically substituted perylene dyes from the corresponding anhydride is straightforward. The bisanhydride is also a very good starting material for the preparation of other perylene derivatives because it can be easily obtained analytically pure, even on a technical scale. As an example, highly pure perylene diimides can be prepared by condensation of (2) with corresponding amines in m-cresol, isoquinoline solvent mixtures (40:1) . Zinc salts like zinc acetate may be used as catalyst for the reaction. Other salts, for example iron or lead or copper salts, can be used, but are less effective [18]. Additionally, the separation of these metal salts from the reaction products can be difficult. The role of zinc salts is not clear, they are denoted as dehydration reagents. A more plausible interpretation is that the zinc salts might be solutizers on the basis of complexation of the anhydride [12]. The bisanhydride, or the bisimide, are insoluble in any organic solvent used for the synthesis; no coloration or no fluorescence! However their solubility is strongly increased by the addition of zinc salts.



(2)

Together with the photostability the dyes are also very stable thermally [30]; some derivatives can be sublimed at temperatures up to 800 °C [29]. Therefore they are very resistant towards ionizing radiation. They can be dissolved in concentrated sulfuric acid and reobtained by dilution without decomposition. Concentrated hypochlorite solutions do not give any bleaching effect.

Most of solid perylene dyes are red. Besides that orange, maroon, bluish black and black derivatives are known. Some of them exhibit an intense bronze like metallic surface lustre. Many of the red dyes have a solid-state fluorescence. The orange colored derivatives are generally fluorescent.

Perylene dyes are interesting for dye laser applications. The photostability of perylene dyes is even higher than that of rhodamin 6G, one of the most stable laser dyes known to date. The laser-light efficiency is a little lower for the latter. This might be due to a small amount of S_1- S_n absorption [34]. Perylene fluorescent dyes may be applied in light concentrating systems for the concentration of diffuse solar radiation. They can be also used as light emitting species in oxalate chemiluminescent devices because of their chemical persistency [18]. The high photostability and fluorescent quantum yield make the perylene dyes ideal tools for highly sensitive fluorescent analysis methods. They have been used in optical fluorescent sensors where the long-term stability is a critical point. A further amplification of the analytical signal is achieved if the dyes are incorporated in the double layer of liposomes. These fluorescent liposomes can be attached to antibodies as a general selectively binding system and thus a universal analysis system can be established. Because of the lightfastness of the dyes even single fluorescent immunoantibodies can be visually observed and their binding site located under a fluorescence microscope.

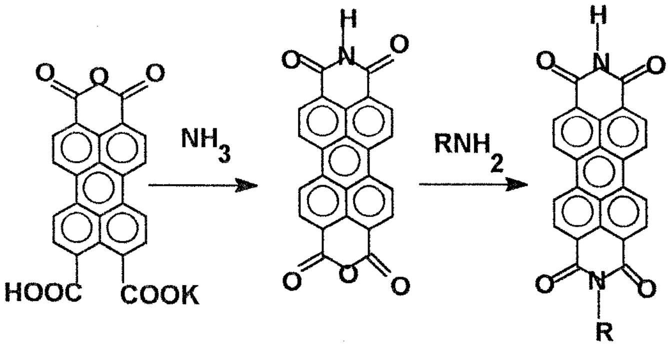
It is not possible to prepare non-symmetrical substituted perylene diimides by a stepwise condensation of the technical bisanhydride with primary amines. A reaction of the bisanhydride with a primary amine as a minor component will not produce 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10-imide [27] as might be expected, rather the amines are completely converted to symmetrical perylene diimides and the excess of bisanhydride remains unreacted.

In this work we have synthesized symmetrical and unsymmetrical [28] perylene diimides. The symmetrical perylene diimides are synthesized in the same way as described before [11]. We have synthesized unsymmetrical perylene diimides via a long synthetic route:

a- Synthesis of monopotassium carboxylate of 3,4,9,10-perylenetetracarboxylic acid monoanhydride

b- Synthesis of 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10-imide.

c- Synthesis of unsymmetrical perylene diimides.



Elemental analyses, absorption spectra, and IR and MS spectra confirm the structures at each level. The fluorescence quantum yield calculation from UV absorption and emission spectra has shown interesting characteristic. The properties of unsymmetrical and symmetrical perylene diimides are compared.

II. THEORETICAL

II.1.1 Colour and Colour Measurement

II.1.1.1 Introduction

Colour plays a remarkably dominant role in our everyday lives. Clothing, carpets, painted walls, plastic veneers, food, all contain these substances. Even so-called white objects, such as a white page, are normally rendered "whiter than white" by the incorporation of special dyes, known as fluorescent brightening agents.

In 1856, William Henry Perkin synthesized the first synthetic dye, Mauveine [4]. Today, virtually all commercially available dyes and pigments are synthetic substances, with the exception of some important inorganic pigments, and every year hundreds of new coloured compounds are described in the patent literature for a multitude of applications [2].

Colour is a subjective phenomenon, as it is the response of brain to the stimulation of the eye by light. The physical origins of colour were the first to receive any systematic attention, and it was early recognized that the absorption spectrum of a dye could give at least a rough indication of the colour of the dye in practical usage.

II.1.1.2 What is Colour?

Colour is no more a *physical* property of an object than is, say, the odour of a rose a physical property of the flower. The causes of both sensations do have a physical interpretation. In the absence of light of any kind, an observer cannot perceive colour, and thus it can be concluded that colour arises from an interaction of light with the eye. Colour is, in fact, the way in which the brain recognizes the different qualities of light falling on the retina. A discussion of colour must therefore begin with an understanding of the properties of light [3,6].

Light has dual characteristics both wave and particle character.

In wave theory, light can be characterized either by its wavelength (λ), *i.e.* the distance required for one complete oscillation of the wave, or by its frequency (ν), the number of oscillations occurring in unit time. The velocity of the wave is thus given by the product of these two quantities [7].

$$c = \nu . \lambda \tag{1.1}$$

In the particle theory, monochromatic radiation is characterized by the energy of each photon. Planck equation relates this photon energy (E) to the frequency of the wave.

$$E = h . \nu \tag{1.2}$$

The quantity h is the Planck constant, and has a value of 6.625×10^{-34} J.s.

The electromagnetic spectrum includes radiation ranging from very short wavelengths (high energy) , such as X-rays and γ-rays, to radiation of very long wavelengths, such as radio waves. Only a very narrow portion of the total spectrum can produce a visual sensation when the radiation is incident on the eye, the limits of the visible region extending from about 400 nm to 800 nm in wavelength usually we refer to radiation in this region as *light* [46]. The different "qualities" of light that are responsible for the sensation of colour are its wavelength, or equivalently, its photon energy.

If a reasonably homogenous mixture of all wavelengths of light between 400 and 800 nm is incident on the retina of the eye, then the sensation of white is manifested. White, like black or grey , is termed an *achromatic* colour [2]. When such a mixture is passed through a suitable prism or diffraction grating, the beam is split up into a continuum of colours, the dominant hues occuring in the well known order: red, orange, yellow, green, blue, and violet as shown in Figure 1.1.

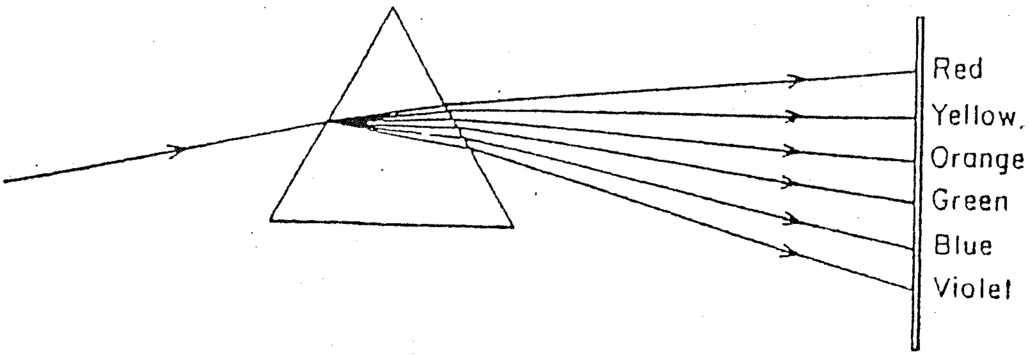


Fig .1.1 The dispersion of white light into the visible spectrum. [2]

The wavelengths of the radiation giving rise to these colours decrease in the same order, from red to violet. Thus a low energy photon (say of 45 kcal.mol^{-1}) gives the sensation of red, whereas a high energy photon (say of 70 kcal.mol^{-1}) gives the sensation of violet [2]. There are 150 different hues identified. However, for normal purposes, the visible spectrum can be divided into nine broad regions, each readily distinguishable from the others, and these can be depicted in the form of a colour circle Figure 1.2 .

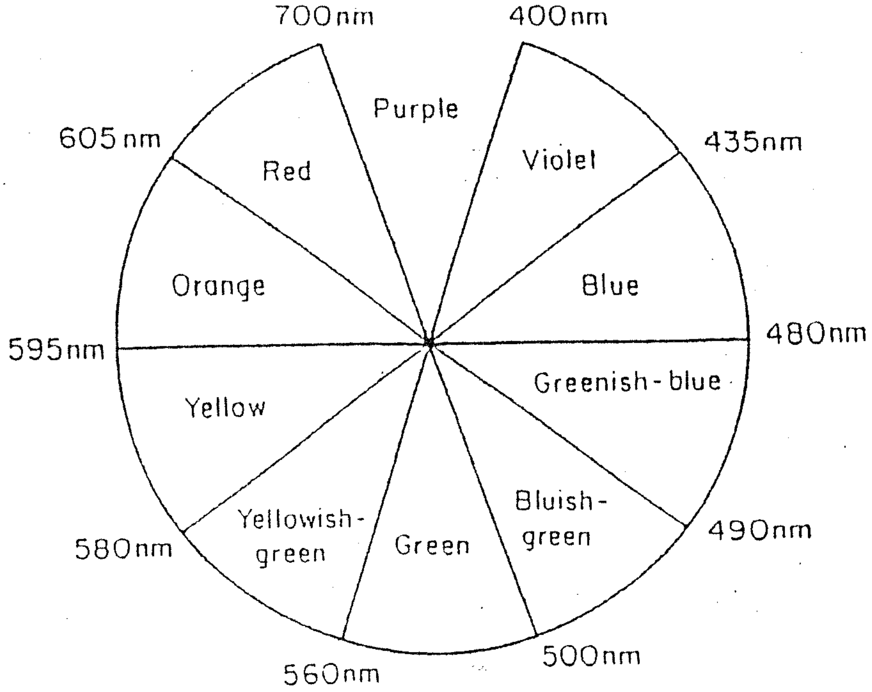


Fig. 1.2 The colour circle. Each sector corresponds to the wavelengths of monochromatic light giving a particular hue. [2]

In Figure 1.2 the wavelength scale around the circumference of the circle has no physical significance, but it will be noted that each sector has another sector diametrically opposed to it and also the colour purple is not duplicated by any single wavelength of light, and this is called a *non-spectral* [2,4] colour.

The colour circle can be used to discuss the aspects of colour and colour mixing. All the colours of the circle, if mixed in the correct amounts, give white light. However, white light, at least as far as the human eye is concerned, is also produced by mixing two monochromatic radiations from any pair of opposite sectors. Such pairs of colour are said to be *complementary* [2]. For example , the complementary colour of blue (sector 435 - 480 nm) will be yellow (580 - 595 nm), and white light can be produced by mixing blue and yellow light.

Mixing radiations in this way is called *additive* mixing [4], since the intensity of the resultant colour increases additively as more components are added to the mixture. For example, the synthesis of the colour yellow by mixing red and green radiations.

A pure spectral hue is afforded by a monochromatic light wave or the same hue can be accurately duplicated by mixing two different monochromatic radiations. In fact, the hue may be synthesized from any number of combinations of monochromatic radiations, and it is apparent that the eye can register the same colour sensation for a wide variation in the quality of the radiation entering the eye. The eye is not capable of assessing the characteristics of light in the same way that a spectrophotometer can.

If three monochromatic radiations are selected so that they are well separated on the colour circle, then it is found that every possible hue can be reproduced by additive mixing of these colours. The trio can then be called *additive primary colours* [2].

In colour television, for example, the remarkably good colour production that can be obtained depends solely on three phosphors, giving the primary colours, red, green and blue.

The vast majority of colours that pervade our environment are not of this type, however, and in fact arise from what is known as *subtractive* [4] colour mixing process. Mixing a pair of complementary colours gives an apparent sensation of white light. If one of the components of such a mixture is removed, e.g. by passing the beam through a filter, then the remaining component will obviously be detected by the eye. A similar situation arises with white light that actually consists of a mixture of all wavelengths, such as daylight. If one wavelength, or a narrow band of wavelengths is removed from the mixture, the colour registered by the eye is *the complementary colour of the radiation removed.* This shows that the light falling on the eye is still an extremely complex mixture of wavelengths. One example, if sunlight is passed through a filter that removes a band of wavelengths in the region of 495 nm (i.e. bluish-green light), the eye will perceive the complementary colour of blue - green , namely red. Colours formed by removal of radiations from white light are said to be produced by *subtractive* colour mixing. Dyes, pigments and other coloured substances appear coloured because of this type of phenomenon, the molecules selectively filtering certain wavelengths from normal daylight.

As the absorption maximum of a substance moves from short to long wavelengths, the colour of light absorbed progresses through the sequence violet, blue, greenish blue, bluish green, green, yellowish green, yellow, orange and red (Figure 1.2). The *observed* sequence of colours can be deduced from Figure 1.2 , by noting the complementary colour of that absorbed. For most purposes only seven complementary colours need to be memorized, and these are, ranging from left to right for the absorption band of a substance on the recorded spectrum : yellow, orange, red, purple, violet, blue and bluish green. This can be understood from Figure 1.3 , which shows the absorption spectra and observed colours of representative dyes.

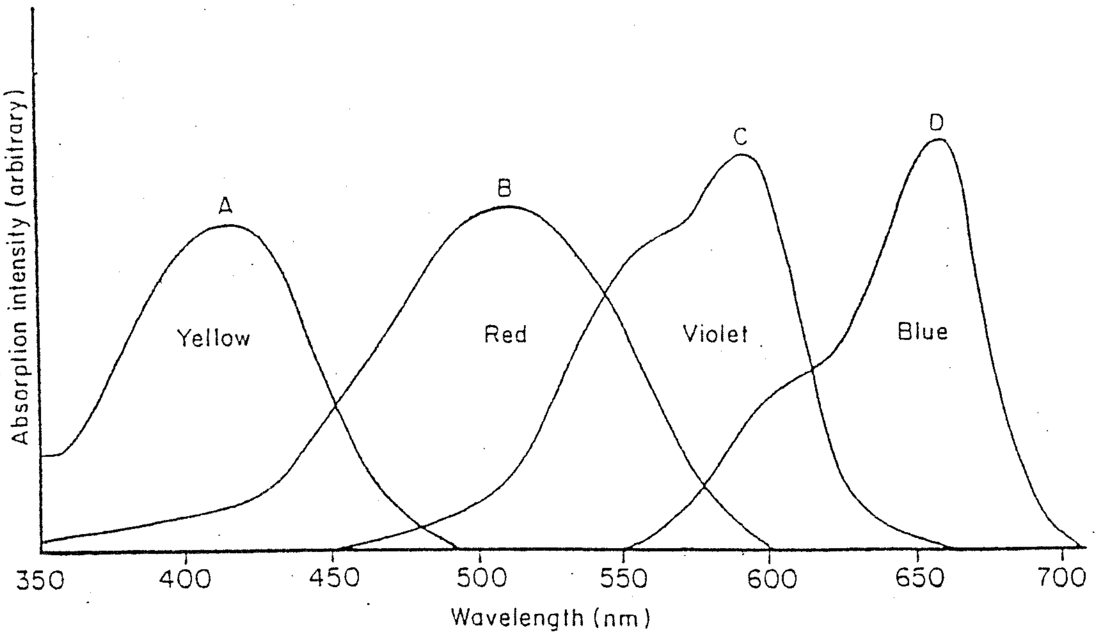


Fig. 1.3 Visible absorption spectra of (A) 2-aminoanthraquinone, (B) 1-methylaminoanthraquinone, (C) Crystal Violet, and (D) Methylene Blue, measured in ethanol. The observed colours of the solutions are indicated. [2]

Figure 1.4 shows the absorption spectrum of a typical green dye, Malachite Green, with two absorption bands in the red and violet regions of the spectrum.

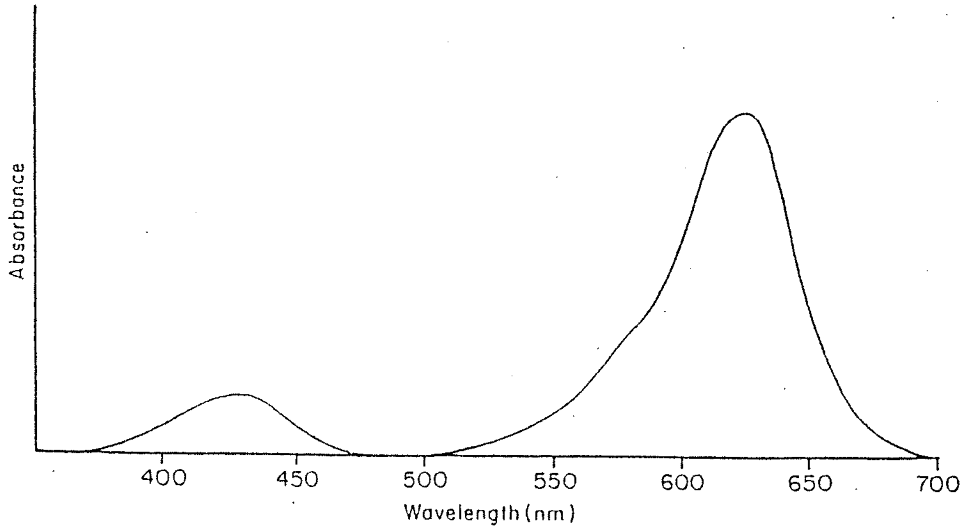


Fig. 1.4 Absorption spectrum of Malachite Green (in ethanol). [2]

The different intensities of the two peaks affects the shade of green observed, and in this example the red-absorbing peak (giving a blue visual sensation) is more intense than the violet-absorbing peak (yellowish green sensation), and thus the observed shade is rather dull green with a blue cast.

When dyes and pigments are mixed together, a wide variety of colours can be produced, as they can be the additive mixing of coloured lights. In the former case however, it is found that as more and more components are added to the mixture, the resultant colour becomes darker and darker, until eventually black is produced, whereas in the latter case, white is produced. The production of black is easy to understand for subtractive mixing, since the addition of more absorbing molecules to the mixture results in an increase in the amount of incident light absorbed, until eventually almost complete absorption occurs.

Some colours produced by subtractive mixing are not easily described by hue alone, and these are the dark or dull shades, such as browns, maroons, olive greens, etc. These shades are actually provided by substances that absorb over a relatively high proportion of the visible spectrum, but which still absorb most intensely at those wavelengths that provide the dominant hue. Single compounds with broad absorption bands, or mixtures of dyes with overlapping bands are used commercially to provide colours of this type. On the other hand, the most brilliant, pure colours are provided by dyes with very narrow absorption bands, or by dyes which fluoresce and absorb light simultaneously.

II.1.1.3 Other Factors Influencing Colour

Although the colour of a substance is controlled very largely by its absorption or reflectance spectrum, other external factors can affect the observed colour. For example, the spectral composition of the illuminant used to observe a coloured surface can affect the apparent colour quite dramatically. The apparent change in the colour with the external illuminating source is a type of *dichroism* [2,4], and is familiar to all of us who have bought clothing when viewed under fluorescent lighting, and have found the colours to be quiet different in normal daylight.

Sometimes two coloured surfaces appear to match perfectly under one illuminant, and differ markedly under another illuminant. This effect is called *metamerism* [2], and is of particular concern in commercial colour matching. This can be pronounced when the dye or pigment has two absorption bands of different intensity.

Another type of dichroism involves the apparent dependence of some colours on concentration, where this is purely physical effect, and is not associated with aggregation of the dye in solution. An example is blood, which normally contains a high concentration of oxyhaemoglobin and has the familiar deep red colour. However in very dilute solutions the colour is yellow , at high concentration the absorption bands of oxyhaemoglobin at 420 and 560 nm have the same intensity, (red colour). However at low concentration the 420 nm band is more intense, (yellow colour).

II.1.1.4 Colour Vision

Young-Helmholtz theory [2] recognizes the experimental fact that all colours can be duplicated to the eye by the additive mixing of a minimum of three primary colours. Thus the theory assumes that the human eye possesses three types of receptor, which are assumed to respond to light of the colours red, green, and blue (or violet). Colour response curves have been evaluated for the receptors, and these would correspond roughly to the absorption spectra of the receptors if they were simple pigments. A typical set of response curves are shown in Figure 1.5.

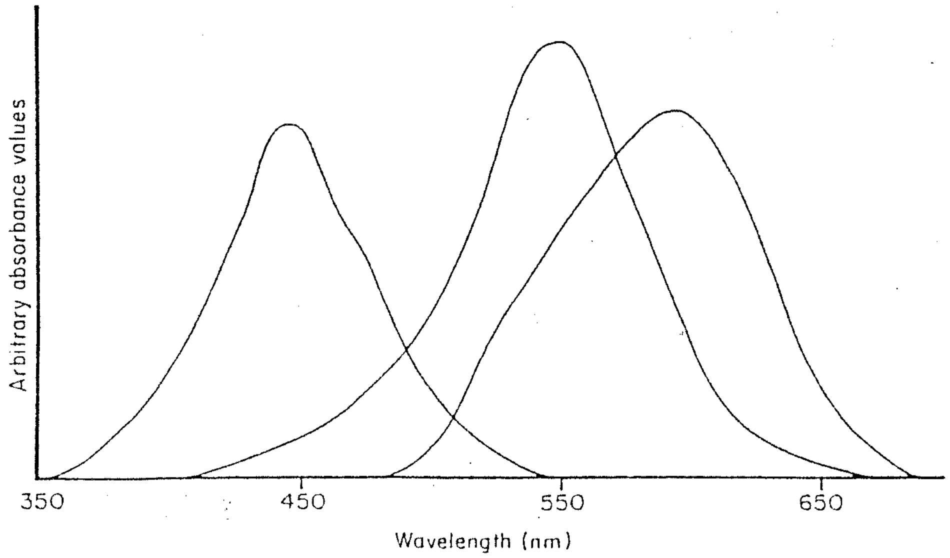


Fig. 1.5 Typical set of colour response curves for the three visual receptors [2]

When all three receptors are simultaneously stimulated by suitable amounts, the colour white is registered, which indicates that the three responses are neutralized in the brain, and no particular hue is dominant. For example, it is known that if daylight is filtered through a solution absorbing in the region 400-480 nm , all blue and violet light will be removed, and the observer will register the emergent colour as yellow. In fact, the emergent beam will not be composed of pure yellow light (580-595 nm), but will be a complex mixture of wavelengths, ranging from 480 to 700 nm. From the response curves of Figure 1.5 , it is apparent that such a mixture of wavelengths will excite the green and red receptors simultaneously, it is also established that the eye will synthesize these two colours as yellow, and thus an apparently pure spectral yellow is registered in the brain.

If, yellow is observed by mixing red and green radiations, how can pure yellow monochromatic radiation (of wavelength in the region of 590 nm) also be registered as yellow. This is explained by means of colour response curves of Figure 1.5. It can be seen that radiation of wavelength 590 nm will stimulate the red and green receptors, and mixing of these two sensations in the brain gives the sensation of yellow.

II.1.1.5 The Measurement of Colour

The measurement of colour can be done in two ways. The most direct approach involves measurement of the complete visible absorption spectrum of the two coloured object, either by transmission or by reflectance. In this way all the colour properties are recorded in the spectrum, and if a mixture of colouring matters is prepared with an identical spectrum, then the two colours will match perfectly under all conditions.

Colour can be matched *visually* with many different formulations of dye mixtures. The visually matched colours may not be identical spectroscopically, but may appear so to the eye. Since all colours can be duplicated by mixing the primary coloured lights, then a colour can be defined by three parameters. If the test object is viewed under a standard white light source, then an adjacent white surface can be brought to match the test colour by irradiating it with the appropriate mixture of primary lights [41]. The relative intensities of the three primaries required to give the match thus afford a set of three numbers that define the test colour. These parameters are called the *tristimulus values*[2] of the colour. This is in fact an over-simplified version of colour measurement , but the widely accepted international system (C.I.E) is essentially based on this approach.

Three properties of colour emerge from the measurement of colour in this way [41,2]. The hue is that property that distinguishes, for example, red from yellow, and corresponds roughly to the dominant primary, or pair of primaries, in the additive mixture. It is also determined largely by the wavelength of the absorption maximum of the substance giving rise to the colour. The *saturation* of the colour is a measure of the proportion of the total light intensity from all three primaries that is provided by the dominant primary. For example, if the red primary was completely dominant, and the green and blue non-existent , then a fully saturated red would be observed. If the background intensities of the green and blue primaries is slowly increased, relative to the red, the overall effect would be a dilution of the red colour with white, producing a pink . Thus pink would be described as a red of low saturation. This procedure would not alter the hue [2].

If the intensity of all three lights were lowered by equal amounts, the hue and saturation would remain unaltered, but the result would be a darker colour. The lightness of the colour is then said to be altered. For example, a red of low lightness would be effectively a brown.

II.1.1.6 Electronic Absorption Spectroscopy

Colour and molecular structure relationships are best discussed with reference to absorption spectra.

Spectra in the near-ultraviolet (200-400 nm) and visible (400-700 nm) regions are measured almost exclusively on automatic recording spectrophotometers at the present time. Monochromatic radiation is passed through the test sample, and the amount of radiation absorbed is measured electronically. The spectrum is obtained by recording the light absorption as a function of wavelength (λ) or wavenumber ($\bar{\nu} = 1/\lambda$) of the incident radiation [2]. The majority of spectra recorded in this way have the scale on horizontal axis linear with respect to wavelength, and the wavelength increases from left to right. Thus the ultraviolet region lies to the left of the spectrum , and the visible region to the right. Spectra are also recorded where the horizontal scale is linear with respect to wavenumber.

The wavenumber scale is directly proportional to the frequency of the wave (1.1) and according to the Planck equation (1.2) [7] the latter quantity is proportional to the photon energy , or the electronic excitation energy of the absorption band. Thus linear wavenumber plots show the shape and disposition of absorption bands as a function of transition energy. On the other hand, a linear wavelength scale corresponds to a reciprocal wavenumber plot, and absorption bands tend to be compressed at the short wavelength end of spectrum, and expanded at the long wavelength end. This presents a distorted picture of relative band positions and band shapes, but the expansion of spectra afforded in the visible region is valuable for colour and constitution studies. The human eye is so sensitive to small changes in transition energy that distinctly different colours may in fact arise from a shift in an absorption band of only a few nanometers. Such shifts are most easily recorded and measured on the expanded plots that are linear with respect to wavelength.

The vertical scale of an absorption spectrum must give an indication of the amount of monochromatic radiation absorbed by the test substance, and this is usually measured relative to reference cell in the spectrophotometer. Beer-Lambert equation (1.3) [7,2] relates the intensities of the incident radiation (I_o) and emergent radiation (I) to the concentration (c) and the pathlength (l) of the solution.

$$\log_{10} (I_o / I) = \varepsilon \, . \, c \, . \, l \qquad (1.3)$$

If the concentration is expressed in moles per liter and the pathlength in centimeters, then the proportionality constant ε is the *molar absorptivity* or *molar extinction coefficient* [4]. This quantity is a measure of the intensity of absorption of radiation of a particular wavelength by the solute. The maximum value of ε (ε_{max}) is commonly quoted for substances as a useful characteristic of their absorption bands, together with the wavelengths (λ_{max} values) at which maximum absorption occurs.

The quantity $\log_{10}$ (I_o / I) is called the absorbance or *optical density* [2] of the solution, and it is this quantity that is normally plotted on the ordinate of most absorption spectra.

The units of electronic absorption spectroscopy refer principally to the wavelength, wavenumber, frequency, and the energy of radiation absorbed. Wavelengths are most popularly expressed in *nanometers* (nm), where $1 \text{ nm} = 10^{-9}$ m. An alternative unit, more favoured by spectroscopists is the Angstrom (Å), where 1 Å = 10 $^{-10}$ meters. The visible spectrum thus extends from approximately 400 nm (4000 Å) to 700 nm (7000 Å). Wavenumbers are expressed in cm^{-1}, and frequencies in *hertz* (Hz). One hertz is equal to a frequency of one cycle per second.

Transition energy [8] is equal to the energy of electromagnetic radiation absorbed, and expressed in *kilocalories per mole.* This is in fact the energy of a "mole" of photons, i.e. an Avogadro number or *einstein* of photons (1 kcal = 4.187 kJ). In SI units, the kilocalorie per mole would be translated into kilojolue per mole (kJ.mol^{-1}), where 1 kcal = 4.187 kJ.

Another common unit of transition energies, is the *electron volt* (eV) , where 1 eV = 23.06 kcal.mol^{-1}. The following equations are useful for converting wavelengths to transition energies [2].

$$E\,(kcal.mol^{-1}) = 28.6 / \lambda\ (\mathrm{nm}) \qquad (1.4)$$

$$E\,(eV) = 1240 / \lambda\ (\mathrm{nm}) \qquad (1.5)$$

Finally, the various terms and phrases used in connection with electronic absorption spectroscopy are the following [2,4,10]:

Bathochromic Shift : The displacement of an absorption band towards longer wavelengths.

Hypsochromic Shift : The displacement of band to shorter wavelengths

Red Shift : Synonymous with the term bathochromic shift, implying a movement towards the red end of the spectrum.

Blue shift : Synonymous with hypsochromic shift, i.e. a movement towards the blue end of the spectrum.

Deepening in colour : This rather ambiguous phrase is occasionally encountered , and refers to a bathochromic shift specially in the visible region of the spectrum. It does not imply an increase in the absorption intensity.

Hyperchromic Effect : An increase in the intensity of an absorption band.

Hypochromic Effect : A decrease in the intensity of an absorption band.

Solvatochromism : The change in position and intensity of an absorption band accompanying a change in the polarity of the solvent.

Halochromism : The colour change (i.e. displacement of the visible absorption band) of a substance accompanying a change in the pH of the solution.

Half-band width : The width of absorption band (usually expressed in wavenumber units) at one half the total peak height.

II.1.2 Qualitative Colour-Structure Relationships

II.1.2.1 The Classification of Coloured Organic Molecules

According to certain distinct characteristics, coloured organic molecules can be divided into four broad classes :

a) $n \rightarrow \pi^*$ chromogens

b) Donor - acceptor chromogens

c) Acyclic and cyclic polyene chromogens

d) Cyanine - type chromogens

Chromophore [2,4] is a covalently unsaturated group which is responsible for electronic absorption. e.g. $-NO$, nitroso dyes; $-NO_2$, nitro dyes; $-N=N-$, azo dyes , etc.

Auxochrome [10] is a saturated group with nonbonded electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption. e.g. $-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}H$, $-\overset{\cdot\cdot}{N}H_2$, $-C\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}H$, $-SO_3H$.

a) $n \rightarrow \pi^*$ chromogens :

Class of chromogens that show $n \rightarrow \pi^*$ absorption band in the visible region.

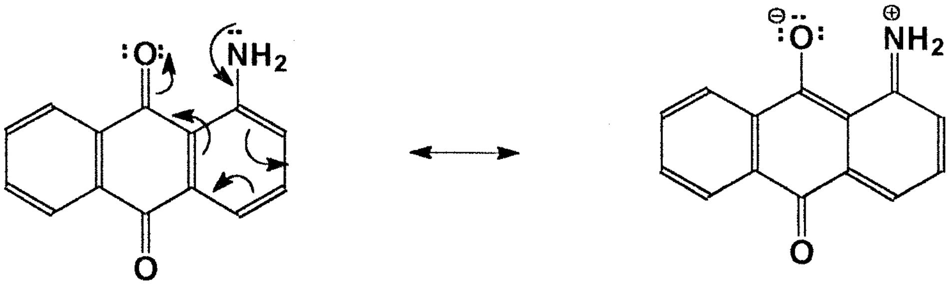
e.g. nitrosomethane and nitrosobenzene differ in overall structure, both are blue in colour, and share the same characteristic $n \rightarrow \pi^*$ chromogen, namely the nitroso group [2,4].

b) Donor - acceptor chromogens :

This class is the largest group and the majority of commercially important dyes and pigments belong to this group.

A donor - acceptor chromogen [2,5,31] contains an electron donor group (*i.e.* an atom possessing lone pair electrons) directly linked to a conjugated π electron system. The orbital containing the lone pair electrons must be aligned with the adjacent p orbital of the conjugated system, so that the lone pair electrons may be partly delocalised into the π system. The visible absorption band of the complete chromogen then corresponds to a migration of electron density away from the donor atom into the rest of the system. If several atoms in the π system show an increase in electron density, then the entire π system is best regarded as an electron acceptor unit, and can be designated as a *complex acceptor* [5].

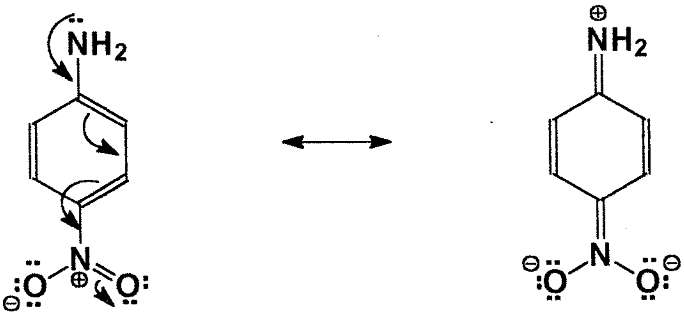
e.g. 1- aminoanthraquinone (1) , where the amino group is the donor, and the anthraquinone residue is the complex acceptor.



1- aminoanthraquinone (1)

If only a small, discrete part of the π system shows a significant build up of electron density in the first excited singlet state, then such a unit can be termed a *simple acceptor*. The remainder π system is virtually unaffected, and merely acts as a conjugating bridge [2] between the donor and acceptor.

e.g. para - nitroaniline (2) , where nitro group is the simple acceptor.



para - nitroaniline (2)

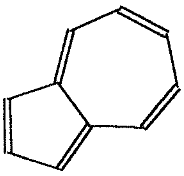
c) Acyclic and Cyclic Polyene Chromogens :

A polyene chromogen [2] is a collection of sp^2 (or sp) hybridized atoms in which complete overlap of all the p orbitals occurs, giving a conjugated π electron system containing as many electrons as there are p orbitals . Such a molecule would show an alternating sequence of single and double bonds forming either open chains or ring systems, or a combination of both. Provided the degree of conjugation is great enough, the longest wavelength transition will occur in the visible region of the spectrum. *e.g.* Acyclic polyenes [8] show a considerable degree of bond alternation, whereas in certain ring systems bond equalisation occurs, and such compounds may be classed as "aromatic". Special properties are also found in cyclic systems containing odd-numbered rings (the nonalternants [2,4]) and these may or may not show some tendency towards bond equalisation. Unlike the donor - acceptor chromogens, the polyene chromogens show no regions of particularly high or low electron density either in the ground state or in the first excited state. Chromogens of the polyene class may be hydrocarbons or heteroatomic systems, as in general, the replacement of a carbon atom by a heteroatom in such a system will have only a minor effect on the absorption spectrum.

Examples of polyene chromogens include :

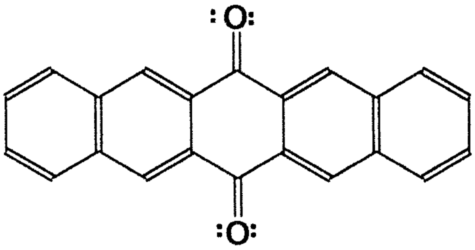
$CH_3(CH{=}CH)_9CH_3$ (3)

Polyolefin (3) where the colour is yellow and $\pi \rightarrow \pi^*$ transition exist [4].



(4)

Nonalternant hydrocarbon azulene (4) where the colour is blue and has $\pi \rightarrow \pi^*$ absorption band [4].



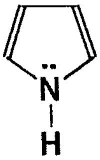
(5)

Heteroatomic system (5) where the colour is yellow shows a visible $\pi \rightarrow \pi^*$ band, thus permitting it to be classed as a polyene chromogen, and also shows a visible $n \rightarrow \pi^*$ band. Thus it can also be classed as an $n \rightarrow \pi^*$ chromogen [4].

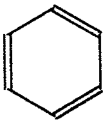
A polyene chromogen should contain as many π electrons as p centers [2], but it is convenient to make an exception to this rule in the case of heterocyclic systems in which the heteroatom contributes two electrons to the π electron systems,

e.g. pyrrole (6) , where the number of π electrons exceeds the number of p centers by one, although the system remains neutral.

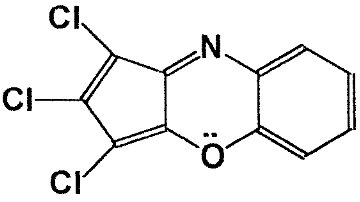
In general, the spectrum of a compound of this type will resemble that of the corresponding neutral hydrocarbon containing the same number of π electrons . For example, pyrrole (6), bears a marked spectral resemblance to benzene (7) and the complex heterocylce (8) shows an electronic absorption spectrum remarkably similar to the iso - π - electronic hydrocarbon 5,6 benzazulene (9) [2].



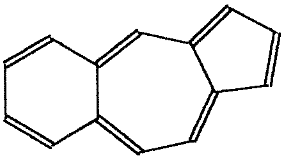
Pyrrole (6)



benzene (7)



Complex heterocycle (8)



5,6 benzazulene (9)

d) Cyanine - Type Chromogens :

If the terminal carbon atoms of such an odd alternant (possess a non-bonding molecular orbital midway between the bonding and antibonding π orbitals) are replaced by heteroatoms (usually nitrogen or oxygen) then the electronic symmetry will not be greatly disturbed, and the resultant system will retain many of the properties of the hydrocarbon anion, including a low energy first electronic transition. As a result a red shift will appear [2,4].

For example, the nitrogen compounds (11) contain the same number of π electrons as the carbanions (10), even though the former bear a positive charge, and they can also be regarded as resonance hybrids of the two extreme forms (11a) and (11b).

$$ {}^{\ominus}CH_2(CH=CH)_nCH=CH_2 \longleftrightarrow CH_2=CH(CH=CH)_nCH_2^{\ominus} $$

(10a) (10b)

$$ R_2\ddot{N}{-}({-}CH=CH)_nCH=\overset{\oplus}{N}R_2 \longleftrightarrow R_2\overset{\oplus}{N}=CH(CH=CH)_n{—}\ddot{N}R_2 $$

(11a) (11b)

The first known dyes containing a chromogen of this type were called *cyanines*, and all coloured systems containing same fundamental π electron systems as (10) and (11) are classed as *cyanine-type* chromogens [2,4].

II.1.2.2 Resonance Theory and Colour

If the molecule can be represented by two resonance forms that are not equivalent in the energy, then the situation is shown in Figure 2.1.

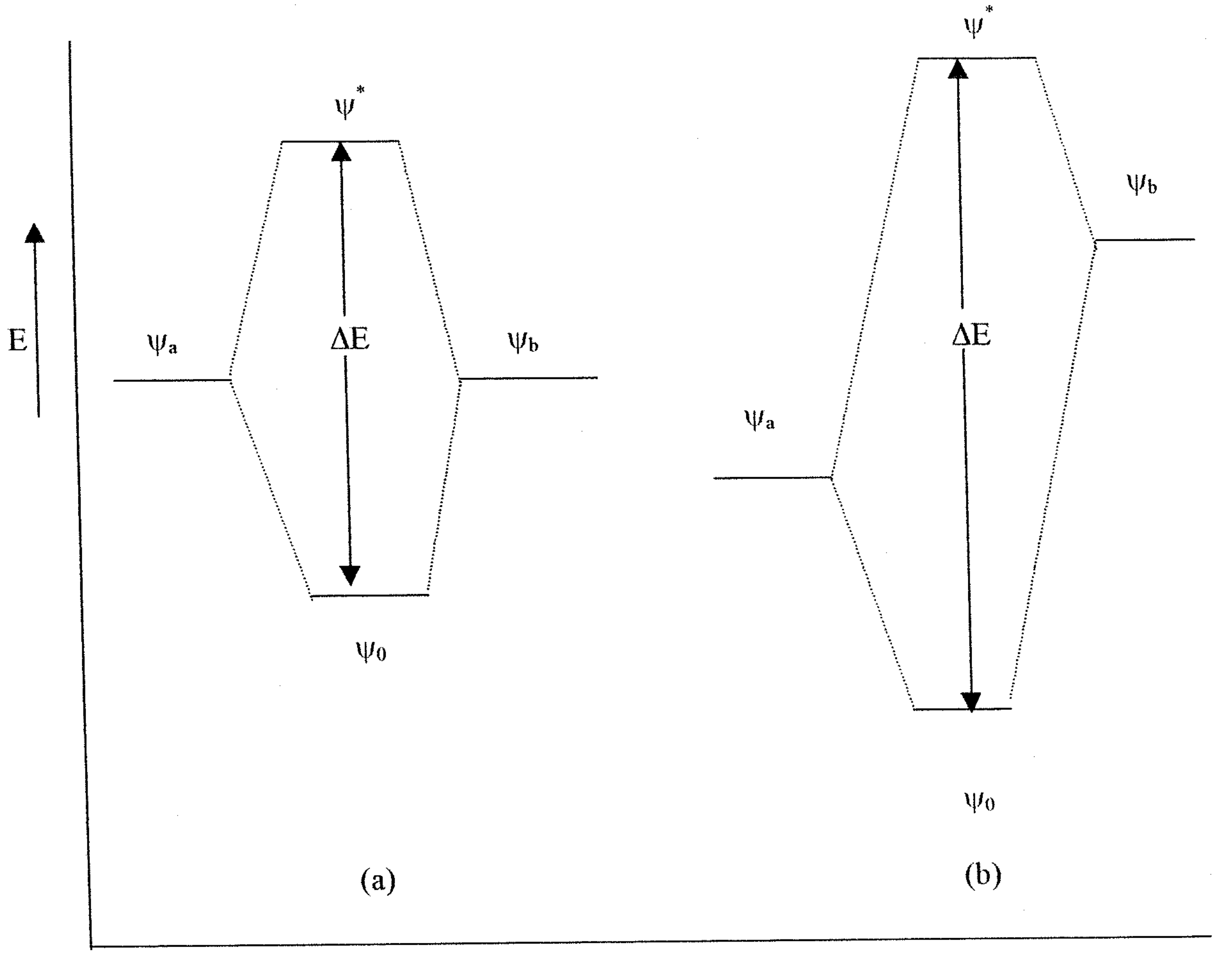


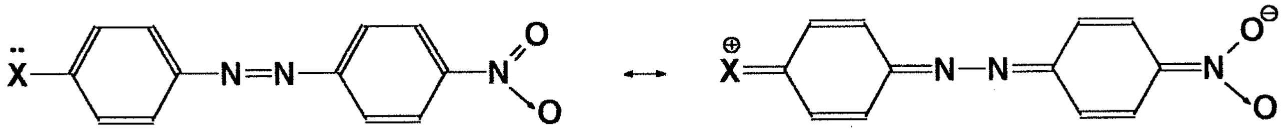
Fig 2.1 The interaction between two classical resonance structures when they are of equal energy and of unequal energy. [2]

An example of such a system would be (12),

(12a) (12b)

in which form (a) should be more stable than (b), since nitrogen bears a positive charge more readily than oxygen. Because the two forms no longer lie at the same level, resonance interaction now gives two states that are farther apart in energy than if they had been degenerate in the first instance, Figure 2.1(b). Thus the effect of this electronic asymmetry is to produce a hypsochromic shift of the visible absorption band. In cyanine series (11) , there are examples which illustrate this phenomenon.

In donor - acceptor chromogens [19], the same considerations appear to apply, although now the two extreme resonance forms always differ considerably in energy. In most cases, the more stable form is neutral, e.g. (13a), and the less stable resonance form shows a separation of charge, e.g. (13b).

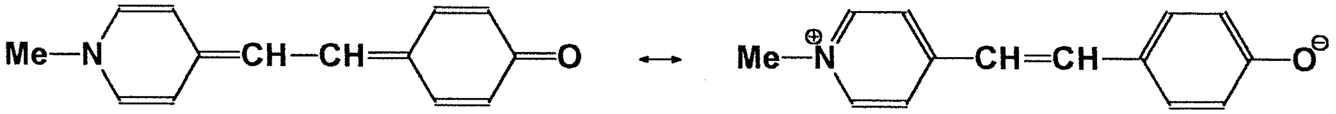


(13a) (13b)

If the donor atom is replaced by another atom which serves to destabilise the charge separated from, then the resonance picture suggests that a hypsochromic shift [24] should result. For example, in (13) if X is an amino group the molecule absorbs at about 440 nm, whereas if X is a hydroxy group the separated form (13b) is appreciably destabilised, and the absorption band shifts to about 380 nm. Intuitively, however, one might expect the former compound to absorb at longer wavelengths since the amino group is a better electron donor than the hydroxy group [24].

Resonance theory can also be applied to the problem of solvatochromism [2,4] which is most pronounced in the case of molecules that can be described as resonance hybrids of two limiting structures that differ markedly in polarity. Cyanines (11) show only small solvent shifts, whereas donor- acceptor chromogens such as (13) have long wavelength bands at the particularly solvent sensitive. Resonance theory can be used to predict the direction of the band displacement with increasing solvent polarity. Using (13) as an example, it is evident that an increase in solvent polarity will have only a small effect on the stability of the neutral form (13a), whereas the stability of the charge separated from (13b) will be greatly enhanced. Thus such a change in the solvent will bring (13a) and (13b) closer together in energy, and after allowing for resonance interaction, the gap between the ground and excited states will be reduced relative to that in a non-polar environment. A bathochromic shift [24] of the absorption band will then result. In agreement with this, it is found that the majority of donor - acceptor chromogens show bathochromic shifts of the first absorption band in solvents of increased polarity.

In a few cases, hypsochromic shifts are observed, and this is peculiar to a type of donor - acceptor chromogen that has a lower energy resonance form of greater polarity than the higher energy resonance form [2]. An example of this type is the merocyanine (14),

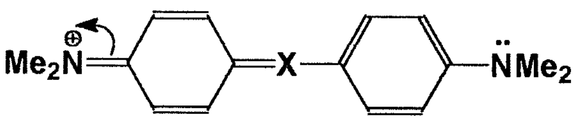


(14a) (14b)

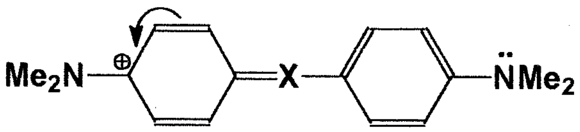
merocyanine

for which the resonance form (14b) is more stable than (14a). The unusual stability of the charge separated form can be considered to arise from the favorable formation of the aromatic benzene and pyridine ring systems. This compound shows large hypsochromic shifts of the visible band in polar solvents.

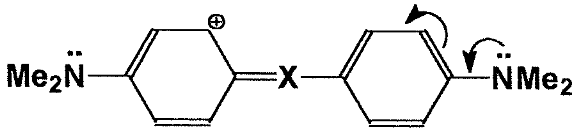
The qualitative success of resonance theory in accounting for variations in the terminal groups of cyanine - type chromogens, led naturally to the applications of the technique to more complex structural changes. Perhaps the first attempts to formulate colour - structure rules based on resonance theory were by Lewis and Calvin and Forster in 1939, and these were later extended and exemplified by Knott in 1951. Knott's rules refer specially to cyanine - type and donor - acceptor chromogens, and enable the spectral effect accompanying a change at an interauxochromic position (i.e. non-terminal position). To apply Knott's rules [2], one must first draw all possible resonance forms of the chromogen, migrating double bond electron pairs and lone pair electrons as appropriate, so that every atom in the system can be assigned either a positive charge or a negative charge. In some cases this may necessitate doubly or triply charged species. The appropriate resonance forms for the cyanine-type chromogen (15) follow from (15a-d) and the overall situation can be summarized by (15e). The charges in (15e) have no physical significance.



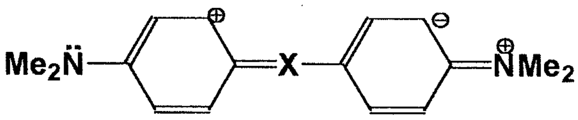
(15a)



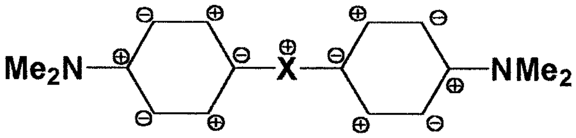
(15b)



(15c)



(15d)

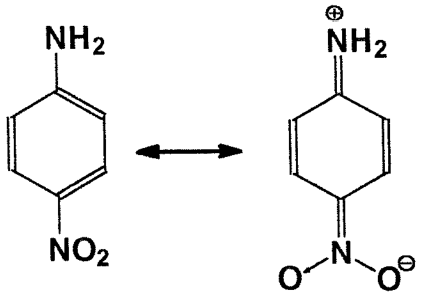


(15e)

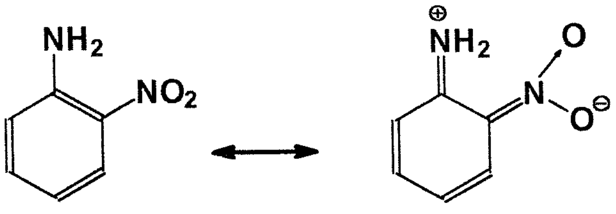
Knott's rules then state that any structural change in the system (e.g. replacement of a carbon atom by a heteroatom, or attachment of an electron donating or accepting group to an atom in the chromogen) will cause a bathochromic shift at the visible band, provided the change serves to destabilize the assigned charge at the position involved. Conversely, if the structural change stabilizes the hypothetical charge, a hypsochromic shift will result. These rules work well for a wide range of coloured systems. As an example of an application of the rules, the dye (15, X=CH) (Michler's Hydrol Blue), which absorbs at about 600 nm. If X is changed from CH to N a green dye is formed (Bindschedler's Green) , absorbing at 725 nm. According to Knott's rules, the hypothetical charge at X in (15) is positive, and since nitrogen is positive , and since nitrogen is more electronegative than carbon, the former atom will destabilize the charge, and should therefore produce a bathochromic shift [2].

II.1.2.3 Failures of Resonance Theory

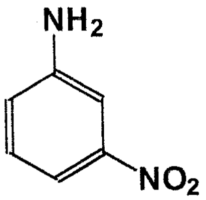
The main attacks on resonance theory provides exceptions to the rules. Nitroanilines are one of the simplest series of coloured donor-acceptor chromogens where resonance theory breaks down, namely the nitroanilines (16)-(18). It is pointed out that para-nitroaniline (16) absorbed at shorter wavelengths than both the ortho- and meta-isomers, (17) and (18) [2],



(16)



(17)

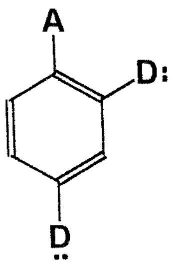


(18)

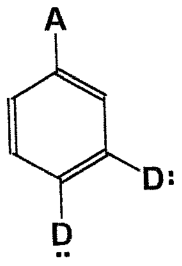
whereas a consideration of resonance interaction would suggest that the meta isomer should be the most hypsochromic member of series. The charge separated forms shown for the ortho- and para- derivatives should not be particularly high in energy, and thus resonance interaction (Figure 2.1) should give rise to a long wavelength absorption band. A charge separated form for the meta- isomer should be much higher in energy, and thus the absorption band should lie at shorter wavelengths. In fact, the absorption maxima of ortho- and meta- nitroaniline lie respectively at 402 and 375 nm in ethanol, whereas that of the para- derivative lies at 371 nm in the same solvent. This general wavelength trend appears to be common to several benzene derivatives substituted by one electron donor and one electron acceptor group, e.g. cyanophenols. The apparent failure of resonance theory in these systems rises from the assumption that only low energy resonance forms need to be considered as contributing to the ground and first excited states. In fact, there is no real justification for ignoring higher energy alternative resonance forms, and their neglect lead to wrong predictions, particularly in small systems such as the nitroanilines. Some other exceptions to the predictions of resonance theory, where the chromogen is relatively small, include aminoquinolines and the ring protonated 3- and 4- aminoquinolines.

When a benzene ring is substituted with one electron acceptor and two electron donors, the absorption band wavelength increases for the various possible situation patterns, (19)-(21), in the order (21) > (20) > (19). Resonance arguments predict that (19) should absorb at longer wavelengths than both (20) and (21), since two relatively low energy forms can be drawn for (19) in which the lone pair electrons on the donor atoms can be transferred to the acceptor group. Wizinger [2] has pointed out the dyes (22) and

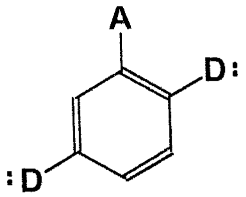
(23) are examples of this type. Thus (22) absorbs at 500 nm, and is red, whereas the seemingly less conjugate dye (23) absorbs at 585 nm, and is violet.



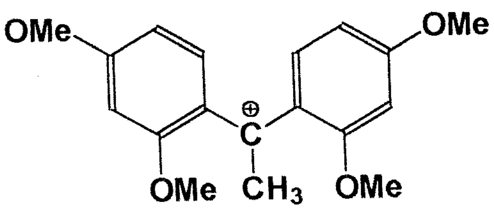
(19)



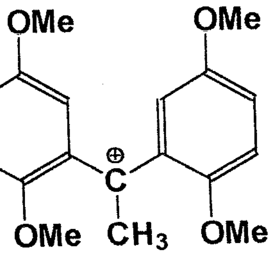
(20)



(21)

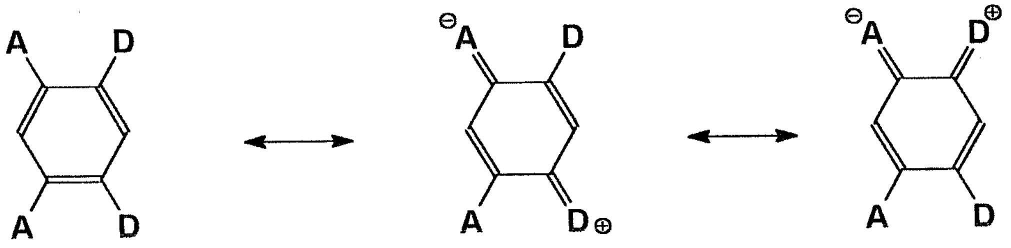


(22)

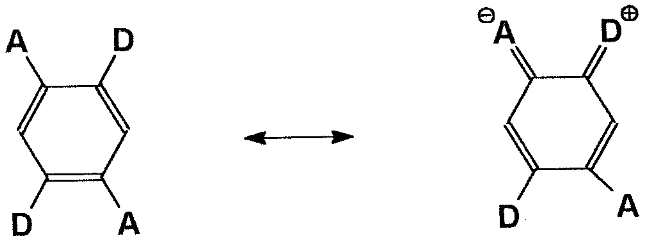


(23)

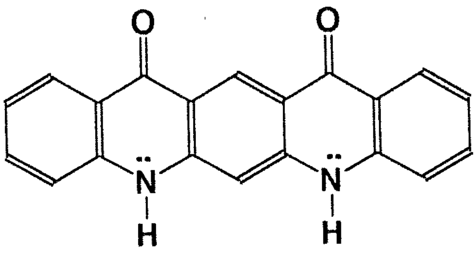
When a benzene ring contains two electron donor and two electron acceptor groups, two substitution patterns that might be expected to provide large bathochromic shifts are (24) and (25) [24]. Structure (24) can be represented by a total of four charge separated quinonoid forms, namely two para structures (e.g. 24b) and two ortho structures (e.g. 24c). On the other hand, (25) cannot be represented by any para quinonoid structures , but only by ortho structures such as (25b). On this basis alone, (24) would be expected to absorb at longer wavelengths than (25), whereas in practice the opposite is found. A good example of this effect is provided by the isomeric dyes (26), which is yellow, and (27), which is violet [2].



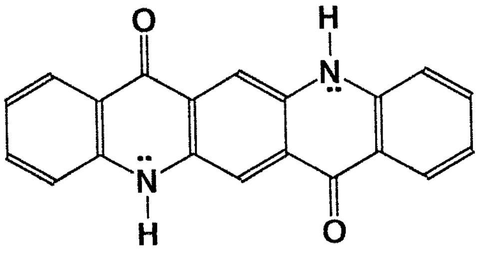
(24a) (24b) (24c)



(25a) (25b)



(26)



(27)

In conclusion, resonance theory should never be used to obtain structural information based on analysis of spectroscopic data.

II.1.2.4 Perturbational Molecular Orbital Theory

Perturbational Molecular Orbital Theory is used to calculate the energy differences between two states. Perturbational theory [2] is applied to the systems where the hydrocarbon is alternant. The perturbations are then the various structural changes that must be made to the hydrocarbon (e.g. replacement of carbon by a heteroatom, or attachment of a particular group to the π framework), in order to generate the chromogen under investigation. For example, pyridine can be regenerated as perturbed from benzene, in which one of the carbon atoms has been replaced by nitrogen.

In order to predict the effects of perturbation on the absorption spectrum, the following special properties of alternant hydrocarbons are utilized [2]

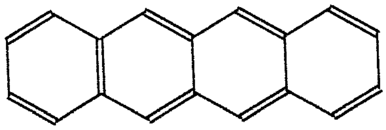
a) In even alternants, the molecular orbitals are "paired" , and the first absorption band corresponds to the excitation of an electron from the highest occupied to the lowest unoccupied orbital, i.e. between the two paired orbitals. The paired orbitals have LCAO coefficients of the same magnitude at corresponding positions, but not necessarily of the same sign.

b) In odd alternants, the highest occupied orbital is usually the NBMO (Non Bonding Molecular Orbital) and the LCAO coefficients at all unstarred positions are zero.

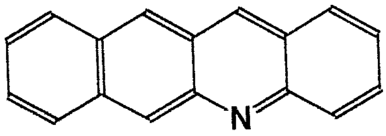
Applications of perturbational theory to electronic absorption spectra :

(i) Alteration of the Electronegativity of an Atom in an Even Alternant System :

Perturbational theory predicts that alteration of the electronegativity at any position in an even alternant [2] have a minimal effect on the position of the first absorption band. For example, tetracene (28) and 5-azatetracene (29) are both orange, the former absorbing at 440 nm, and the latter at 450 nm.



(28)



(29)

Replacement of carbon by boron in various cyclic even alternant systems has also been shown to have little effect on spectra.

(ii) Alteration of the Electronegativity of an Atom in an Odd Alternant System :

A very large number of chromogens are iso-π-electronic with odd alternant [2] hydrocarbon anions, i.e. they contain the same number of conjugated p orbitals, the same topography, and the same number of π electrons . For example, the aminoaldehyde (30), is iso-π-electronic with the hydrocarbon anion (31), as is the cyanine (32), even though the overall charge on each is different. The three compounds contain the same number of p centers and the same number of π electrons.

$$Me_2\ddot{N}{-}CH{=}CH{-}CH{=}O \qquad (30)$$

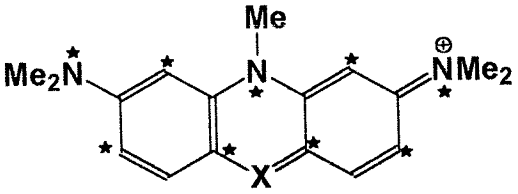
$$^{\ominus}CH_2{-}CH{=}CH{-}CH{=}CH_2 \qquad (31)$$

$$Me_2\ddot{N}{-}CH{=}CH{-}CH{=}\overset{\oplus}{N}Me_2 \qquad (32)$$

Cyanine type chromogens, which have a similar uniformity of bonding to the odd alternant anions, are probably the best systems for application of the rules. Donor acceptor chromogens (e.g. (30)), on the other hand, show a high degree of bond alternation, and is less justifiable to apply the rules to these systems. Nevertheless, Dewars' rules [2] work remarkably well, even for these systems.

Dewar Rules :

a) Increasing the electronegativity at an unstarred position gives a bathochromic shift.

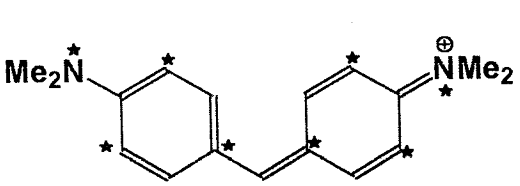


(33)

X = CH, λ_{max} 491 nm

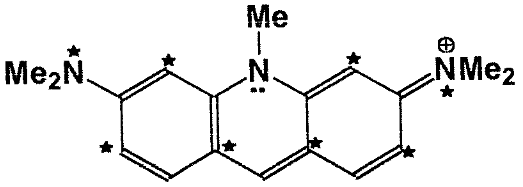
X = N, λ_{max} 564 nm

b) Decreasing the electronegativity at an unstarred position gives a hypsochromic shift.



(34)

λ_{max} 610 nm

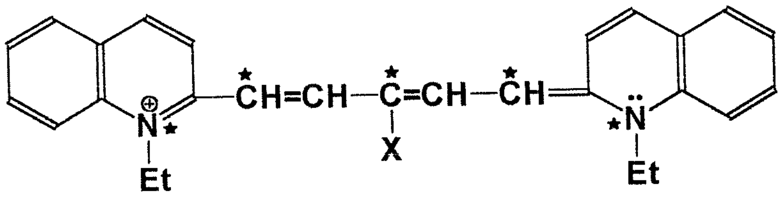


(35)

λ_{max} 491 nm

In this case the mesomeric electron donor group, -NMe- , is linked across two unstarred positions. Qualitatively, this has the same effect as lowering the electronegativity at the positions of attachment.

c) Increasing the electronegativity at the starred position produces a hypsochromic shift.

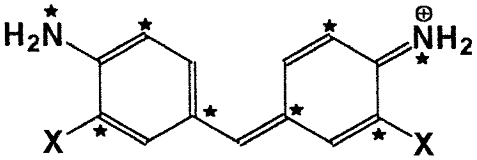


X = H, λ_{max} 708 nm

X = NO_2 , λ_{max} 580 nm

(36)

d) Decreasing the electronegativity at the starred position produces a bathochromic shift.



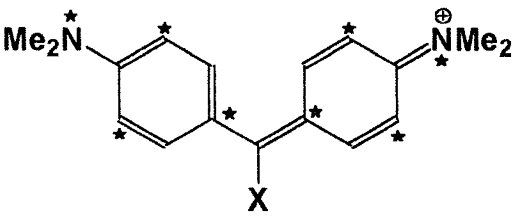
(37)

X = H, λ_{max} 558 nm

X = Me, λ_{max} 561 nm

The shift is rather small in this case, since there is a tendency for the methyl groups to rotate the amino groups out of conjugation because of steric hindrance. This gives a hypsochromic shift, which diminishes the net bathochromic displacement of the visible absorption band. An additional example of this rule is afforded by a comparison of (34), λ_{max} 610 nm, and (37 ,X=H). The large bathochromic shift for the former compound is due to the methyl groups attached to the terminal nitrogen atoms. These can be considered to be attached to a starred position, thus lowering the electronegativity of the nitrogen atoms.

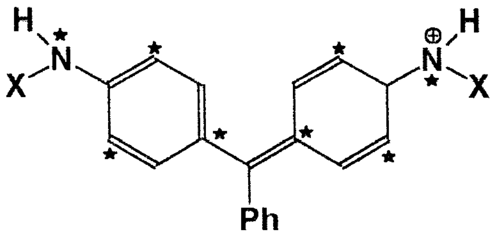
e) Extending the conjugation with a neutral unsaturated group always produces a bathochromic shift, irrespective of the point of attachment.



X = H, λ_{max} 610 nm

X = Ph, λ_{max} 621 nm

(38)



X = H, λ_{max} 562 nm

X = Ph, λ_{max} 637 nm (39)

II.1.2.5 Other Empirical Approaches to Substituent Effects

The sensitivity of human eye to small wavelength changes means that a 20 nm shift can be observed as a distinct shade change, to predict the wavelength shifts arising from the introduction of new groups into a molecule, empirical correlations can be used.

Simple chromophores containing two or three conjugated double bonds handled by summation rules, which enable the wavelength of the first $\pi \rightarrow \pi^*$ absorption band to be predicted accurately. For example, a heteroannular diene [2], i.e. one where the two conjugated double bonds are not in the same ring, can thus be assigned a base λ_{max} value of 217 nm (the value for butadiene), and to this is added 5 nm for each alkyl substituent attached to a double bond, and 5 nm for each double bond exocyclic to a six-membered ring. Homoannular dienes, with both double bonds in the same ring, are treated in the same way, but assuming a base value of 253 nm.

Similar rules have been proposed for the first $\pi \rightarrow \pi^*$ transitions of α, β-unsaturated ketones and conjugated dienones, and these have all been of considerable value in the structure evaluation of natural products, e.g. steroids, terpenes.

In donor-acceptor chromogens [23,24], substituent effects are more complex, and simple additivity rules are unsuccessful. If steric effects are neglected, a substituent can be characterized by its electron donating or electron withdrawing properties. Electron donation or withdrawal can be divided into a mesomeric (or resonance) effect and a field effect. Resonance effect operates through π bonds thus the field effect considered to operate through space, or through the σ-bond framework to which the substituent is attached, σ- mode of transmission referred to as *inductive effect* [2]. The first electronic transition of a chromogen will involve a certain degree of electron density redistribution, and it is obvious that if there is a decrease in electron density at the position to which an electron withdrawing group is attached, the group will impede the charge redistribution, and will cause an increase in the transition energy, or a hypsochromic shift. Similar arguments for electron donating groups, which would be expected to be bathochromic at a position of decreasing electron density, and hypsochromic at a position of increasing electron density.

If the electron donating or withdrawing strengths of substituents is assigned as numerical values then these quantities in an empirical manner can be related to spectral shifts. Electronic effects of benzene ring substituents suggested by Hammett [2] that a quantitative measure of the electronic effect would be given by the difference between the pK_a of a substituted benzoic acid and that of benzoic acid itself. Electron withdrawing groups will favour dissociation, and thus lower pK_a, and conversely, electron donating groups will raise pK_a. If the dissociation constants for substituted benzoic acid and the benzoic acid itself are K_x and K_o, respectively, then the parameter σ, characteristic of the substituent, will be given by [2]:

$$\sigma = \log K_x - \log K_o$$

From the above expression it follows that electron withdrawing groups will have positive σ values, increasing with their withdrawing strength, and electron donating groups will have negative values. Hydrogen will, have a zero value.

The magnitude of the σ-constant of a particular group will depend on the position of attachment of the latter to the benzene ring. In most cases, σ value will be greater in the *para* position than in the *meta* position, although the halogen substituents are notable exceptions. Substituent constants for groups attached to the *ortho* position of the ring are not easy to define because one should take into account the steric effects.

Substituent	σ_{meta}	σ_{para}
NH_2	-0.16	-0.66
OH	0.12	-0.37
CH_3	-0.07	-0.17
H	0.00	0.00
Cl	0.37	0.23
CH_3CO	0.38	0.50
CN	0.56	0.66
NO_2	0.71	0.78
NMe^+_3	0.88	0.82

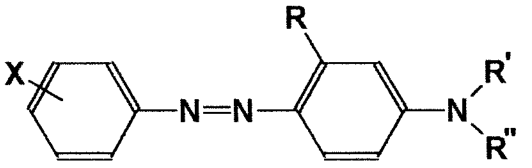
Table 2.1 Some typical Hammett σ - constants for *Meta* and *Para* Substituents.[2]

If a benzene ring is attached to a chromogen, but plays little part in the electronic excitation process (i.e. electron density changes in the ring are minimal), then substituents attached to the ring may influence the position of the absorption band indirectly by their electron donating or withdrawing effect. Thus the electron density at the atom in the chromogen to which the benzene ring is attached will be modified in the proportion to the Hammett σ-constant [2,4]. The orbital energies will also be modified in the proportion to σ, and consequently so will the transition energy. Thus, provided the substituent is not directly involved in the excitation process, the change in the excitation energy of the absorption band due to the substituent should be proportional to the Hammett σ-constant. Thus:

$$\Delta\nu = \nu_x - \nu_H = \rho \cdot \sigma_x \tag{2.1}$$

where ν_x and ν_H are the absorption frequencies of the substituted and unsubstituted chromogens, respectively, and σ_x is the Hammett constant for the substituent X. The constant ρ is a measure of the sensitivity of the absorption band to substituent effects, and, for example, if ρ is positive then the band will move to longer wavelengths with increasing electron donating strength.

If the substituent is directly involved in the electronic excitation process, then its electronic properties (i.e. its σ value) will be altered in the excited state. As this change will not be uniform for all substituents, this means that the linear correlation between $\Delta\nu$ and σ (2.3) will not hold. Examples that give good correlations are Malachite green system, 1-arylazoazulenes and the acyl- and aryl- aminoanthraquinones. Examples that give poor correlations are the aminoazo dyes (40) , are of great technical importance as colorants for the newer synthetic fibers.



(40)

II.1.2.6 Steric Effects in Electronic Absorption Spectra

Steric crowding [36] in a molecule has a pronounced effect on the electronic absorption spectrum. These effects are noticed in colour systems.

It is important to examine first the nature of the distortion that occurs in a molecule when bulky substituents are introduced into it. The ideal π-chromogen has all p-centers lying in the same plane, with all bond angles near 120° and all bond lengths in the range 1.34 to 1.48 Å. If a bulky group is introduced into such a chromogen, then a large increase in energy could result, since compression of electron clouds to accommodate the group is extremely difficult. To avoid this type of compression , the molecule can alter its geometry in three different ways. The first type of deformation can take the form of stretching or compressing a bond needs high energy, ~3-7 kcal.mol^{-1}, a second distortion process involves increasing or decreasing bond angles still needs high energy, and the third, the molecule can undergo bond rotation about a pure single bond requires no energy and a pure double bond requires only 0.2 $kcal.mol^{-1}$. A molecule will always distort by bond rotation if steric interactions are significant.

Bond rotation gives a non-polar molecule, and also causes a reduction in the overlap between adjacent p orbitals. The general decrease in overlap causes a decrease in the intensity of absorption bands, this is the way of showing the presence of steric crowding in a chromogen [2,4]. The change in atomic orbital overlap alters molecular orbital energies, and affects the wavelength of a particular band. The direction of the shift is not characteristic of steric hindrance, since, it may be bathochromic or hypsochromic, or even zero in a few cases.

In a typical π-chromogen each bond can be defined by its total π bond order. If it is zero, it is purely single bond, if it is unity, it is pure double bond. Rotation about a pure single bond does not alter the energy of the molecule, rotation about a pure double bond increases the energy. A particular bond in a molecule is twisted because of steric crowding, and if the π bond order of the bond is known, then it can be deduced whether or not the energy of the molecule is increased by the distortion. This gives a qualitative indication of the effect of the steric interaction on the ground state energy.

For the first excited state molecule, one can make use of the generalization that π bond orders in the first excited state are roughly the opposite of those in the ground state. Bond in the ground state has a π bond order of near zero, then in the excited state the value will be near unity. Conversely, a high bond order in the ground state will have a low value in the first excited state. If bond rotation causes a small increase in the energy of the ground state then it will cause a large increase in the energy of the excited state, and a hypsochromic shift [19] of the first absorption band will occur. Similarly, rotation about a bond of high order in the ground state will produce a bathochromic shift [19].

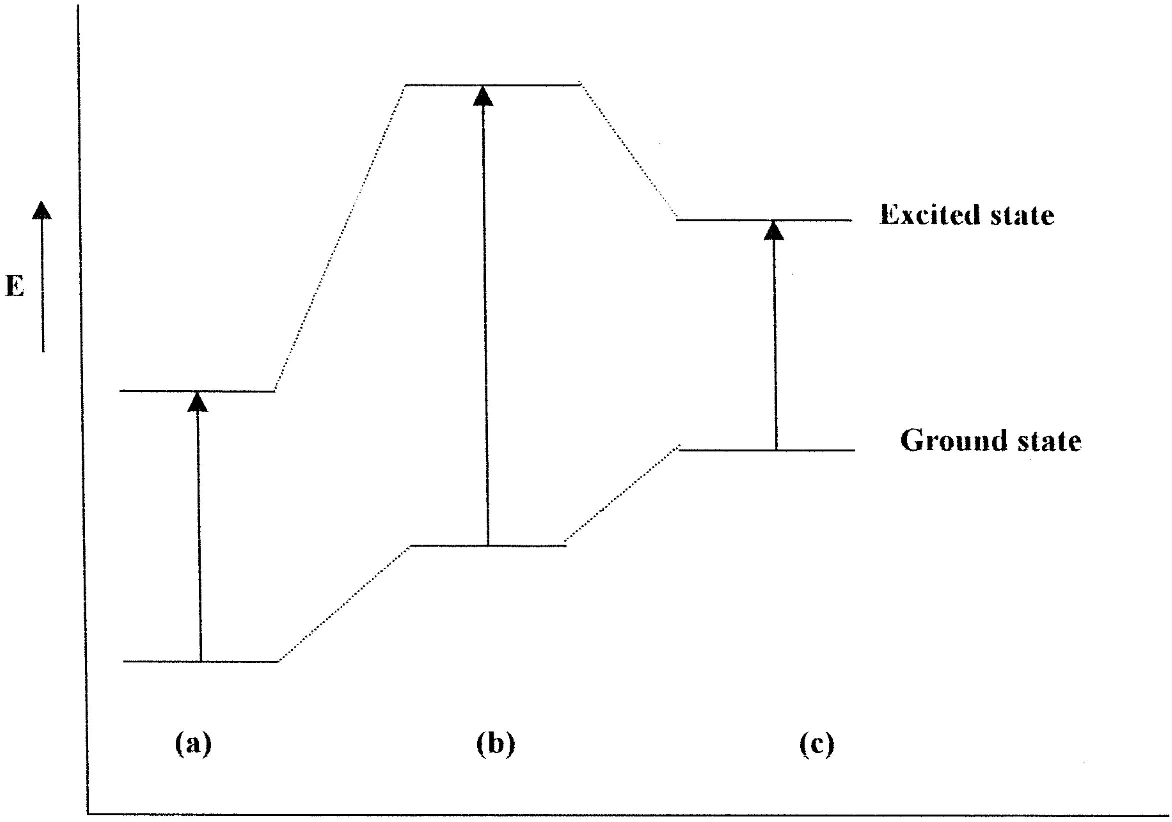
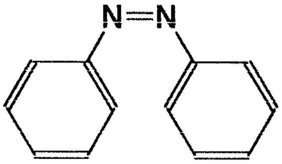


Fig 2.2 The effect of bond rotation on the ground and excited state of a molecule : (a) planar situation, (b) rotation about a bond of increased bond order in the excited state (hypsochromic shift), and (c) rotation about a bond of reduced bond order in the excited state (bathochromic shift) [2].

In summary, if steric crowding causes rotation of an essentially single bond there will be hypsochromic shift, whereas if it causes rotation of an essentially double bond, there will be a bathochromic shift.

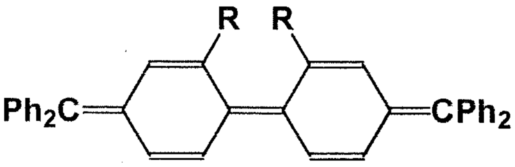
It is easier to twist a single bond than a double bond, so the former is preferred. Thus most crowded molecules give hypsochromic shifts, irrespective of where a bulky group may be present in the system.



e.g. cis-azobenzene (41)

in which there is a considerable steric interaction between the two phenyl groups.

Bathochromic shifts accompanying steric crowding are only observed in special cases where rotation about single bonds is effectively prevented. e.g. , the hydrocarbons (42a and 42b)



(42)

a: R = H, λ_{max} 574 nm, log ε 4.9

b: R = CH_3, λ_{max} 597 nm, log ε 3.6

contain all essentially single bonds within the two six-membered ring. Steric crowding caused by the methyl groups of (42b) can only be relieved by rotation about the central double bond, and thus a bathochromic shift is observed.

II.1.2.7 Steric Effects in Cyanine Type Chromogens

Cyanine-type chromogens [4] are analogues of the odd alternant hydrocarbon anions, and show both orbital pairing properties, and the presence of a non-bonding molecular orbital. These properties enable several useful generalizations to be made concerning the effects of steric crowding in such chromogens. First of all, the total π bond orders are considered in order to discuss the effect of bond rotation on the first absorption band of a conjugated system. The excitation of a molecule from the ground state to the first excited state can be approximated by the promotion of a single electron from the highest occupied orbital to the lowest unoccupied orbital. Thus it is only necessary to consider the *partial* bond orders of the two orbitals involved in the transition in order to explain the effects of bond rotation on the absorption band.

A positive partial π bond order [2] implies that there is in-phase overlap of the adjacent atomic orbital wave functions, or in other words, that there is a region of bonding between the two atoms concerned. Twisting the bond will diminish the degree of in-phase overlap, and will thus raise the energy of the *molecular orbital.* A negative partial π bond order [2] implies that there is out-of-phase overlap , and a region of antibonding between the atoms. Twisting the bond creates a more favorable situation since this diminishes the amount of out-of-phase overlap [2], and thus the energy of the molecular orbital is *lowered.* Provided the partial bond orders for the highest occupied and lowest unoccupied orbitals are known , it is then an easy matter to predict whether rotation about a particular bond will bring the orbitals together (giving a bathochromic shift) or move them farther apart in energy (giving a hypsochromic shift).

The highest occupied orbital of a cyanine-type chromogen is the NBMO [2], all partial bond orders in an NBMO are zero. Thus bond rotation has no effect on the energy of the highest occupied orbital. Because of bond equalization in odd alternants, there are no bonds that can be regarded as essentially pure single or double bonds, and thus in general, the introduction of a bulky substituent will cause all bonds to rotate by roughly the same amount. Since the lowest unoccupied orbital will contain one or more node than the NMBO, the wave profile for the former orbital will show more partial bond orders that are negative than positive bond orders. Thus a uniform rotation of all bonds will lower the energy of the antibonding orbital. This situation is shown in Fig. 2.3, and obviously causes a bathochromic shift of the absorption band.

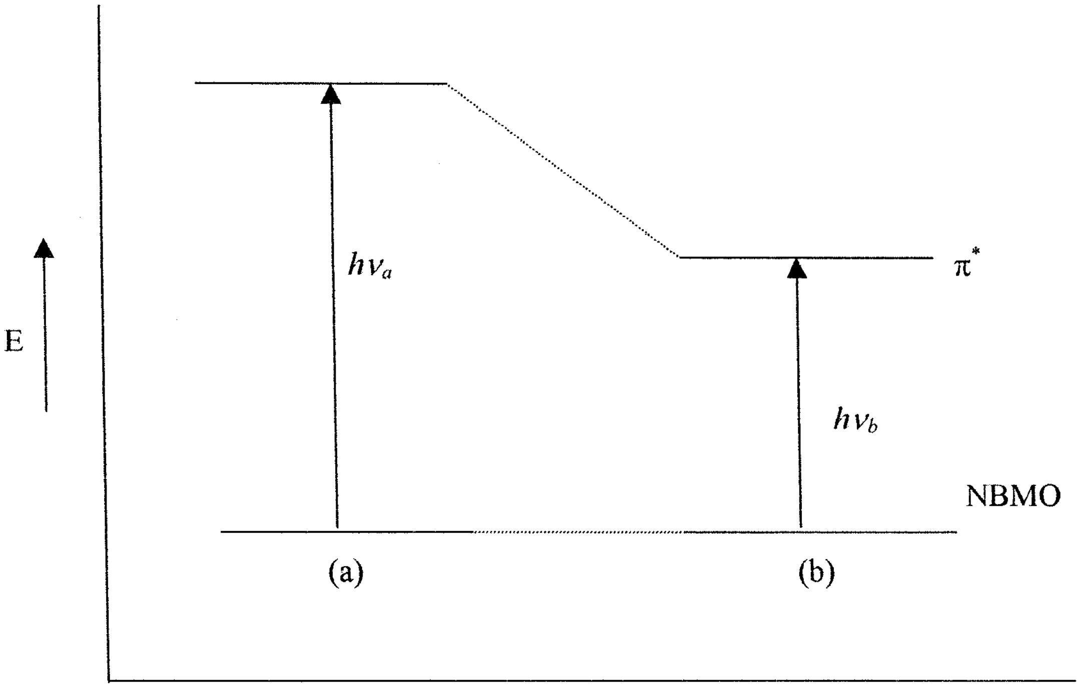
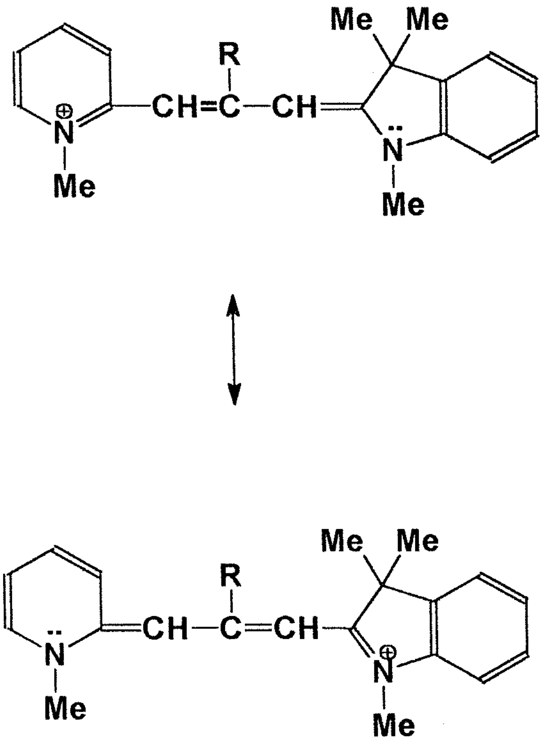


Fig. 2.3. The effect of bond rotation on the highest occupied (NBMO) and lowest unoccupied orbitals of an odd-alternant system; (a) planar, (b)non-planar situation. [2]

Consider what happens as the electrical symmetry of cyanine type chromogen is increased, for example by including terminal groups of different basicities. This will favour one resonance form over the other, and thus increase bond alternation. At some stage, bond alternation will be sufficiently pronounced for selective rotation to occur about the low order bonds, when a hypsochromic shift should result, rather than the bathochromic shift normally encountered in the cyanine type chromogens. This phenomenon is well exemplified by the unsymmetrical system .(43)



R = H, λ_{max} 509 nm

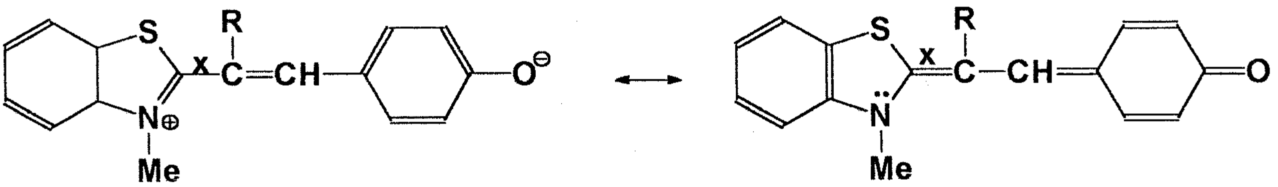
R = Ph, λ_{max} 460 nm

(43a) - (43b)

Because of the strong tendency for the pyridinum system to retain its structure, resonance form (43a) is greatly favoured relative to (43b) , and thus there is a strong bond alternation. The introduction of a bulky group, as in (43, R=Ph) now causes a hypsochromic shift of the absorption band of some 49 nm.

In practice, a gradual transition from a bathochromic shift to a hypsochromic shift is observed as the electrical asymmetry of a chromogen is increased, and the magnitude of the shift can be used as a measure of bond alternation in a given series of closely related compounds.

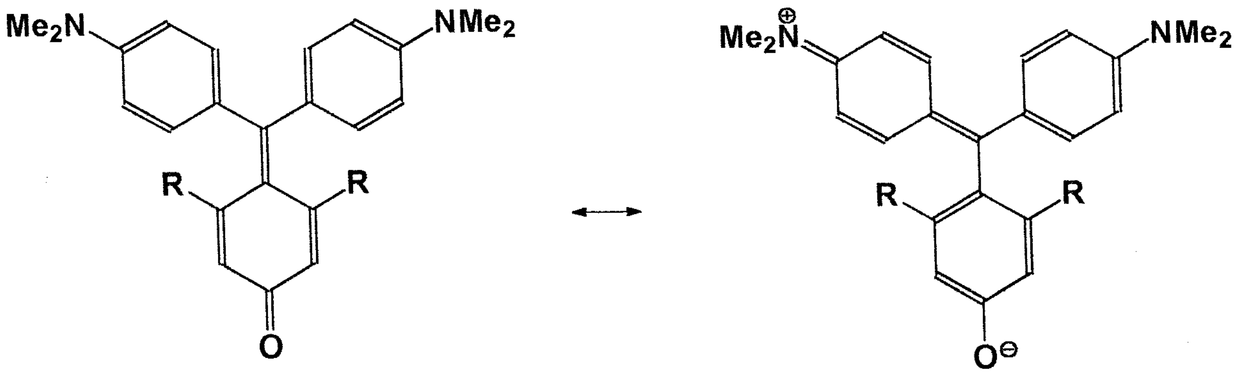
Bond alternation [2] can also be influenced by solvent polarity, and thus the nature of the solvent may influence the displacement of an absorption band by steric crowding. For example, (44) may be regarded as a resonance hybrid of the higher polar form (44a) and the neutral form (44b). The degree of bond alternation will depend on the relative energies of these two extreme forms. In polar solvents (44a) will be favoured, and thus bond x will be an essentially single bond. In (44, R=Me) there will be a strong steric interaction between the methyl group and the benzthiazole ring, and thus rotation about bond x will occur. As this is a bond of low order in polar solvents, a hypsochromic shift should result. In fact, in water a hypsocromic shift of some 65 nm is observed. In marked contrast, however, the same molecule shows a bathochromic shift of about 12 nm in chloroform, relative to the unhindered molecule. This can be interpreted as arising from a change in the bond alternation pattern, caused by a decrease in solvent polarity. In chloroform, the non-polar resonance form (44b) is dominant, and thus bond x is of high order. The steric effect of the methyl group causes rotation about this essentially double bond, and a bathochromic shift occurs.



(44a) (44b)

II.1.2.8 Allopolar Isomerism

Type of isomerism which is shown by a few chromogens with a branched π-electron system, is known as *allopolar isomerism* [2]. This arises from a combination of steric and electronic effects. In the fuchsone series (45), the chromogen can be regarded as a resonance hybrid of two extreme forms (45a) and (45b). In the unhindered molecule (45, R=H) a reasonably planar configuration is possible, and the system is best represented by the non-polar resonance form (45a).



(45a) (45b)

A single visible absorption band is observed, near 555 nm, and corresponds to a migration of electron density from the N,N-dimethylamino groups into the cyclohexadienone ring.

However, the substituted fuchsone (45, R=Me) shows two well defined visible bands, one near 600 nm and the other near 500 nm, and the relative intensities of the two bands show a marked dependence on solvent polarity. This can be attributed to the presence of two different molecular species in solution. The methyl groups of

(45, R=Me) prevent the system achieving coplanarity, and two isomeric species are then possible. The first can be represented by (45a), in which the two N,N-dimethylaminophenyl rings are twisted out of the plane of the cyclohexadienone ring. This species is called the *meropolar* [2] form, and gives rise to the band at 500 nm. The second species can be represented by (45b), in which the ionized hydroxyphenyl ring is perpendicular to the planar cyanine-type chromogen encompassing both N,N-dimethylaminophenyl rings. This isomer is called the *holopolar*[2] form, and shows an absorption band at 600 nm. The two species are no longer resonance forms, but are distinct chemical entities. The solvent and temperature dependence of the equilibrium is examined and found that an increase in solvent polarity or decrease in temperature favoured the holopolar form.

This type of isomerism was discovered by Brooker [2], and he has described several other systems that exhibit allopolar isomerism. All are characterized by possessing branched π-electron systems and a relatively high degree of steric crowding.

II.1.3 Theory of Fluorescence and Phosphorescence

II.1.3.1 Photochemical Reactions

Photochemical energy, most often causes reactions from the potential energy surfaces of various electronically excited states. The electronically excited molecules can react by fragmenting into neutral molecules or free radicals, by electron transfer, by isomerization, or by addition to some other molecules. In general, the production of electronically excited molecules permits occurrence of highly selective reactions. Complicated molecules can be constructed in one or a few steps from relatively inexpensive raw materials and at low temperatures. Reaction temperatures as low as -269°C has been used; however, industrial photoreactions normally occur at 0-125°C [1,3,5,7,8].

II.1.3.2 Jablonski Diagrams

Jablonski diagrams [3,8] provide a useful means of representation of the excited states of polyatomic molecules having polydimensional energy surfaces. In order to appreciate a Jablonski diagram it is necessary to understand the concept of spin multiplicity. Ordinary organic molecules have an even number of electrons. In the ground state, most organic molecules have all electrons paired. Molecular states with all electrons paired are called *singlet states* (S_n) [46]. Absorption of light occurs without spin inversion, and the initial excited state produced is a singlet excited state. Singlet excited states may undergo spin inversion, giving a new excited state with two unpaired electrons. Molecular states with two unpaired electrons are called *triplet states* (T_n) [46].The singlet and triplet designation derive from the fact that singlet states do not split in a magnetic field , whereas triplet states split into three different energy levels. Free radicals that have one unpaired electron give rise to two energy levels in a magnetic field and thus known as *doublet states* [5]. Electronic transitions between states of the same multiplicity, i.e., singlet-singlet and triplet-triplet transitions, are spin-allowed, and transitions between states of different multiplicity, i.e., singlet-triplet or triplet-singlet transitions, are spin-forbidden transitions and can be observed only by the use of special techniques. Spin-forbidden transitions between excited singlet and triplet states (intersystem crossing) occur in many molecules.

The major events that occur following light absorption may be summarized in terms of a Jablonski diagram. Imagine absorption of a quantum of light of sufficient energy to induce a transition from S_o to S_2, as shown in Figure 3.1. In solution, the excess vibrational energy of S_2 will be rapidly dissipated by radiationless process (vibrational cascade) to the solution. The S_2 state will undergo radiationless internal conversion to an upper vibrational level of S_1, which in turn will rapidly lose its excess vibrational energy to the medium. All of these processes will occur in about 10^{-11} seconds; i.e., the lifetime of upper excited singlet states is generally less than 10^{-11} sec [3,5].

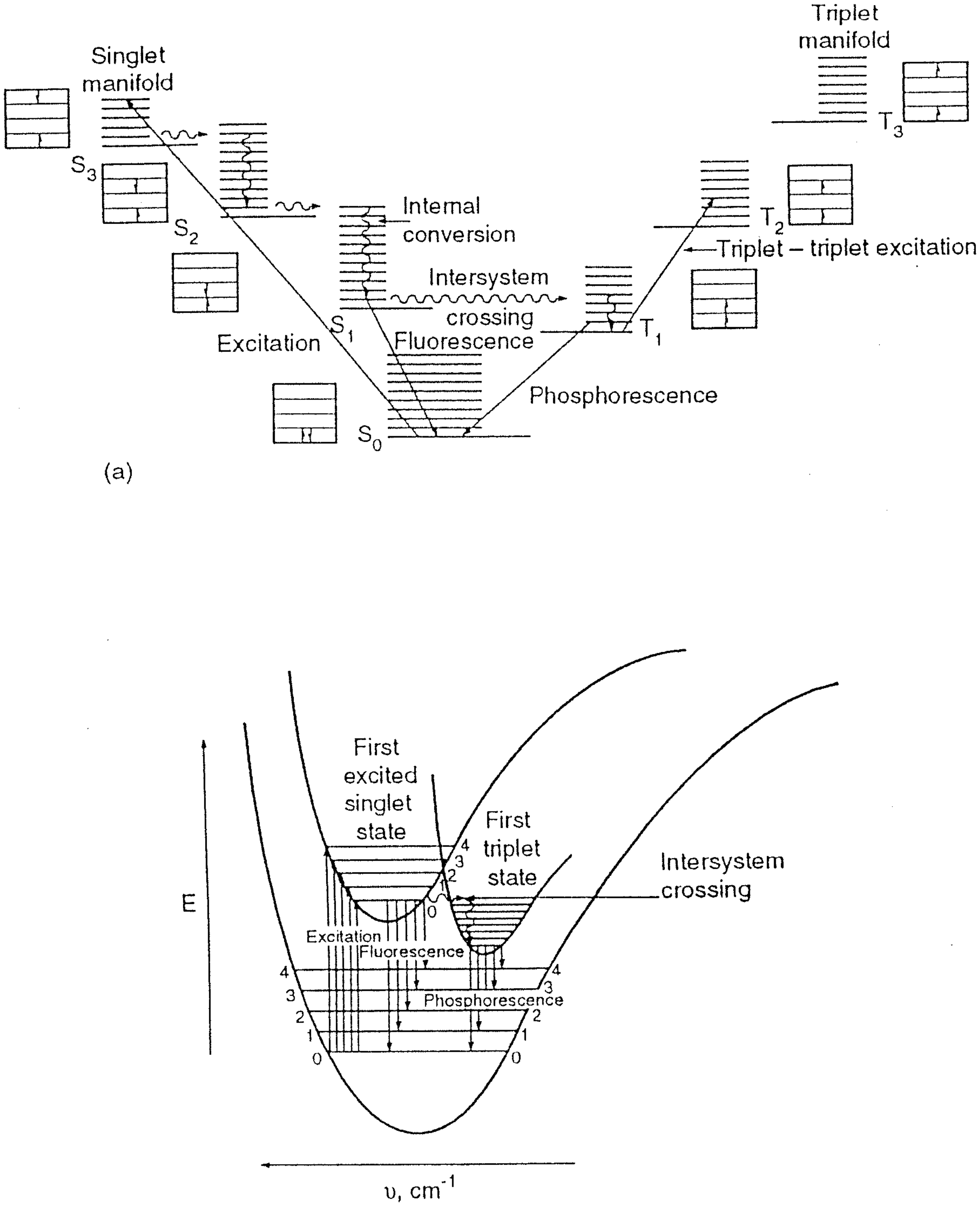


Fig. 3.1 **(a)** Modified Jablonski diagram.

(b) Schematic representation of relative energies of fluorescence and phosphorescence. [9]

The thermally equilibrated low-lying singlet excited state S_1 (v_o) has relatively long lifetime (~ 10^{-8} sec). The lifetime of this state is limited by four important processes: (1) fluorescence, (2) chemical reaction, (3) radiationless decay to the ground state, and (4) intersystem crossing. Fluorescence is the emission of light from a singlet excited state as it returns to the ground state. Fluorescence is, in a sense, the opposite of the lowest energy singlet-singlet light absorption process. Nondissociative chemical reactions are more probable in long-lived excited states. For this reason, S_1 and T_1 are the major reactive states in photochemical processes. Radiationless transition from S_1 to S_o may be thought of as internal conversion from S_1 to vibrationally S_o followed by vibrational cascade to S_o (v_o) with the medium absorbing the excess thermal energy. Intersystem crossing involves and gives rise to a lower energy triplet state. This process is very important in photochemistry, because the triplet state T_1 produced is even long lived than S_1. Low lying triplet states in general have lifetimes greater than 10^{-6} sec, and molecules with triplet lifetimes longer than one second are known. On the other hand, upper triplet excited states have very short lifetimes, just as upper singlet states do. The lifetime of the T_1 state is limited by (1) phosphorescence, (2) chemical reaction, and (3) radiationless decay to S_o. Phosphorescence is the emission of light from a triplet state as it turns to the ground state. Phosphorescence and internal conversion of T_1 to S_o are spin forbidden processes, and this contributes to the relatively long lifetime of low lying triplet excited states. Chemical reaction, especially intermolecular reaction, is favoured by the longer lifetime of the T_1 state relative to the S_1 state [1,3,4,5,7,8,10].

II.1.3.3 Intersystem Crossing

Intersystem crossing [5] ($S_1 \rightarrow T_1$) is formally spin-forbidden process. In some molecules, however it occurs with 100% efficiency, whereas in others it does not occur to any measurable extent. The efficiency in intersystem crossing depends, among other factors, on the difference in energy between the low-lying singlet and triplet state (the S_1 - T_1 energy gap). When this energy difference is small, there is considerable overlap of the two excited states and spin identity is less apparent. In such systems intersystem crossing is efficient. When the energy difference is large, spin-forbiddenness is quite important and intersystem crossing efficiency is low or zero. Generally speaking, ketones have high intersystem crossing efficiencies, aromatic compounds have intermediate to high intersystem crossing efficiencies, and olefins have low intersystem crossing efficiencies. The presence of heavy atoms (sulphur, chlorine, bromine, iodine, etc.) in a molecule enhances intersystem crossing efficiency. Jablonski diagrams are given in Figure 3.2 (a) for benzophenone, which intersystem crosses with 100% efficiency, and Figure 3.2 (b) for 1,3-butadiene which the intersystem crossing efficiency approaches zero [3].

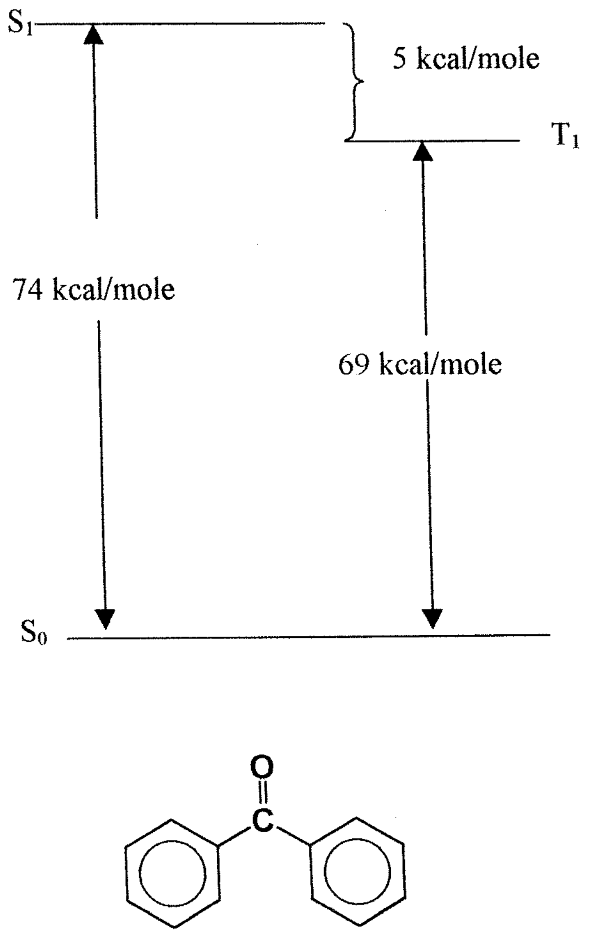


Fig.3.2(a) Jablonski diagram for benzophenone

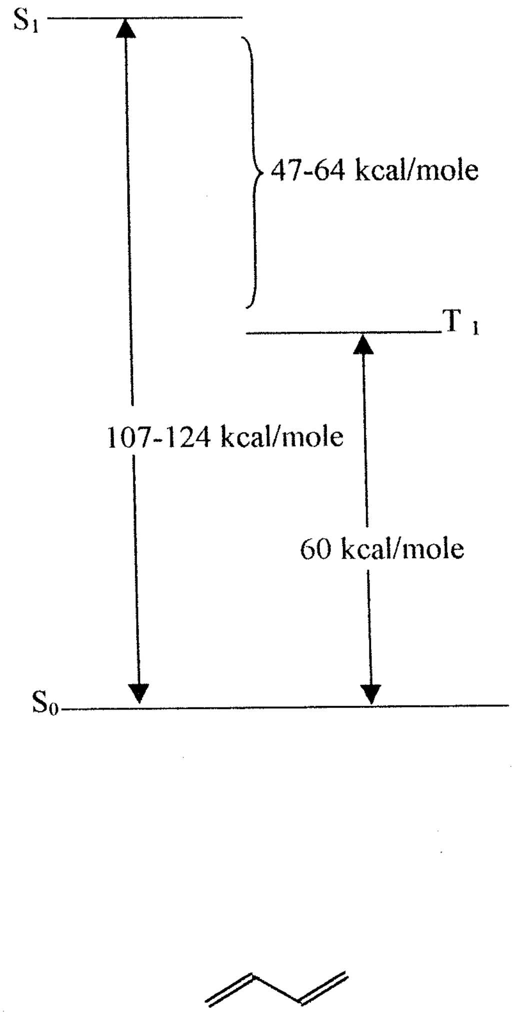


Fig.3.2(b) Jablonski diagram for 1,3-butadiene [3]

II.1.3.4 Energy Transfer

Transfer of excitation energy from an electronically excited molecule to the ground state of another molecule, is generally used for producing triplet excited states. Singlet excitation energy can be transferred, but the probability is limited by the lifetimes of excited singlet states (~10^{-8} sec), which are relatively short compared to the lifetimes of triplet excited states (>10^{-6} sec). Triplet energy transfer in its simplest form requires that the triplet energy [$E_T = E(T_1) - E(S_o)$] of the donor be 3 kcal /mole or more greater than the triplet energy of the acceptor molecule. If this condition is met, triplet energy transfer will occur at every collision between a triplet excited donor molecule and a ground state acceptor molecule. Such reactions are said to be *diffusion - controlled* reactions and have pseudo first-order rate constants [3] of 10^9 to 10^{10} sec^{-1}. Imagine a donor (D) – acceptor (A) system such that only the donor absorbs the incident light, and the triplet energy of the donor is at least 3 kcal/mole greater than the triplet energy of the acceptor [3,5,17].

Light absorption by the donor produces singlet excited donor ^1D.

$$D + h\nu \longrightarrow {}^1D$$

which undergoes intersystem crossing, giving triplet excited donor, ^3D .

$$^1D \xrightarrow[\text{crossing}]{\text{intersystem}} {}^3D$$

Triplet excited donor then collides with acceptor, producing triplet acceptor ^3A and ground state donor D.

$$^3D + A \longrightarrow D + {}^3A$$

The concentration of the acceptor must be kept low enough to make collision with singlet excited donor improbable. This concentration will be determined by the singlet lifetime of the donor. If ^3A gives the products of interest, this is called *sensitization mechanism.*

$$^3A \longrightarrow \text{products (sensitization)}$$

If the products of interest are derived from ^3D , A is a quencher and this is a *quenching mechanism.*

$$^3D \longrightarrow \text{products (quenching)}$$

Sensitization [7,8] and quenching [7,8] are important methods for determining the spin multiplicity of excited states responsible for photochemical reactions. Sensitization is also an important method for producing the triplet states of molecules in which the efficiency of intersystem crossing is low or zero.

II.1.3.5 Aggregation

Dye-dye self-association in solution is called "*aggregation*". It is consequently of great importance in analyzing in any phenomenon in which dye molecules or ions take part. In dye aggregation multiple equilibria need to be considered, i.e. dimeric, trimeric, etc. aggregates are formed [4,16].

$$D + D \overset{K_2}{\rightleftharpoons} D_2 \qquad (3.1)$$

$$D_2 + D \overset{K_3}{\rightleftharpoons} D_3 \qquad (3.2)$$

$$D_{n-1} + D \overset{K_n}{\rightleftharpoons} D_n \qquad (3.3)$$

The aggregation of dyes in solution has been investigated by a variety of methods, i.e. conductometry, calorimetry, polarography, measurements of diffusion coefficients, solubility, activity of counter (sodium) ion, light scattering, fluorescence quenching, X-ray diffraction, sedimentation, evaluation of colligative properties, ^{1}H- and ^{19}F-NMR, and, most frequently, by visible light absorption.

An increase in temperature results in a decrease in the value of the aggregation constants, as expected for entropy reasons. At higher ionic strengths, however, ionic dye aggregation becomes more dominant.

Aggregation of dyes also takes place on and in the substrates during the dyeing process and after treatments. In many cases the lightfastness is increased by that aggregation. If the spectra of Methylene Blue is analyzed, which is adsorbed on glass plates, demonstrates that higher aggregates, up to the tetramer, exist in this system. Therefore, aggregation equilibria are superimposed on dyeing equilibria. This phenomenon is likely to be a major reason for the complex character of dyeing equilibria. In the context of dye aggregation in solid substrates, solutions of (mainly) oligomeric compounds have to be mentioned which lead to many types of inclusion compounds with dyes. Cyclodextrins [4] constitute such a family. Cyanine dyes form complexes with cyclodextrins and that cyclodextrine induces dimerization of these dyes.

Dye aggregation was applied in order to study model systems of biological structures, in which molecules organize themselves to form functional entities.

Figure 3.3 shows electronic spectra of the dye given in Figure 3.4 at four concentrations in the range from 2.96 x 10^{-5} to 1.48 x 10^{-3} mol.L^{-1}. Calculations show that at concentrations below 10^{-5} mol.L^{-1} practically only the monomer exists and that above 10^{-2} mol.L^{-1} various higher aggregates appear, giving poly associated system.

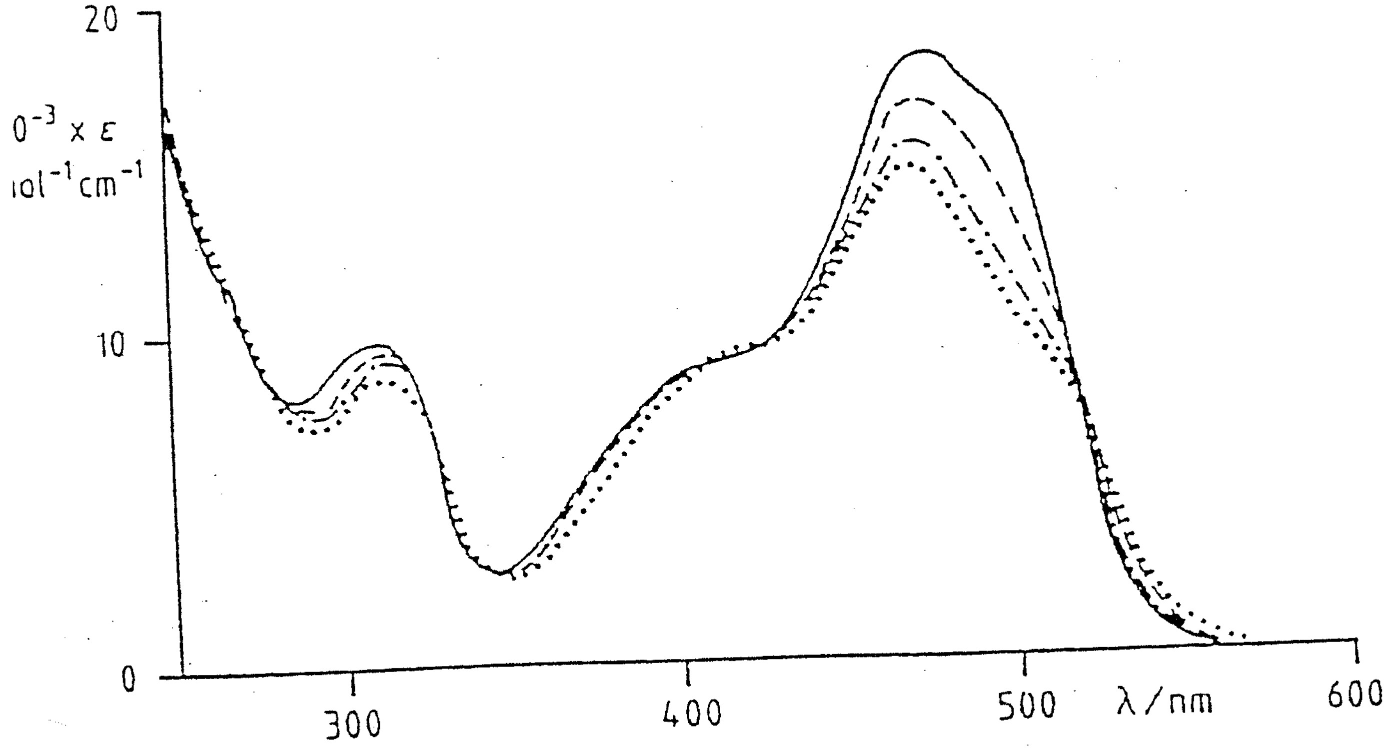


Fig 3.3 Absorption spectra of aqueous solutions of dye (3.4) at 25°C. [4]

—— : 2.96×10^{-5} mol.L^{-1}

- - - : 2.96×10^{-4} mol.L^{-1}

- . - : 7.88×10^{-4} mol.L^{-1}

.... : 1.48×10^{-3} mol.L^{-1}

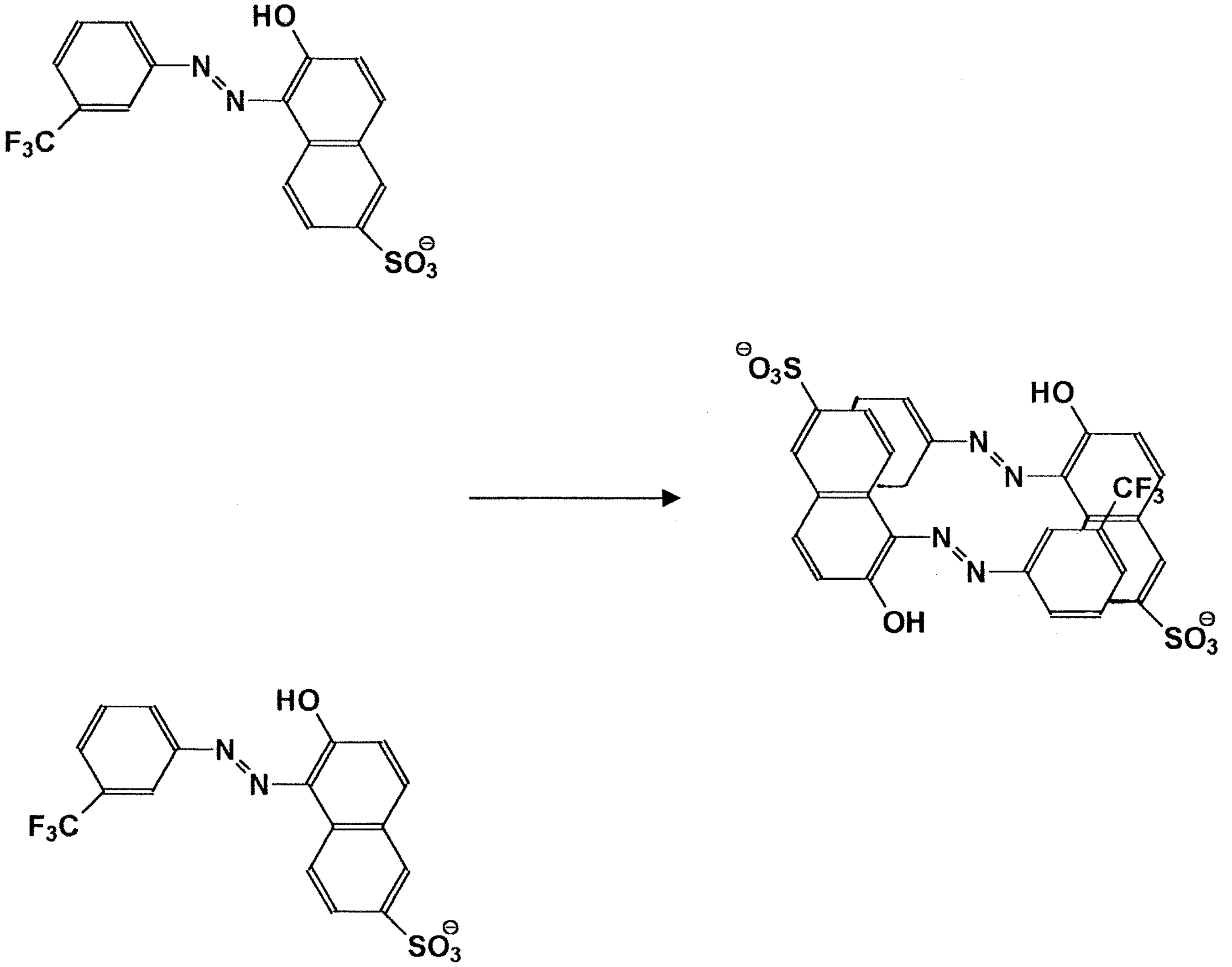


Fig. 3.4 Schematic representation of dimer formation of dye (3.4) through hydrophobic interactions. [4]

II.1.3.6 Photosensitization and Quenching

$$R_0 \longrightarrow R^{*v} \longrightarrow R^{*} \xrightarrow{Q} R_0 + Q^{*}$$

In the bimolecular pathway, R^* can interact with and transmit its excitation energy to another molecule Q to form Q^* (quencher or sensitizer) is a process called "quenching" or "sensitization".

Photosensitization and quenching play an important role in many aspects of organic photochemistry [32]. Photosensitization and quenching processes which involve in energy transfer of the type $D^* + A \longrightarrow D + A^*$ may be used to control photochemical sequences and to study reaction mechanisms [5,7,8].

For example, singlet – singlet and triplet – triplet energy transfer may be used to indirectly populate A^* states or to quench D^* states. Of special importance is triplet - triplet energy transfer, because the *quenching* of D_T^* by energy transfer often limits its lifetime. For example, a unimolecular typical triplet lifetime in a non – reactive organic solvent is ~ 10^{-4} sec. This corresponds to a unimolecular decay rate constant, k_D, of 10^{-4} sec^{-1}. The *actual* rate constant of decay of the triplet is given by [46]:

$$k_D^{OB} = \text{rate constant decay of } D_T^* = \underset{\text{True 1}^{\text{st}}\text{ order}}{k_D} + \underset{\text{Pseduo 1}^{\text{st}}\text{ order}}{k_q[Q]}$$

If $k_q = 10^{10}\ M^{-1}\ sec^{-1}$, then for $[Q] = 10^{-6}$ M, 50% of D_T^* molecules will be quenched by Q. Since exothermic energy - transfer rate constants, k_{ET}, are of the order of $10^9 - 10^{10}\ M^{-1}\ sec^{-1}$, it is clear that very small amounts of impurities (which may serve as exothermic energy – transfer quenchers) can limit the lifetime of D_T^*.

On the other hand, numerous compounds possess inefficient intersystem crossing yields, so that T_1 is not easily produced by *direct* photoexcitation. Triplet – triplet energy transfer may allow for the efficient *indirect* production of such triplets. A *triplet photosensitizer* is one capable of transferring its triplet excitation to an acceptor.

Judicious selection of triplet photosensitizers is required in many specific cases in order to avoid the complications of singlet quenching of D_S^* , photoreactions of D_S^* , direct excitation of A_S^* , etc. An *"ideal"* triplet photosensitizer would posses the following characteristics [5,46].

1. A fast rate of intersystem crossing relative to other deactivation of S_1 .(i.e. $k_{ST} >> k_F$, so that $\phi_{ST} \sim 1.0$).
2. A high triplet energy, E_T, which would allow energy transfer to be exothermic with respect to a broad range of acceptors.
3. A long triplet lifetime, τ_T , in order to maximize the efficiency of the energy – transfer process (i.e. $k_{ET}[A] >> k_T$ at accessible contractions of A).
4. A substantial absorption in a region of the spectrum where A does not significantly absorb.
5. A low chemical reactivity in order to avoid photochemical reactions with A.

There is no "ideal" photosensitizer in a general sense. However, the rational choice of photosensitizer can be made by examiming the above characteristics for potential candidates. The most important single parameter in the selection of a triplet photosensitizer is the energy gap between D_T^* and A_T^* , since only if the energy transfer is exothermic can it possess a maximum value of k_{ET}. Thus, knowledge of $E_T(D^*)$ and $E_T(A^*)$ is of crucial importance in the selection of a triplet photosensitizer.

	E_S	E_T	τ_S^b	τ_T^b		
Compound	(kcal/mole)	(kcal/mole)	(sec)	(sec)	Conf. T_1	ϕ_{ST}
Benzene	110	84	~10^{-7}	10^{-6}	π,π^*	0.2
Acetone	~85	~78	10^{-9}	10^{-5}	n,π^*	1.0
Xanthone		74	-	-	π,π^*	1.0
Acetophenone	~79	74	10^{-10}	10^{-4}	n,π^*	1.0
4-CF_3-Acetophenone		71	-		n,π^*	1.0
Benzophenone	~75	69	10^{-11}	10^{-4}	n,π^*	1.0
Triphenylene	83	67	~$5x10^{-8}$	10^{-4}	π,π^*	0.9
Thioxanthone	78	~65	-	-		-
Anthraquinone	-	62	-	-	n,π^*	1.0
4-Ph-benzophenone	77	61	-	10^{-4}	π,π^*	1.0
Michler's ketone	-	61	-	-	-	1.0
Naphthalene	92	61	10^{-7}	10^{-4}	π,π^*	0.7
2-Acetonaphthalene	78	59	-	10^{-4}	π,π^*	1.0
1-Acetonaphthalene	76	57	-	10^{-4}	π,π^*	1.0
Chrysene	79	57	$5x10^{-8}$	-	π,π^*	0.8
Biacetyl	~60	55	10^{-8}	10^{-3}	n,π^*	1.0
Benzil	~59	54	~10^{-8}	10^{-4}	n,π^*	1.0
Camphorquinone	~55	50	~10^{-8}	-	n,π^*	1.0
Pyrene	77	49	~10^{-6}	-	π,π^*	0.3
Anthracene	76	47	~$5x10^{-9}$	10^{-4}	π,π^*	0.7
9,10-Dichloroanthracene	~74	40	~$5x10^{-9}$	10^{-4}	π,π^*	0.5
Perylene	66	~35	$5x10^{-9}$	-	π,π^*	0.005

TABLE 3.1 Important Parameters for Triplet Photosensitizers. [46]

A list of triplet energies E_T (energy of 0-0 transition, $T_1 \longrightarrow S_0$) of selected compounds is given in Table 3.1, which also tabulates the configuration of T_1, singlet energies (E_S) and approximate experimental singlet and triplet lifetimes (τ_S and τ_T respectively). The values of E_S and E_T are usually only slightly solvent dependent (± 1-2 kcal/mole). The tabulated data refer to nonpolar, chemically "inert", "oxygen-free" solvents. In addition to the data given in the above Table 3.1 which allows one to rationally select a triplet sensitizer and appropriate concentration of quencher, the excition coefficients of sensitizer become very important (crucial) if the quencher absorbs in the same region that the sensitizer absorb.

In contrast to the desirability that τ_T be as long as possible for triplet sensitizer , a desirable triplet quencher should have a very short lifetime and still be “chemically inert” to net reaction. The short lifetime is desirable to avoid participation of the triplet quencher (produced by energy transfer) in subsequent photoreactions.

Compound	E_S	E_T
$CH_3 CH = CHCH_3$	~120	78
$PhC \equiv CH$	~100	72
Ph – Ph	~95	66
Ph – Ph – Ph (Orto-tert phenyl)	~90	62
CH_2=CH-CH=CH_2	~90	60
CH_3CH=CHCH=CH_2	~90	59
Ph – Ph – Ph (Para-terphen)	~105	58
Cyclopentadiene	~90	58
Cis-stilbene	~95	57
1,3-cyclohexadiene	~80	53
Trans – stilbene	~90	50
Azulene	~40	~30
Tetracene	~45	~29
Oxygen		23

TABLE 3.2 Energies of some common quenchers. [46]

Table 3.2 lists some commonly employed "triplet" quenchers which are not acceptable as triplet photosensitizers (e.g. because of their poor absorption characteristics or lifetimes). Of course the compounds listed in Table 3.1 are potential triplet quenchers also.

Ketones often possess the best compromise of desirable characteristics of a triplet photosensitizers. For example, acetophenonon possesses a relatively high triplet energy (~72 kcal/mole), a long inherent unimolecular lifetime (~ 100μs), a high value of ϕ_{ST} (~ 1.0), and a short singlet lifetime. It has the disadvantages of not possessing a high absorption maximum ($\varepsilon_{max} \sim 100$) and of possessing a relatively reactive T_1 (n,π^*) state [5,46].

II.1.4 Photochemical Aspects of Perylene 3,4,9,10-Tetracarboxylic Acid-bis-N,N'-aryl(alkyl) Diimides :

Rademacher, Markle and Langhals investigated the preparation of several 3,4,9,10-Perylenebis(dicarboximides) and determine their photostability. The substitution of the insoluble perylene dye pigments with tert-butyl groups causes solubility in organic solvents leading to the high quantum yields of the dyes. [44]

İcil, Uzun and Paşaoğulları investigated a new thermal and photostable reference probe for ϕ_f measurement in aqua: water soluble N,N'-bis-(2-hydroxy-4-benzoic acid)-3,4,9,10-perylenebis(dicarboximide). Together with photostability the dye is also very stable thermally. The fluorescence quantum yield is measured as 1. The diimide dissolves in water at PH=8 completely. The diimide is an ideal reference probe for fluorescence quantum yield measurements in 500-650nm region and an attractive photosensitizer for the photoreactions occuring in water. [29]

Kleine, Fritz, Schruring, Eberhard, Dassler and Walter investigated that the black pigments are used for camouflage. Perylenetetracarboxylic diimides are used as black pigments with IR-reflective properties for camouflage paints and plastics. [39]

Langhals investigated Perylene-3,4,9,10-tetracarboxylic diimide multichromophoric dyes, their preparation and their usage. The dyes are obtained by the condensation of a perylenetetracarboxylic monoimide with $Ar(NHCHO)_2$ which are suitable for coloration of plastics, security printing, machine-readable inks, nonimpact printing toners, and electroluminescent devices. Thus, N-(1-hexylheptyl)-3,4,9,10-perylene tetracarboxylic acid anhydride imide was condensed with 2,4,6-triaminopyrimidine triformamide in the presence of imidazole to give a trichromophoric perylene dye. [40]

Samy A. and El Daly investigated fluorescence quenching of N,N'-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenebis(dicarboximide)DBPI by Co^{+2} ion. He found out that bimolecular quenching rate constant k_q is viscosity and temperature dependent[38]. İcil has pointed that a Förster resonance energy transfer mechanism is dominant in energy transfer from all perylene diimides, to cobalt ions. [17]

Langhals, Sprenger and Brandherm investigated perylene-3,4,9,10-tetracarboxylic acid 3,4-anhydride-9,10-imides are condensed with primary diamines to a number of new basic chromophores with amidine-imide structures. Lighfast dyes are obtained which exhibit a strong fluorescence in solution. The absorption and fluorescence spectra of the perylenamidine-imide compounds are bathochromically shifted compared to those of the perylene dyes. [22]

Lukac and Langhals have investigated the synthesis and fluorescence of 2,3,4,4a,10a,11,12,13-octahydro-1,4a,10a,14-tetraazaviolanthrone derivatives. The tetramethyl derivatives of the above compound was prepared by the condensation of neopentanediamine with 3,4,9,10-perylenebis(dicarboxylic anhydride). The spectra of absorption and fluorescence with λ_{max} = 541 and 563 nm, respectively, show a bathochromic shift versus those of the perylene dyes. The quantum yield of fluorescence is 60 percent. The analogue condensation of the anhydride with ethylenediamine gives a perylene fluorescent dye as an intermediate which contains an amino group and may, therefore, be used in acid aqueous solutions. [43]

The emission characteristics and photostability of N,N'-bis (2,5-di-tert-butyl phenyl)-3,4,9,10-perylene bis (dicarboximide) have been investigated by M. Ebeid and Daly [35].They found that the dye undergoes, molecular aggregation both in the ground state (at a critical concentration of ca. 2 x 10^{-4} mol dm^{-3}) and in the excited state (giving excimerlike emission at ca. 600 nm). It displays solvatochromism in both emission and UV-Visible absorption spectra.. [35]

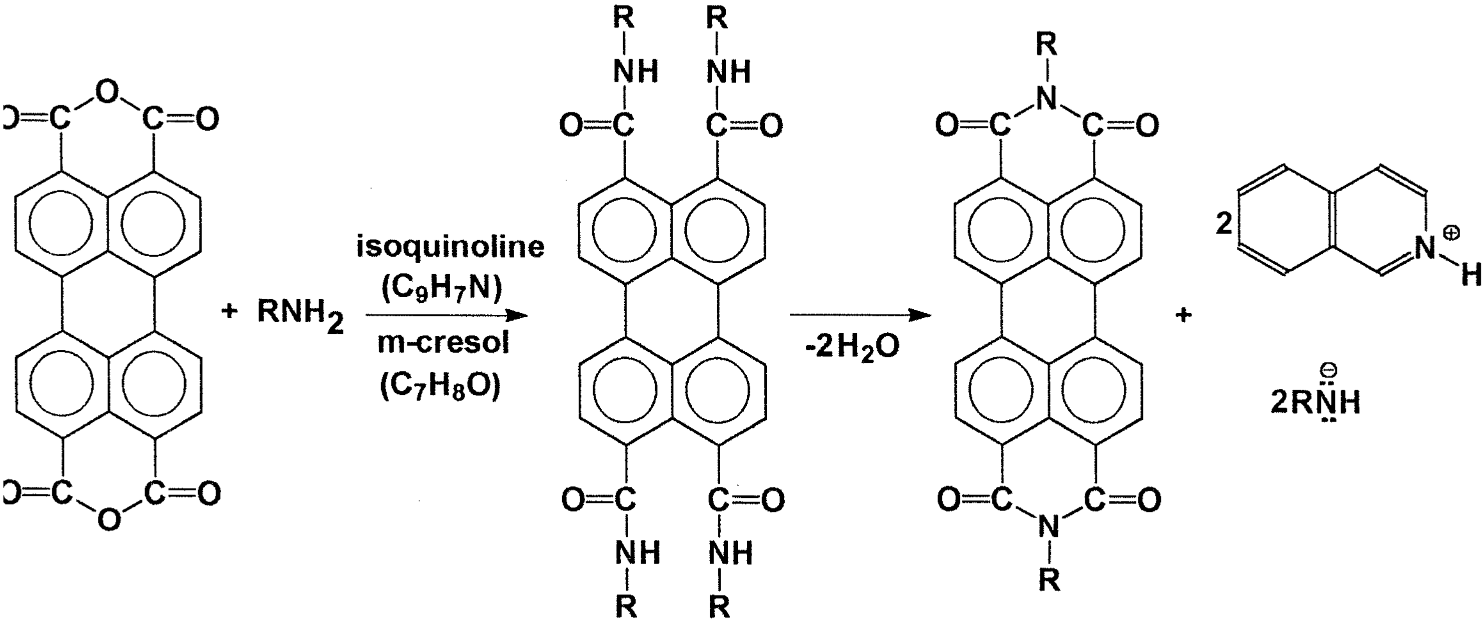
Bird and Sandrai investigated the laser action of perylene-3,4,9,10-tetracarboxylic acid-bis-N,N'(2',6' xylidyl) diimide [34]. They found out that this dye in dimethylformamide absorbs a main maximum at 527 nm. From their investigations they pointed that, this dye is more stable than even rhodamine 6G, which is the most stable of that class. [34]

III. SYNTHETIC EXPERIMENTAL

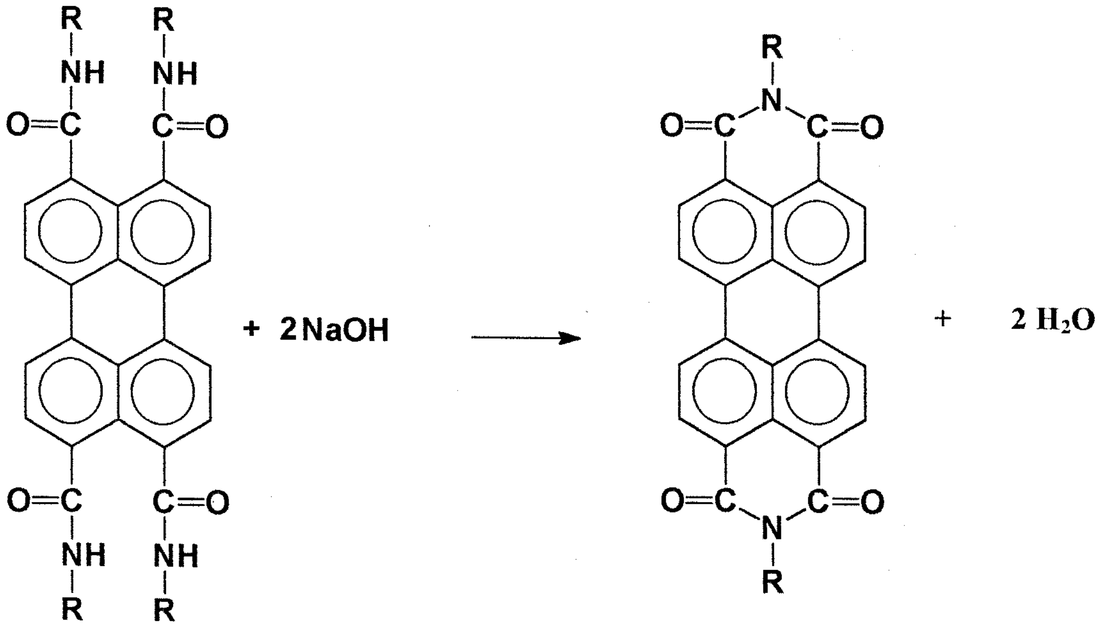
In this section, the preparative description of the synthetical method, the analytical and spectroscopic data of the synthesized compounds are given [18].

III.1 Method of Synthesis of Symmetrically Substituted Perylene Fluorescent Dye

The method of synthesis which was undertaken and applied successfully for the preparation of symmetrically substituted perylene diimide [33] is shown in the scheme below.



In order to convert amides to imides; the amide was treated with NaOH solution.



$R = CH_3(CH_2)_{17}—$

The perylene N,N′- disubstituted imide [11.13] was synthesized by condensation of perylene 3,4,9,10-tetracarboxylic dianhydride [42] and alkyl primary amine in the presence of m-cresol and isoquinoline. Refluxing periods were varied between 10-15 hours. The temperature of reactions was nearly 200°C. The unreacted reactants were taken out by direct washing with hot solvents and product filtered while hot. The wet cake was dried in vacuum oven and refluxed for 1 hour with 10% NaOH (~100 ml) in order to convert amides to imides. After filtration, the product was treated with 10% HCl (~100 ml), heated to 90°C with stirring, filtered hot and dried in vacuum.

The imide have very low solubility (about 1.8 mg in 100 ml of chloroform), very high melting point (above 360°C) and give violet-red colour with concentrated H_2SO_4.

Reactants were heated in a 100 ml two neck flask, fitted with a thermometer and a condenser. It was found that the temperature range and heating period critically affected the yields. The best results were obtained when a reaction phase stayed as a homogeneous liquid, for at least 2 hours at 80°C, and then increase of the temperature upto 200°C slowly. The imide was purified by column separation over silica gel and identified by elemental analysis, IR, MS, UV and Emission spectroscopy [25]. Identification of perylene diimides by NMR Spectroscopy was found to be unpractical due to low solubilities [1].

Synthesis of N,N′-DiOctadecyl-3,4,9,10-Perylene Bis-(Dicarboximide):

A mixture of perylene-3,4,9,10-tetracarboxylic acid dianhydride (1g, 2.55×10^{-3} mol), octadecylamine (1.375g, 5.1×10^{-3} mol), m-cresol (40 ml) and isoquinoline (4 ml) was stirred at 80°C for 2 hours. Then the solution was heated at 120°C for 2 hours, the temperature was raised to 160°C and kept for 2 hours. The reaction was then completed by stirring at 200°C for another 9 hours. The warm solution was poured into 250 ml of acetone, and the precipitate was filtered out and dried at 50°C under vacuum. The crude product was washed with ethanol in order to get rid of the unreacted amine and then refluxed for 1 hour with 10% NaOH (~100 ml) in order to convert amides to imides and also in order to remove unreacted perylene dianhydride. Then in order to remove high boiling solvents, m-cresol and isoquinoline, the crude product was treated with ethanol in a soxhlet apparatus for 48 hours. The product is treated with 10% HCl heated to 90°C, filtered hot and dried in vacuum oven. (50°C). The product is further purified by column separation (silica gel, chloroform) [10,45].

Yield : ~38 %, **colour of the imide** : dark brown , **colour of the imide in conc. H_2SO_4** : violet-red, **melting point** > 360°C, **R_f** (kieselgel,$CHCl_3$) : 0.78, **IR**(KBr pellets) : ν = 2922.6, 2848.4, 1696.7, 1656.4, 1593.9, 1578, 1465.6, 1438.9, 1406.2, 1343.8, 1257.6, 1080.4, 853.7, 809.2, 793.9, 747.3, 630.5, 435.7 cm^{-1}. **UV** ($CHCl_3$): λ_{max} (ε)= 458 nm (18580), 489 (52850), 525 (86100), 582 (12500). **Fluorescence** ($CHCl_3$): λ_{max} (ε)= 535.95 nm, 575.57, 624.68. **Q_f** = 0.8. **MS**: m/z = 895(M^+), 622, 533.

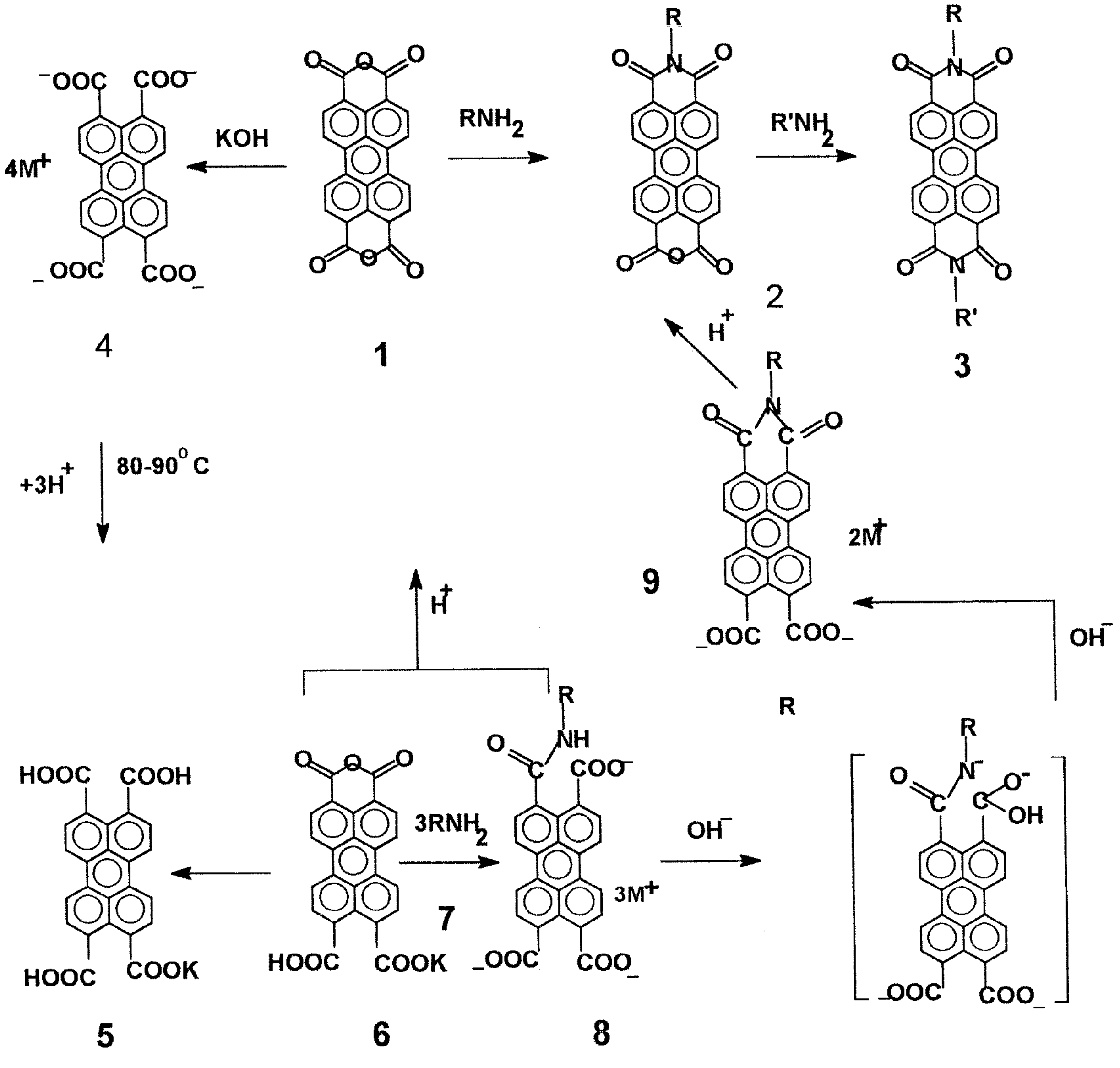
$C_{60}H_{82}N_2O_4$	Calc.	C 80.49	H 9.23	N 3.13
		C 80.26	H 9.25	N 3.07

The origin of the chemicals used for the synthesis of octadecyl diimide are listed below:

Perylene 3,4,9,10-tetracarboxylic acid; pure grade, isoquinoline, 97% and octadecylamine were obtained from "Aldrich". m-cresol, 98%, was supplied by "Fluka", and used without further purification [9].

III.2 Method of Synthesis of Unsymmetrically Substituted Perylene Fluorescent Dye:

The method of synthesis which was undertaken and applied successfully for the preparation of unsymmetrically substituted perylene diimide is shown in the scheme below [20].



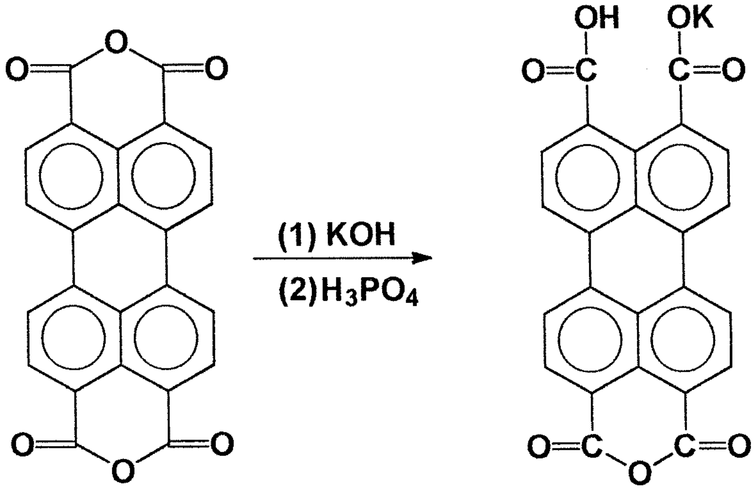
The synthesis of unsymetrically substituted perylene diimide is followed in three steps [14,15.21]:

1 - Synthesis of Monopotassium Carboxylate of 3,4,9,10-Perylenetetra-Carboxylic Acid Monoanhydride

2 - Synthesis of 3,4,9,10-Perylene Tetracarboxylic-3,4-Anhydride-9,10- Imide

3 - Synthesis of N-Octadecyl-3,4,9,10-Perylenetetra-Carboxy Diimide

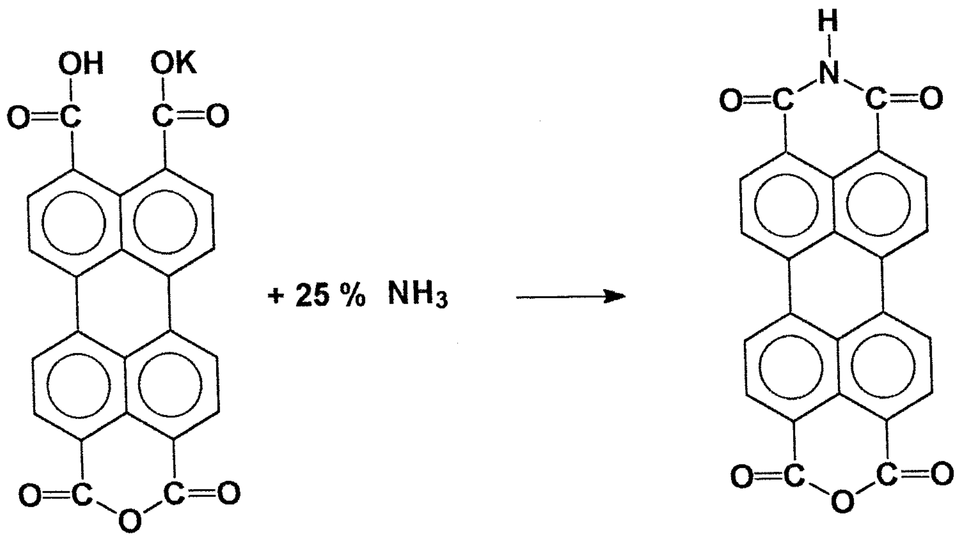
1 - Method of Synthesis of Monopotassium Carboxylate of 3,4,9,10-Perylenetetra-Carboxylic Acid:



3g (7.647×10^{-3} mol) perylene-3,4,9,10-tetrecarboxylic acid dianhydride was refluxed at 90°C for 3-4 hours with 35 ml 5% KOH. After reflux, 12.5 ml of 10% H_3PO_4 was added and refluxed for 1 hour at 90°C and filtered.

Yield : 47 % , **colour of the monopotassium carboxylate of 3,4,9,10-perylenetetracarboxylic acid monoanhydride** : reddish - bordeaux, **IR**(KBr pellets) : ν = 3437 cm^{-1}, 3065, 2460, 1935, 1770, 1727, 1593, 1508, 1407, 1376, 1342, 1315, 1302, 1232, 1211, 1183, 1151, 1122, 1017, 939, 854, 818, 809, 766, 740, 687, 641, 612, 536, 499, 485, 463, 450, 436, 424, 415. **UV** ($CHCl_3$): λ_{max} (ε) = 452.5 nm (11400), 481 (26000), 518 (37800).

2 - Method of Synthesis of 3,4,9,10 - Perylene Tetracarboxylic - 3,4-Anhydride - 9,10 – Imide:

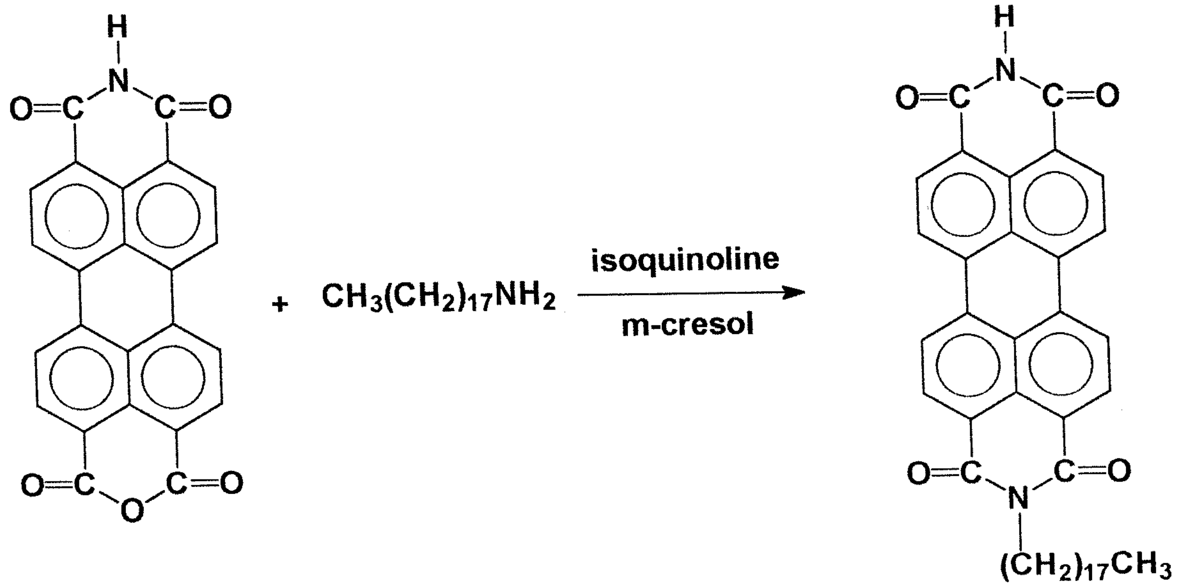


1g (2.23x10^{-3} mol) monopotassium carboxylate of 3,4,9,10-perylenetetracarboxylic acid monoanhydride, 50 ml H_2O and 6 ml 25% NH_3 were refluxed at 0-5°C for 4 hours. Then the solution was heated at 90°C for 2 hours and 12.5 ml 25% K_2CO_3 was added and refluxed for 1 hour at 90°C. The product was filtered at room temperature and washed with 2% K_2CO_3. The reaction mixture was heated to 95°C for 5 minutes after the addition of 3.5% KOH and filtered while hot. The filtrate was acidified with 10% HCl and filtered. The crude product is purified via sublimation (-3 mbar, 300° C)

Yield: ~36.13 %, **colour of the 3,4,9,10 - perylene tetracarboxylic -3,4 - anhydride-9,10 - imide**: dark brown, **IR** (KBr pellets): ν = 3449 cm^{-1}, 1781, 1757, 1687, 1595, 1403, 1372, 1322, 1273, 809, 735, 656. **UV** ($CHCl_3$): λ_{max} (ε) = 480.00 nm (139600), 517.00 (138300), 558.50 (54600). **Fluorescence** ($CHCl_3$):λ_{max} (ε) = 535.02 nm, 574.50, 624.68, **Q_f** = 0.81, **MS**: m/z = 392(M^+), 359, 341, 313, 299, 288, 271, 257, 239, 219.

$C_{24}H_9O_5N$	Calc.	C 73.66	H 2.32	N 3.58
		C 73.61	H 2.30	N 3.55

3 - Method of Synthesis of N-Octadecyl-3,4,9,10-Perylenetetra-Carboxy Diimide :



A mixture of 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10-ammonium imide (1g, 2.26×10^{-3} mol), octadecylamine (6.89g, 2.56×10^{-2} mol), m-cresol (40 ml) and isoquinoline (4 ml) was stirred at 80°C for 1 hour. Then the solution was heated at 100°C for 1 hour, the temperature was raised to 120°C for 1 hour, 140°C for 1 hour respectively. The reaction was then completed by stirring at 160°C for another 4 hours. The warm solution was poured into 250 ml acetone, and the precipitate was filtered out and dried at 50°C under vacuum. The crude product was treated with ethanol for 24 hours in a soxhlet apparatus in order to get rid of unreacted amine and to remove high boiling point solvents, m-cresol and isoquinoline and then washed with 10% NaOH in order to remove unreacted monoimide and convert amides to imides.

The product is further purified by column separation (silica gel, chloroform) [10,45].

Yield: 79.96%, **colour of N-Octadecyl - 3,4,9,10 – Perylenetetra - Carboxy Diimide**: reddish brown , **IR**(KBr pellets) : $\nu = 3450\ \text{cm}^{-1}$, 3158, 3046, 2953, 2919, 2849, 1695, 1677, 1656, 1595, 1578, 1508, 1466, 1439, 1402, 1372, 1276, 1244, 1183, 1090, 882, 852, 811, 795, 743, 656, 435. **UV** ($CHCl_3$): λ_{max} (ε) = 457.0 nm (57700), 484.0 (70900), 524.0 (79300), 604.0 (54900). **Fluorescence** ($CHCl_3$): λ_{max} (ε) = 531.32 nm, 576.11, 624.68, **Q_f** = 0.37, **MS**: m/z = 643.3(M^+), 554.5, 391.2, 359.2, 341.2, 313.2, 267.2, 239.2.

$C_{42}H_{46}O_4N_2$	Calc.	C 78.47	H 7.21	N 4.36
		C 78.67	H 7.19	N 4.34

The origin of the chemicals used for the synthesis of N-octadecyl - 3,4,9,10 – perylene tetracarboxy diimide are listed below:

Perylene 3,4,9,10-tetracarboxylic acid; pure grade, isoquinoline, 97% and octadecylamine were obtained from "Aldrich". m-cresol, 98%, was supplied by "Fluka", and used without further purification. Chloroform and 25% NH_3 were purchased from "Aldrich" [9].

III.3 IR Spectra and Elemental Analysis:

Solid state analysis by IR and elemental analysis gave consistent results for purities and structural characteristics. Elemental analysis were obtained from a Carlo Erba-1106 C,H,N analyzer.

The IR Spectra were taken with KBr pellets using a Bruker IFS66 IR spectrometer.

The two perylene diimides have given characteristic carbonyl-I and carbonyl-II bands with neighboring imide-I and imide-II bands (CONRCO) at decreased intensities [12].

III.4 UV Absorption Emission Spectra:

The UV Absorption Spectra were recorded using an UV-2102 PC UV-VIS Scanning spectrophotometer. The solutions for symmetrically substituted perylene fluorescent dye and for the unsymmetrically dye solutions were prepared in chloroform ($CHCl_3$).

The UV emission spectra were recorded using a Spex Fluorolog. The solutions were prepared in chloroform at 10^{-5} M concentration.

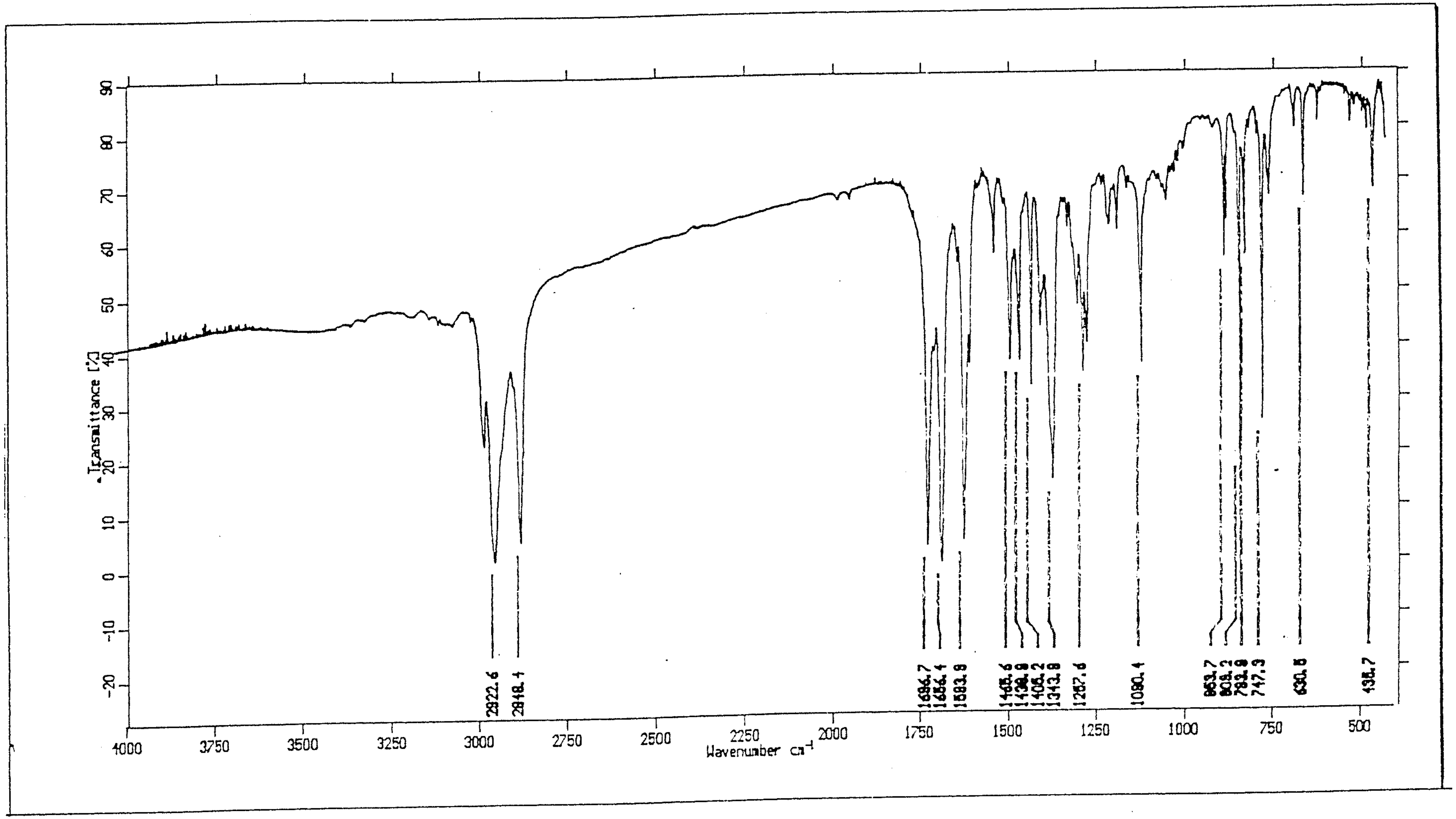


Fig III.1 IR Spectrum of N,N′- dioctadecyl- 3,4,9,10 - perylene bis(dicarboximide).

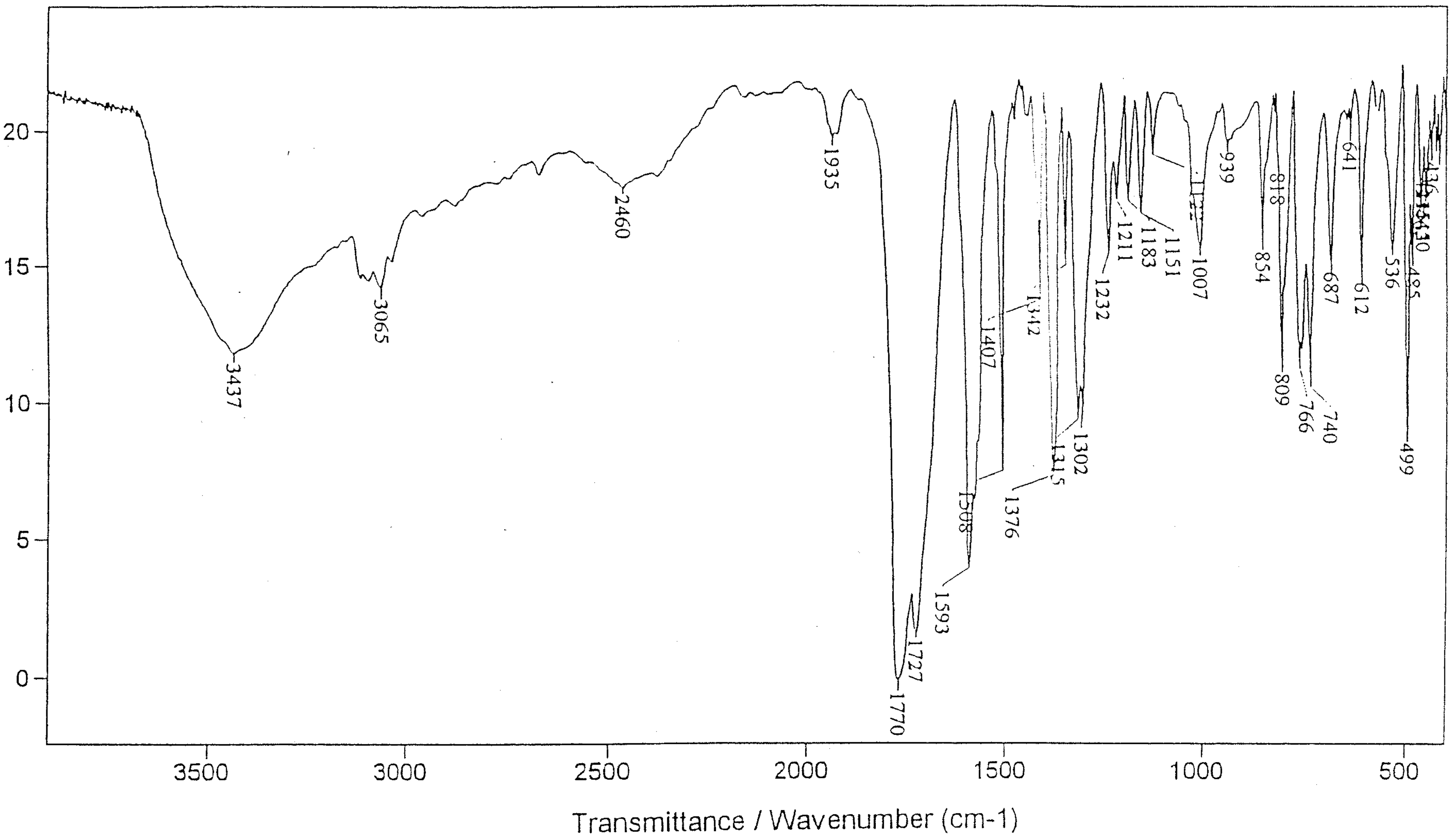


Fig III.2 IR Spectrum of monopotassium carboxylate of 3,4,9,10-perylenetetra-carboxylic acid monoanhydride

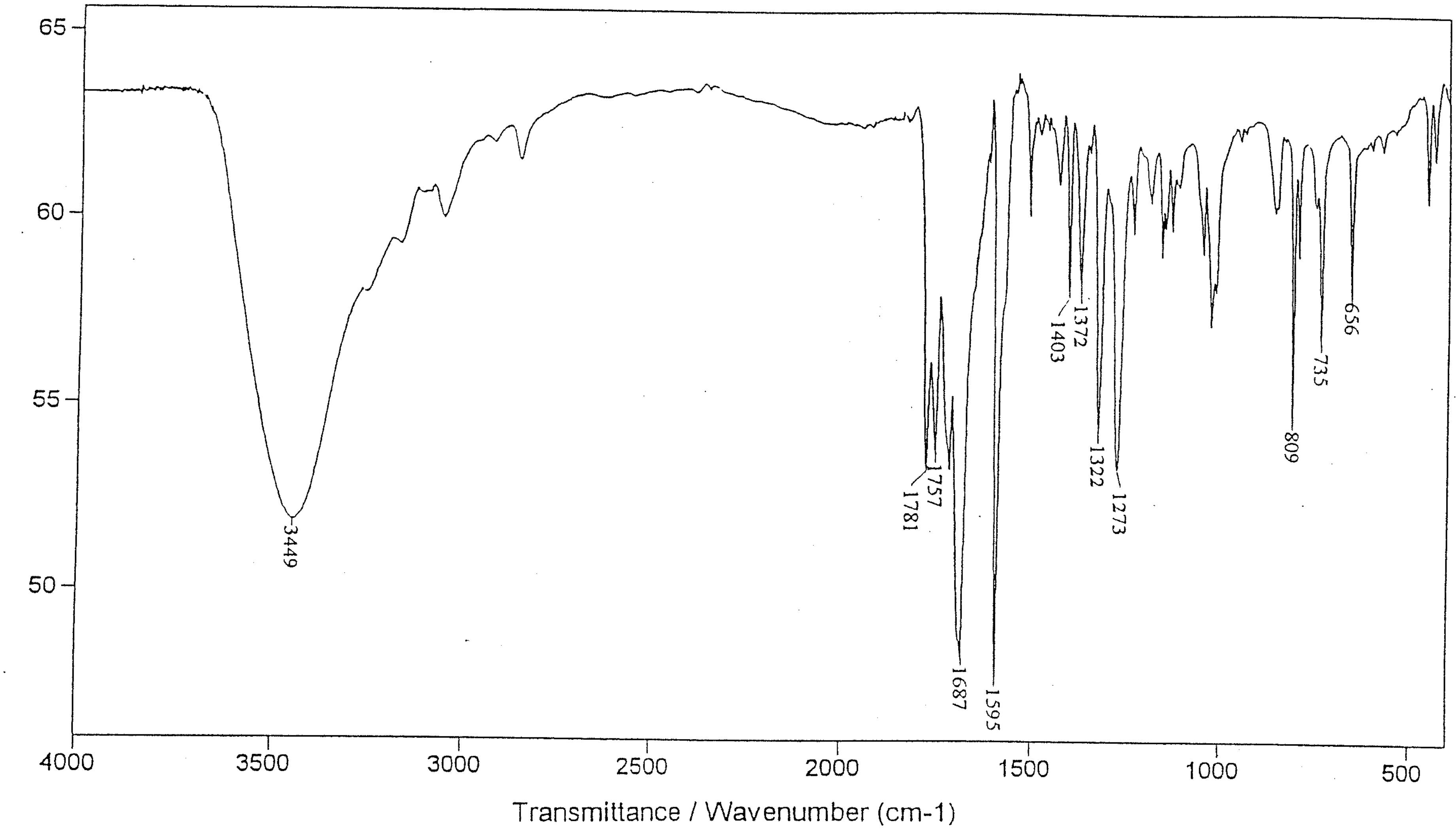


Fig III.3 **IR Spectrum of 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10- imide**

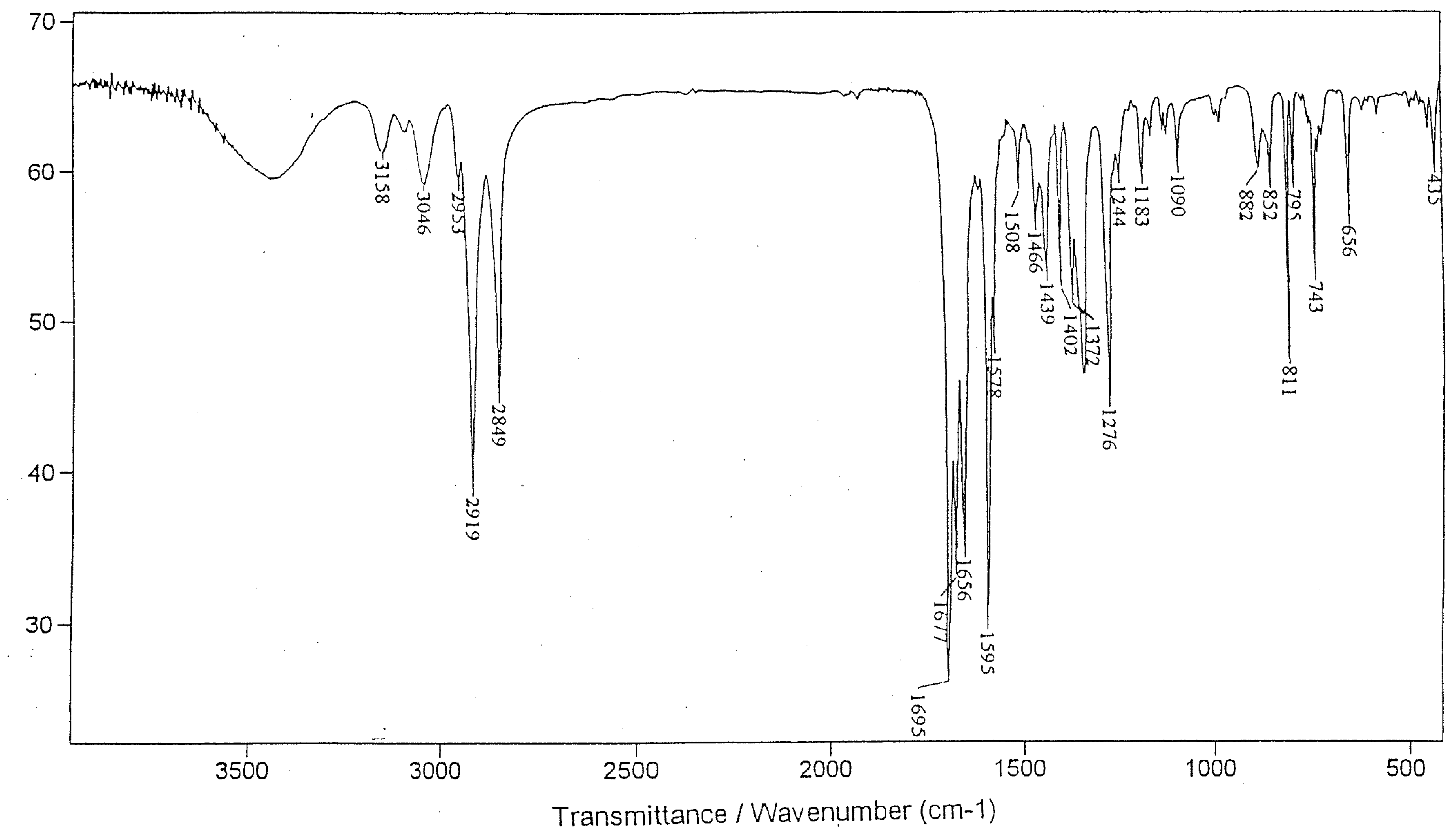


Fig III.4 **IR Spectrum of N-octadecyl-3,4,9,10-perylenetetra-carboxy diimide**

III.5 Mass Spectra:

The Mass Spectra were recorded using a MAT 95 Spectrophotometer.

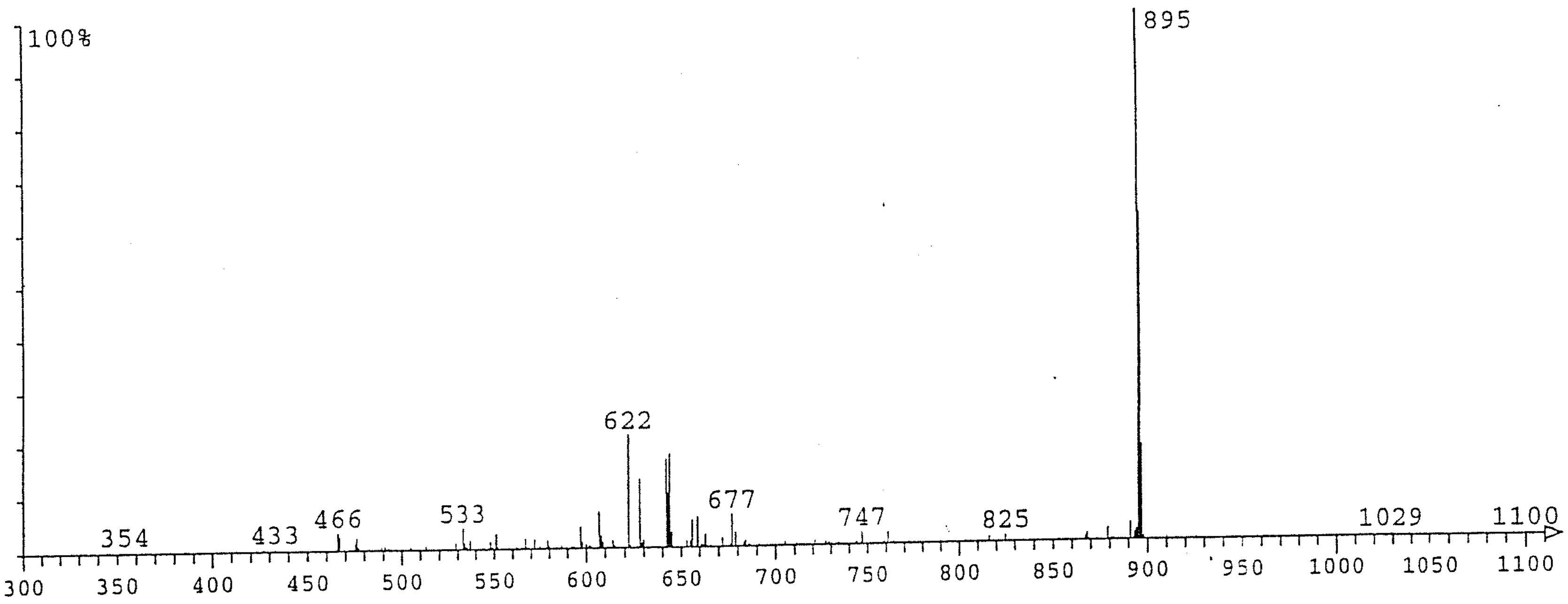


Fig III.5 Mass Spectrum of N,N′- dioctadecyl- 3,4,9,10 - perylene bis(dicarboximide)

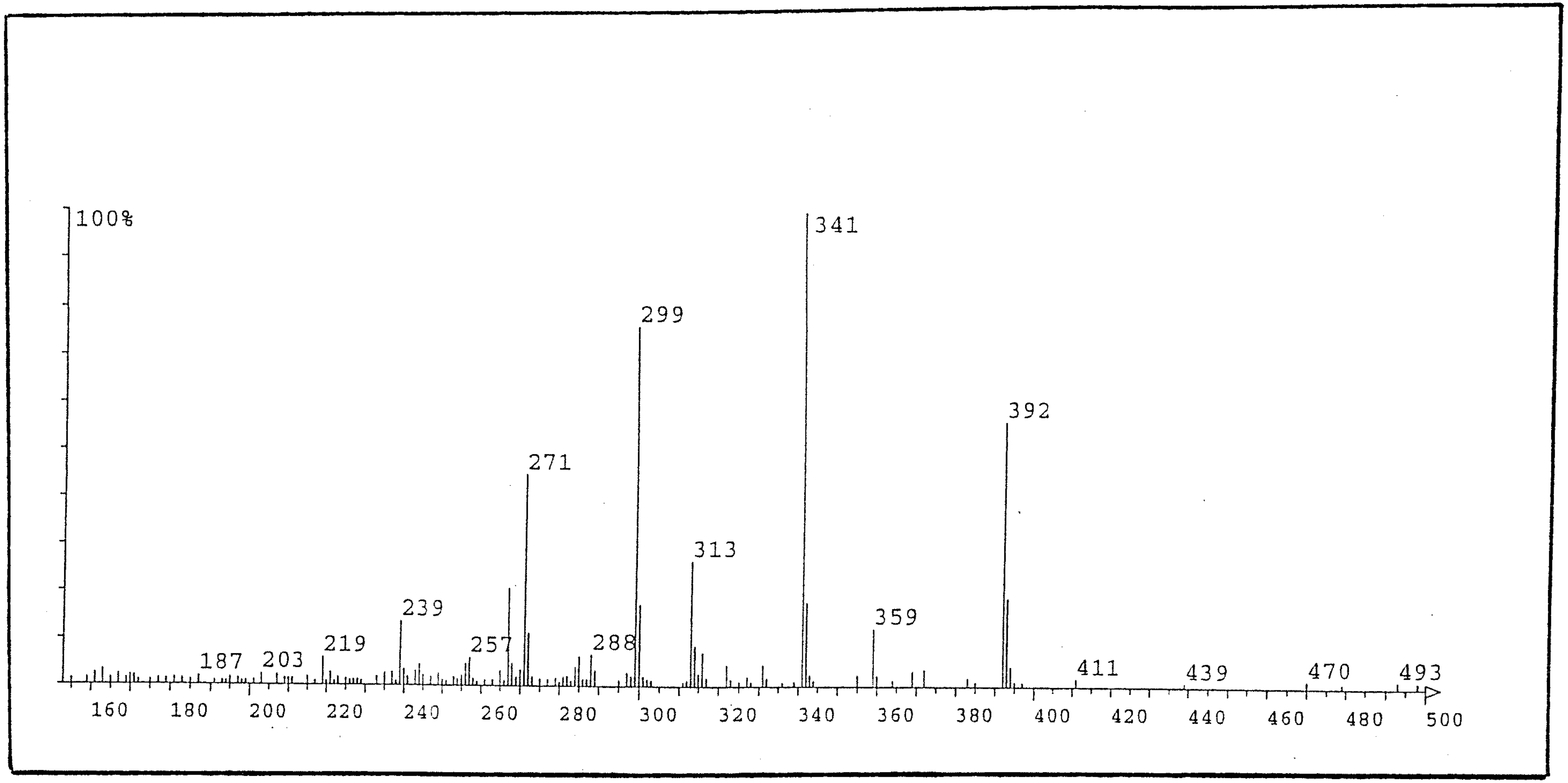


Fig III.6 Mass Spectrum of 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10 - imide

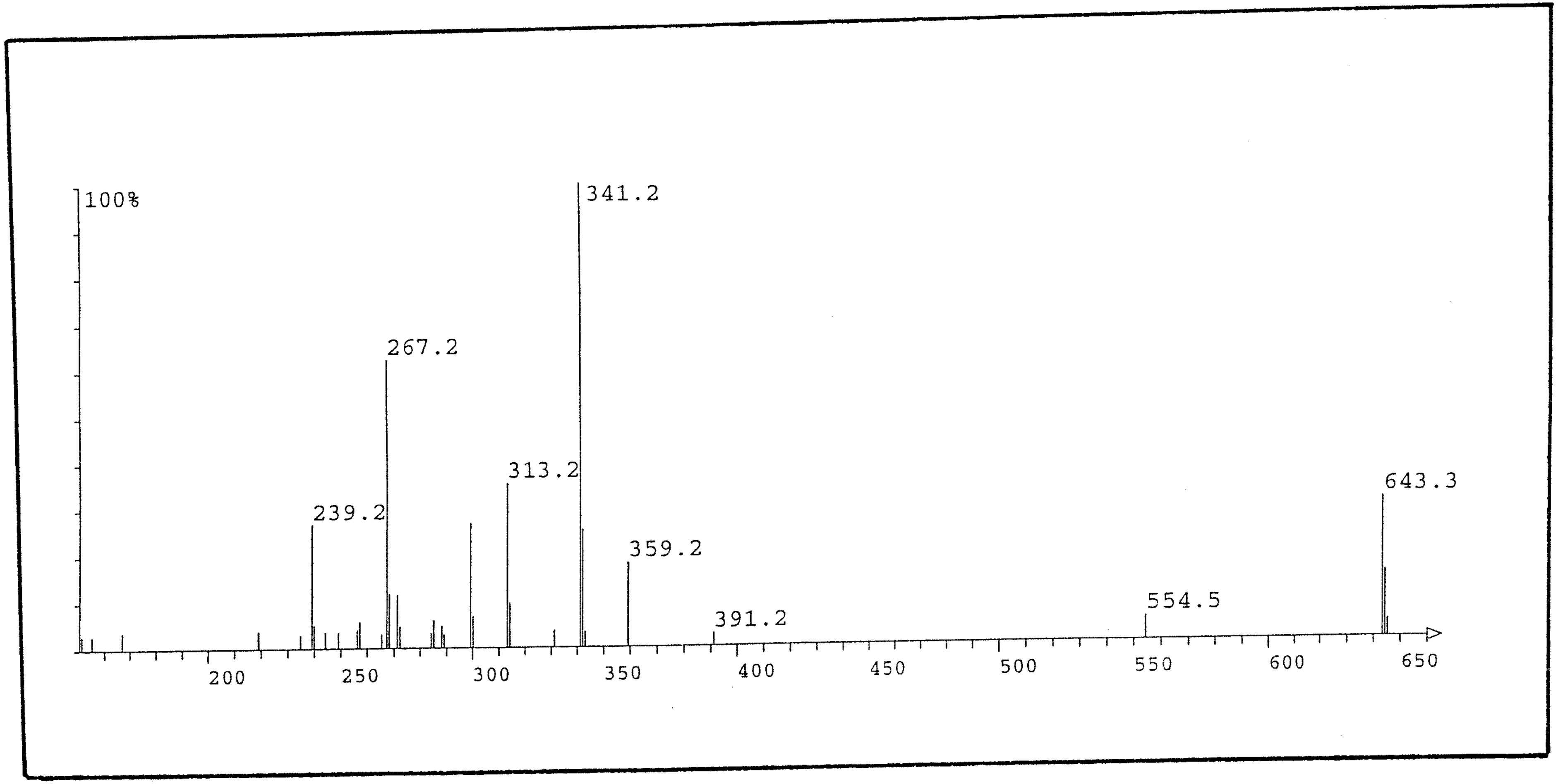


Fig III.7 Mass Spectrum of N-octadecyl-3,4,9,10-perylenetetra-carboxy diimide

IV. DATA and RESULTS

IV.1 Theoretical Aspects of Quantum Yield

A photochemical reaction requires activation by light. The quantitative relationship between the number of molecules which react or are formed and the number of photons absorbed in a unit time is given by the quantum ϕ, which may be defined for a given system as

$$\phi = \frac{\text{number of molecules undergoing a particular process}}{\text{number of quanta absorbed by the system}} \qquad (4.1)$$

The number of molecules reacting or formed per unit time is measured by any convenient analytical kinetic technique, and the number of photons absorbed per unit time is measured by an actinometer (a chemical or physical device capable of " counting" photons). Thus, if for every photon absorbed a molecule undergoes a certain photochemical process, the quantum yield for the process is unity [46]. If other processes compete with the one under consideration, the quantum yield will be less than unity. Free radical chain processes have quantum yields as high as several thousand. This arises from the fact that the photochemical reaction is the initiation step in a free radical chain process. The free radical chlorination of methane, for example, has a high quantum yield. The chain propagation steps occur many times before the chain terminates [38].

$Cl_2 + h\nu \rightarrow 2\ Cl\ .$ initiation

$Cl\ . + CH_4 \rightarrow CH_3\ . + HCl$

propagation

$CH_3\ . + Cl_2 \rightarrow CH_3Cl + Cl$

$CH_3\ . + Cl \rightarrow CH_3Cl$

$2CH_3\ . \rightarrow CH_3 - CH_3$ termination
$2Cl\ . \rightarrow Cl_2$

The quantum yields of photochemical reactions are important because they inform us of the paths by which the electronically excited molecule disposes of its energy.

The primary quantum yield ϕ of a photochemical process may be different from the overall measured quantum yield ϕ. For example, if a molecule undergoes a particular photochemical cleavage which is then reversed, the primary quantum yield may be high for dissociation even though the overall quantum yield for measured net reaction is nearly zero.

Finally, one must be careful to differentiate between the organic chemist's "yield" and the quantum yield. The former indicates the extent of side reactions and the ultimate efficiency of conversion of starting material into product, irrespective of the number of quanta absorbed [6].

IV.2 Calculation of Maximum Extinction Coefficients of Symmetrical and Unsymmetrical Perylene Bis (Dicarboximide) Derivatives at Different Wavelengths

As can be seen from the UV absorption spectra optical density (A) is plotted according to wavelength. By using the formula below we can calculate the maximum extinction coefficients at different wavelengths [8,7].

$$A = \log \frac{1}{T} \qquad (4.2)$$

$$\varepsilon_{max} = \frac{A}{c \, . \, l} \qquad (4.3)$$

A is absorbance, T is transmission, ε is maximum extinction coefficient ($L.mol^{-1}.cm^{-1}$) c is the concentration (M) and l is the pathlength of the cell (cm).

Maximum extinction coefficient calculation at different wavelengths.

ε_{max} of N,N′- Dioctadecyl-3,4,9,10-Perylene Bis-(Dicarboximide) :

M.W : 895.32216 g/mol

c : 1×10^{-5} M

l : 1 cm

$$A = \log \frac{1}{T}$$

$$\varepsilon_{max} = \frac{A}{c \cdot l}$$

$\boxed{\lambda = 458 \text{ nm}}$ A = 0.1858

$$\varepsilon_{max} = \frac{0.1858}{1 \times 10^{-5} \times 1} = \boxed{18580}$$

$\boxed{\lambda = 489 \text{ nm}}$ A = 0.5285

$$\varepsilon_{max} = \frac{0.5285}{1 \times 10^{-5} \times 1} = \boxed{52850}$$

$\boxed{\lambda = 525 \text{ nm}}$ A = 0.8610

$$\varepsilon_{max} = \frac{0.8610}{1 \times 10^{-5} \times 1} = \boxed{86100}$$

ε_{max} of Monopotassium Carboxylate of 3,4,9,10-perylenetetra-carboxylic acid monoanhydride:

M.W : 448.42956 g/mol

c : 1×10^{-5} M

l : 1 cm

$$A = \log \frac{1}{T}$$

$$\varepsilon_{max} = \frac{A}{c\,.\,l}$$

$\boxed{\lambda = \mathbf{452.50\ nm}}$ A = 0.114

$$\varepsilon_{max} = \frac{0.114}{1 \times 10^{-5} \times 1} = \boxed{11400}$$

$\boxed{\lambda = \mathbf{481.00\ nm}}$ A = 0.260

$$\varepsilon_{max} = \frac{0.260}{1 \times 10^{5} \times 1} = \boxed{26000}$$

$\boxed{\lambda = \mathbf{518.00\ nm}}$ A = 0.378

$$\varepsilon_{max} = \frac{0.378}{1 \times 10^{-5} \times 1} = \boxed{37800}$$

ε_{max} of 3,4,9,10 – Perylene tetra carboxylic - 3,4 – anhydride- 9,10 – imide:

M.W : 391.3392 g/mol

c : 1×10^{-5} M

l : 1 cm

$$A = \log \frac{1}{T}$$

$$\varepsilon_{max} = \frac{A}{c \, . \, l}$$

$\boxed{\lambda = 480.00 \text{ nm}}$ A = 1.396

$$\varepsilon_{max} = \frac{1.396}{1 \times 10^{-5} \times 1} = \boxed{139600}$$

$\boxed{\lambda = 517.00 \text{ nm}}$ A = 1.383

$$\varepsilon_{max} = \frac{1.383}{1 \times 10^{-5} \times 1} = \boxed{138300}$$

$\boxed{\lambda = 558.50 \text{ nm}}$ A = 0.546

$$\varepsilon_{max} = \frac{0.546}{1 \times 10^{-5} \times 1} = \boxed{54600}$$

ε_{max} of N – Octadecyl – 3,4,9,10 - Perylene tetracarboxy diimide :

M.W : 642.83832 g/mol

c : 1×10^{-5} M

l : 1 cm

$$A = \log \frac{1}{T}$$

$$\varepsilon_{max} = \frac{A}{c\,.\,l}$$

$\boxed{\lambda = 457.0 \text{ nm}}$ A = 0.577

$$\varepsilon_{max} = \frac{0.577}{1 \times 10^{-5} \times 1} = \boxed{57700}$$

$\boxed{\lambda = 484.0 \text{ nm}}$ A = 0.709

$$\varepsilon_{max} = \frac{0.709}{1 \times 10^{-5} \times 1} = \boxed{70900}$$

$\boxed{\lambda = 524.0 \text{ nm}}$ A = 0.793

$$\varepsilon_{max} = \frac{0.793}{1 \times 10^{-5} \times 1} = \boxed{79300}$$

$\boxed{\lambda = 604.00 \text{ nm}}$ A = 0.549

$$\varepsilon_{max} = \frac{0.549}{1 \times 10^{-5} \times 1} = \boxed{54900}$$

IV.3 Fluorescence Quantum Yield

IV.3.1 Method of Measurement of Fluorescene Quantum Yields

Two methods are commonly used. Primary methods include the use of scattering surface or solutions to calibrate the detector / excitation system absolutely, the use of actinometers in place of , and surrounding the sample, and the use of integrating spheres or calorimetric techniques. Secondary methods are much more preferred by most experimentalists. These involve the use of standard materials and rely on comparison of the integrated areas under the flourescene spectra of the standard materials and rely on comparison of the integrated areas under the fluorescence spectra of the standard and the unknown under identical conditions of incidence irradiance [12].

Method A

The use of scattering solutions. e.g., colloidal silica, or reflective surfaces such as $BaSO_4$ is recommended if this method is used. Refractive index corrections and wavelength sensitivity factors must be considered when using this approach. The use of actinometric methods is not recommended for dilute solutions, and therefore is of little value.

Method B

This is the method of choice for solution determinations. The formula used for calculation is as following

$$\phi_u = [(A_S S_u n^2) / (A_u S_s n_o^2)] \phi_S \qquad (4.4)$$

where the u subscript refers to the unknown and s to the standard and other symbols have the following meanings : ϕ is the quantum yield. **A** is the absorbance at the excitation wavelength, **S** the integrated emission area across the band, and is respectively, index of refraction of the solvent containing the unknown (n) and the standard (n_o) at the sodium D line and the temperature of the emission of the measurement. (The D line is used assuming dispersion among standard solvents to be small).

The need for refractive index corrections arises from two sources. As radiation passes from the solution into air (i.e. , from high to low index region), its intensity changes because of the refraction. Second, internal reflection within a cell can occur.

Suitable reference compounds for comparative determinations of quantum yields of fluorescence in solution are given in Table 4.1. For use of the compounds in Table 4.1, concentrations should be 10^{-5} M in the specified solvent. All solutions should be degassed, solvents should be of spectral grade and must be checked for spurious emission. Temperature should be maintained at 20 ± 1°C.

Region (nm)	Compound	Solvent	ϕ_f
270-300	Benzene	Cyclohexane	005 ± 0,02
300-380	Tryptophan	H_2O (pH 7.2)	0.14 ± 0,02
300-400	Naphthalene	Cyclohexane	0.23 ± 0.02
315-480	2-Aminopyridine	0.1N H_2SO_4	0.60 ± 0.05
360-480	Anthracene	Ethanol	0.27 ± 0.03
400-500	9,10-Diphenylanthracene	Cyclohexane	0.90 ± 0.02
400-600	Quinine bisulfate	1N H_2SO_4	0.546
600-650	Rhodamine 101	Ethanol	1.0 ± 0.02
600-650	Cresyl violet	Methanol	0.54 ± 0.03

Table 4.1 Recommended fluorescence quantum yield references in various emission ranges [19]

Far red and near IR standards are not known in the literature.

IV.3.2 Fluorescence Quantum Yields Calculations For The Synthesized Perylene Dyes :

The calculations are done for 485nm excitation wavelength by the method B. As a standard Rhodamine 101 is taken for the ϕ_f calculation of N,N′-DiOctadecyl-3,4,9,10-Perylene Bis-(Dicarboximide) and N,N′-DiDodecyl-3,4,9,10-Perylene Bis (Dicarboximide) is taken as a standard for ϕ_f calculation of 3,4,9,10-Perylene tetra carboxylic–3,4-anhydride-9,10-imide and for N–Octadecyl–3,4,9,10-Perylene tetracarboxy diimide. The integrated emission area is given from the emission spectra at 485 nm excitation wavelength. Calculation of fluorescence quantum yield (ϕ_f) is done with the formula 4.4. Excitation spectrums at different emission wavelength showed that most suitable wavelength is 485nm [12].

ϕ_f of N,N′-DiOctadecyl - 3,4,9,10 - Perylene Bis (Dicarboxamide) :

Rhodamine 101 is taken as standard. $\boxed{\phi_{Rh} = 1}$

$\boxed{\lambda = 485\text{nm}}$ $\quad l = 1$ cm $\quad \dfrac{A_{Rh}}{A_{per}} = 1$

$S_{Rh} = 1.3914 \times 10^8$ counts / (cm x sec)

$S_{per} = 1.1131 \times 10^8$ counts / (cm x sec)

$$\phi_{per} = \frac{A_{Rh}}{A_{per}} \times \frac{S_{per}}{S_{Rh}} \times \phi_{Rh}$$

$$\phi_{per} = 1 \times \frac{1.1131 \times 10^8}{1.3914 \times 10^8} \times 1 = 0.8$$

$\boxed{\phi_{per} = 0.80}$

ϕ_f of 3,4,9,10-Perylene Tetracarboxylic-3,4-Anhydride-9,10 - Imide :

N,N´-DiDodecyl-3,4,9,10 -Perylene Bis-(Dicarboximide) is taken as standard.

$$\boxed{\phi_{DOD} = 1}$$

$$\boxed{\lambda = 485\mathrm{nm}} \qquad l = 1\ \mathrm{cm} \qquad \frac{A_{DOD}}{A_{per}} = 1$$

$S_{DOD} = 2.2074 \times 10^{10}$ counts / (cmxsec)

$S_{per} = 1.8220 \times 10^{10}$ counts / (cmxsec)

$$\phi_{per} = \frac{A_{DOD}}{A_{per}} \times \frac{S_{per}}{S_{DOD}} \times \frac{(n_{per})^2}{(n_{DOD})^2} \times \phi_{DOD}$$

$$\phi_{per} = 1 \times \frac{1.8220 \times 10^{10}}{2.2074 \times 10^{10}} \times (1.4305 / 1.4422)^2 = 0.81$$

$$\boxed{\phi_{per} = 0.81}$$

For refractive index corrections [9]

	Chloroform	DMF
N_D:	1.4422	1.4305

ϕ_f of N – Octadecyl – 3,4,9,10 - Perylene Tetracarboxy Diimide :

N,N′-DiDodecyl - 3,4,9,10 - Perylene Bis (Dicarboxide) is taken as standard.

$\boxed{\phi_{DOD} = 1}$

$\boxed{\lambda = 485nm}$ l = 1 cm $\dfrac{A_{DOD}}{A_{per}} = 1$

$S_{DOD} = 3.3621 \times 10^8$ counts / (cmxsec)

$S_{per} = 9.1390 \times 10^8$ counts / (cmxsec)

$$\phi_{per} = \frac{A_{DOD}}{A_{per}} \times \frac{S_{per}}{S_{DOD}} \times \phi_{DOD}$$

$$\phi_{per} = 1 \times \frac{3.3621 \times 10^8}{9.1390 \times 10^8} \times 1 = 0.37$$

$\boxed{\phi_{per} = 0.37}$

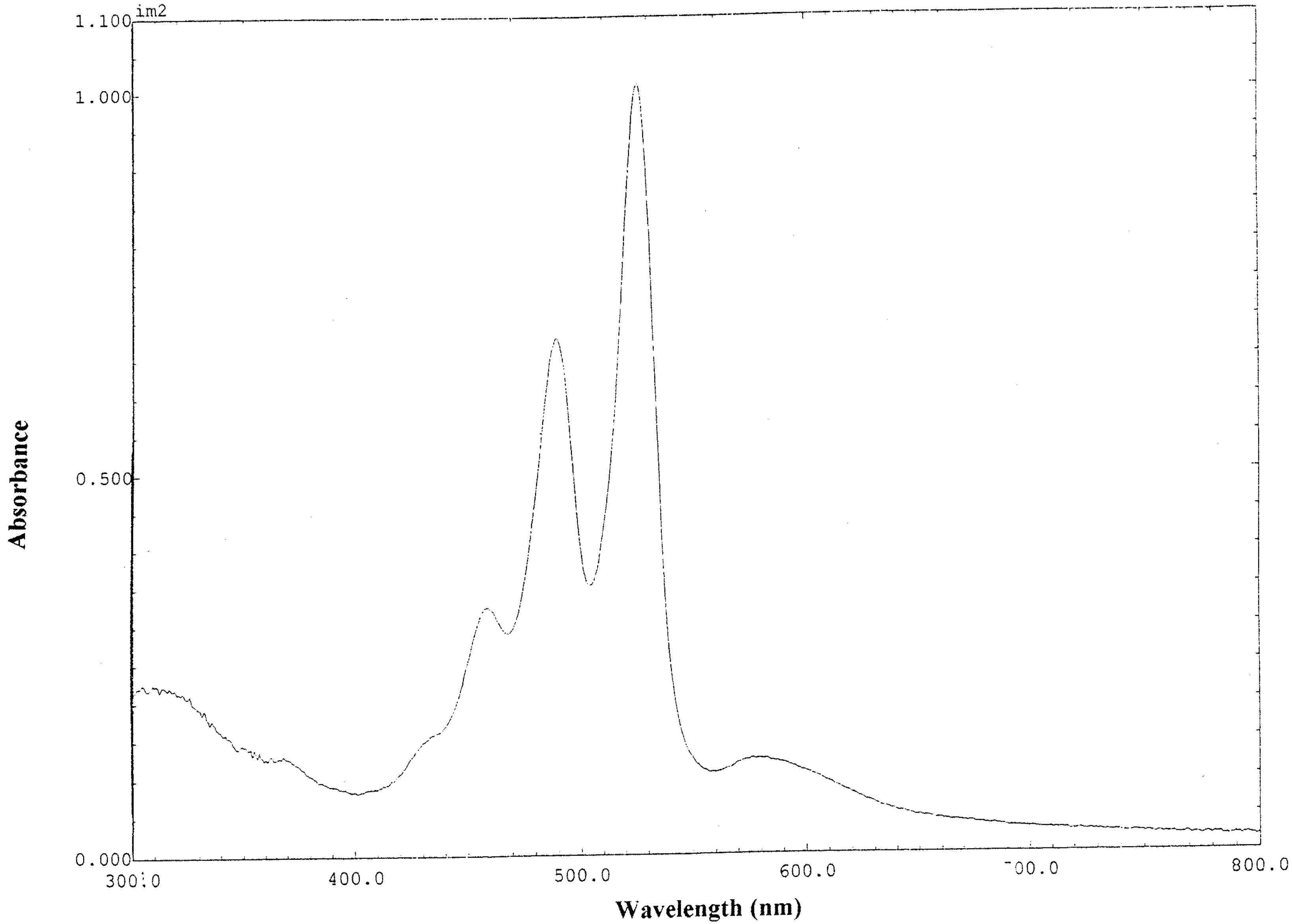


Fig IV.1 UV Spectrum of N,N′- dioctadecyl- 3,4,9,10 - perylene bis(dicarboximide), in chloroform

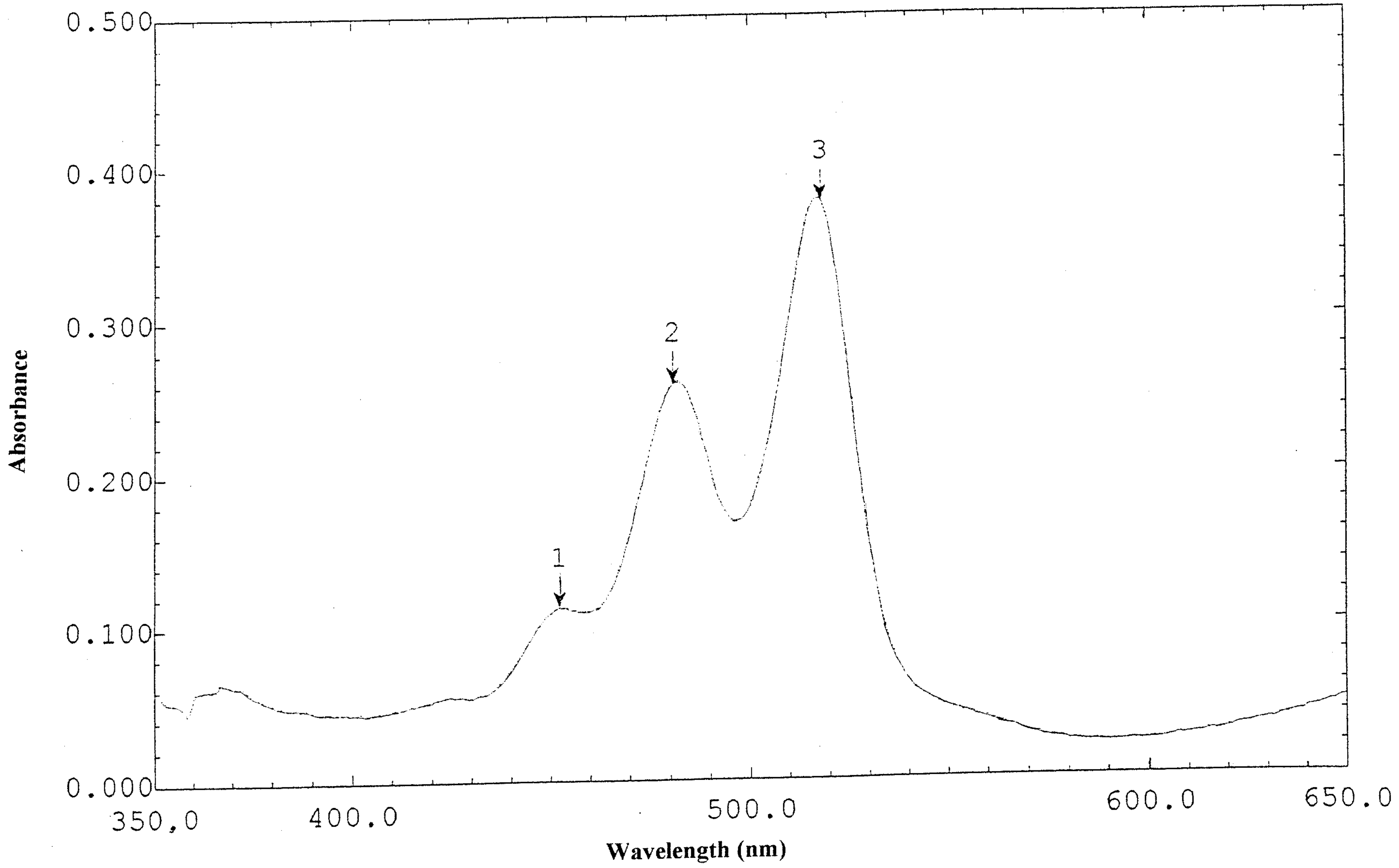


Fig IV.2 UV Spectrum of monopotassium carboxylate of 3,4,9,10-perylenetetra-carboxylic acid monoanhydride, in Chloroform

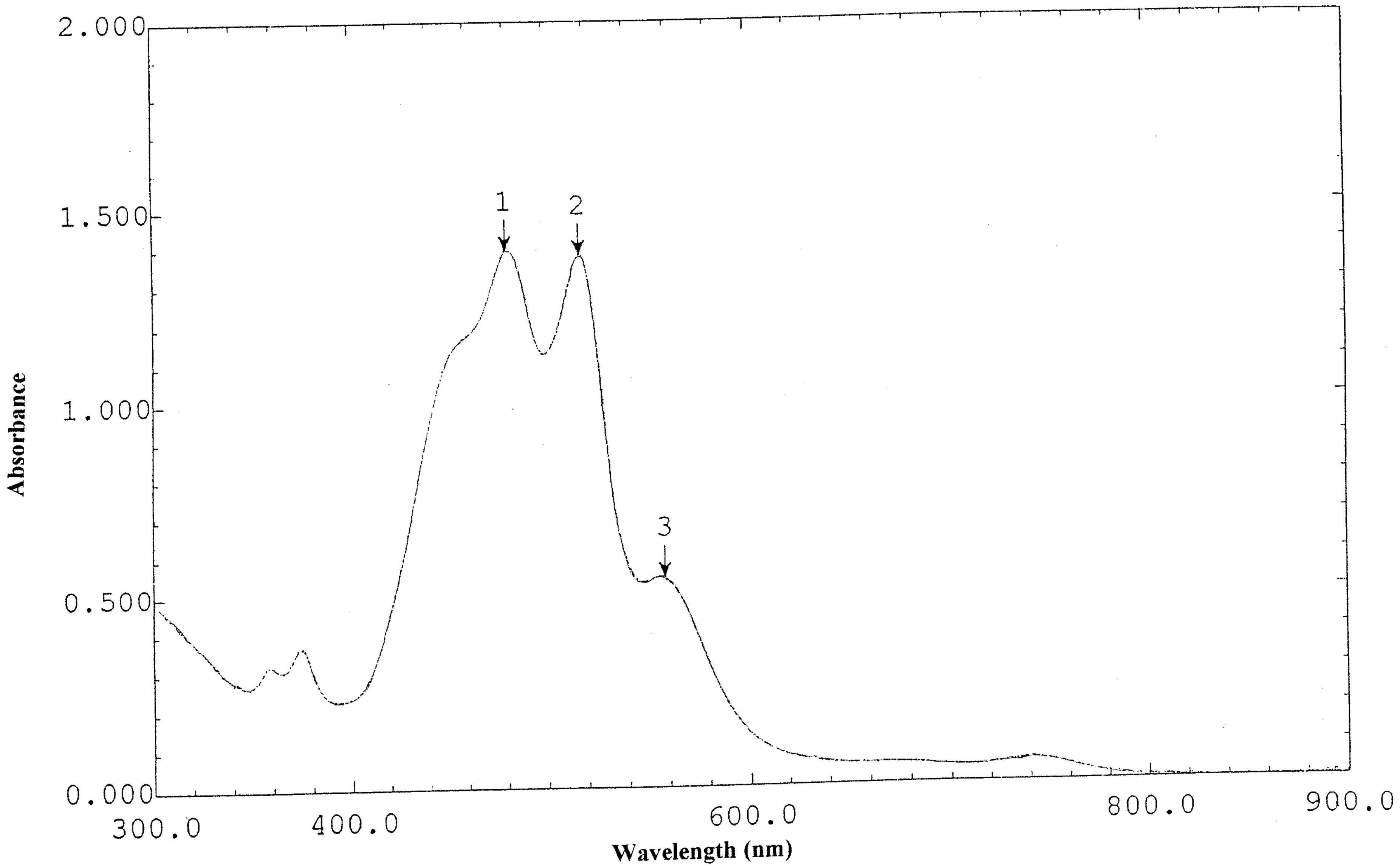


Fig IV.3 UV Spectrum of 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10 - imide, in Chloroform

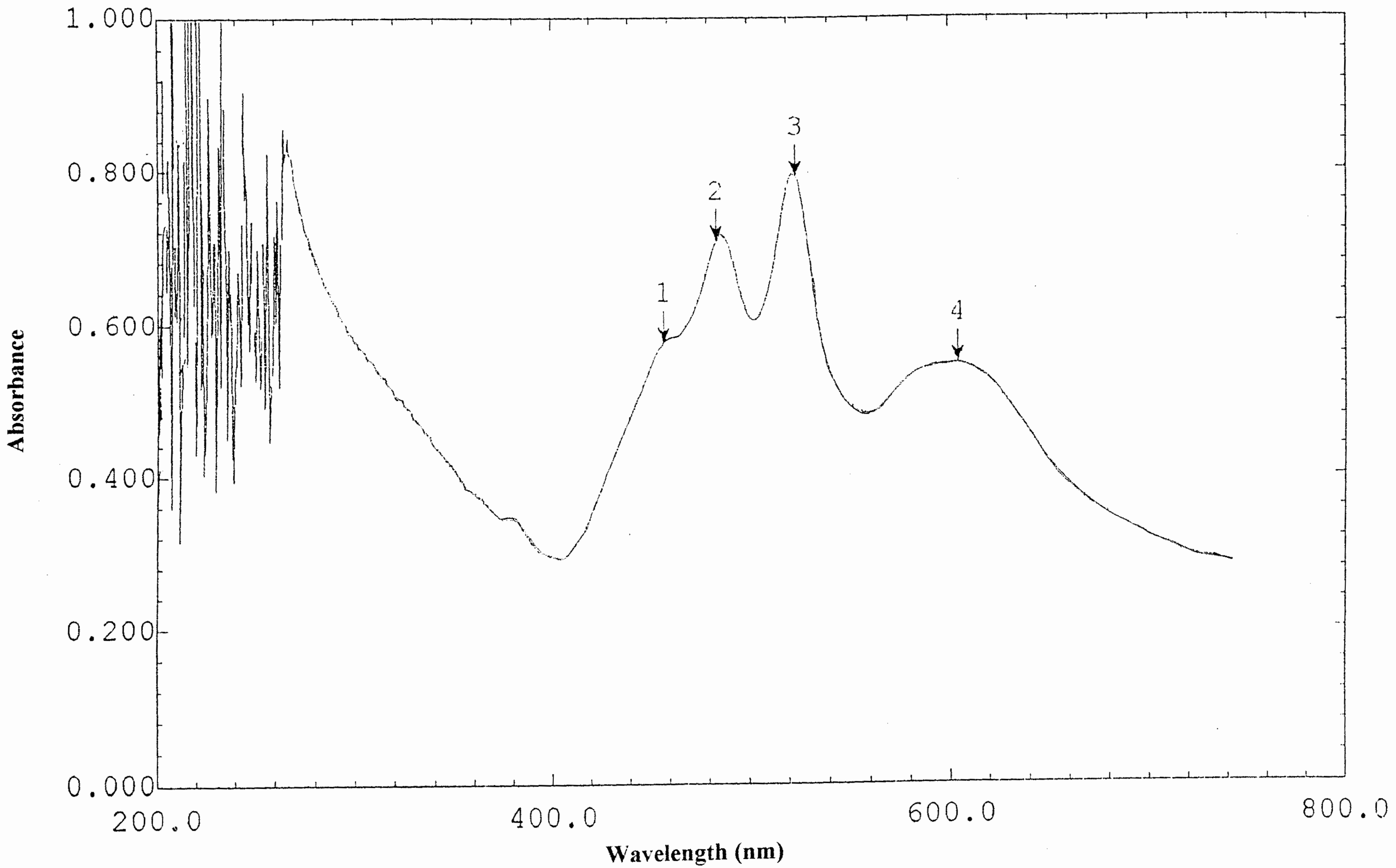


Fig IV.4 UV Spectrum of N–octadecyl– 3,4,9,10 - perylene tetracarboxy diimide , in Chloroform

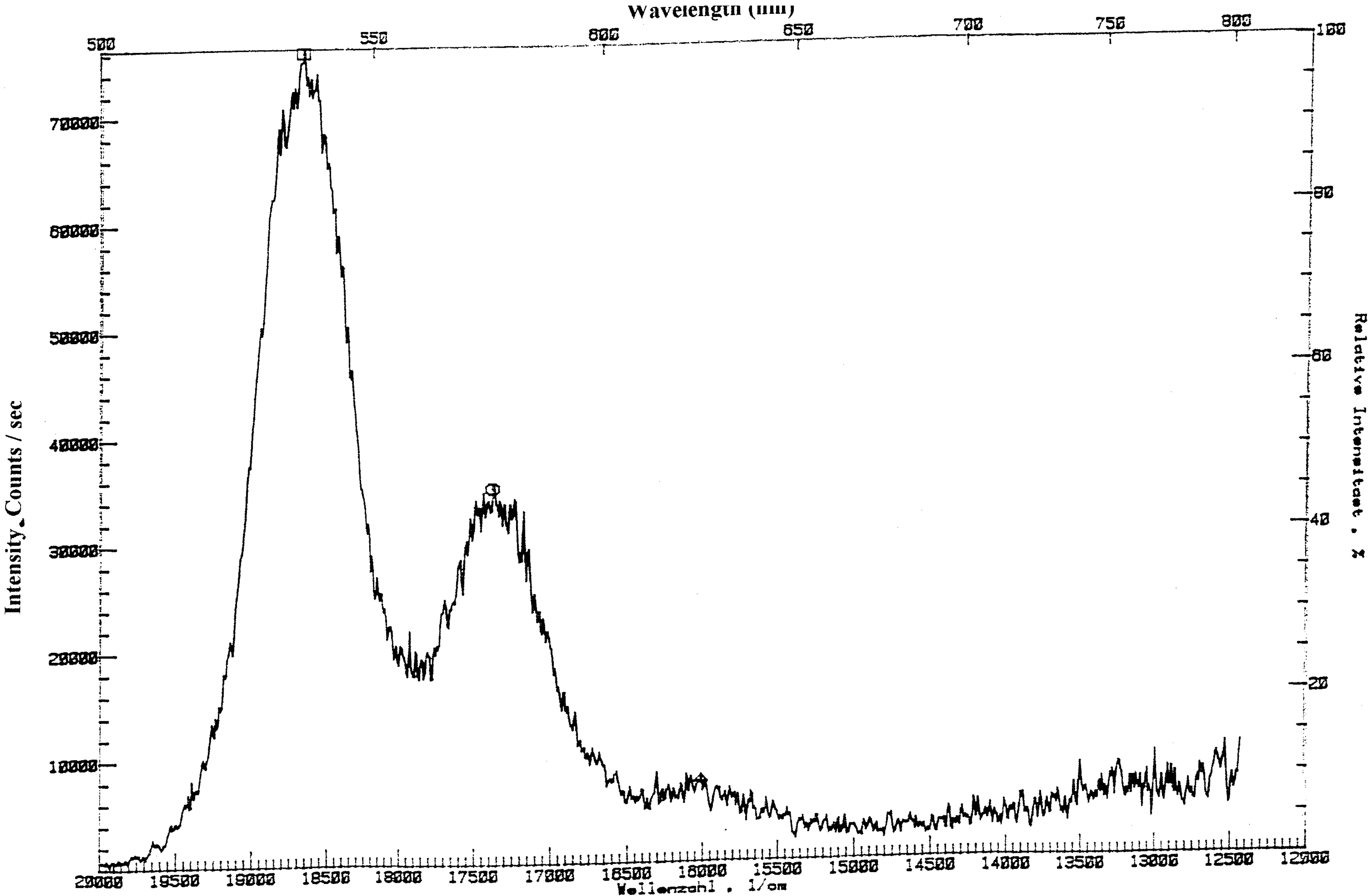


Fig IV.5 Emission Spectrum of N,N´- dioctadecyl- 3,4,9,10 - perylene bis(dicarboximide), in chloroform

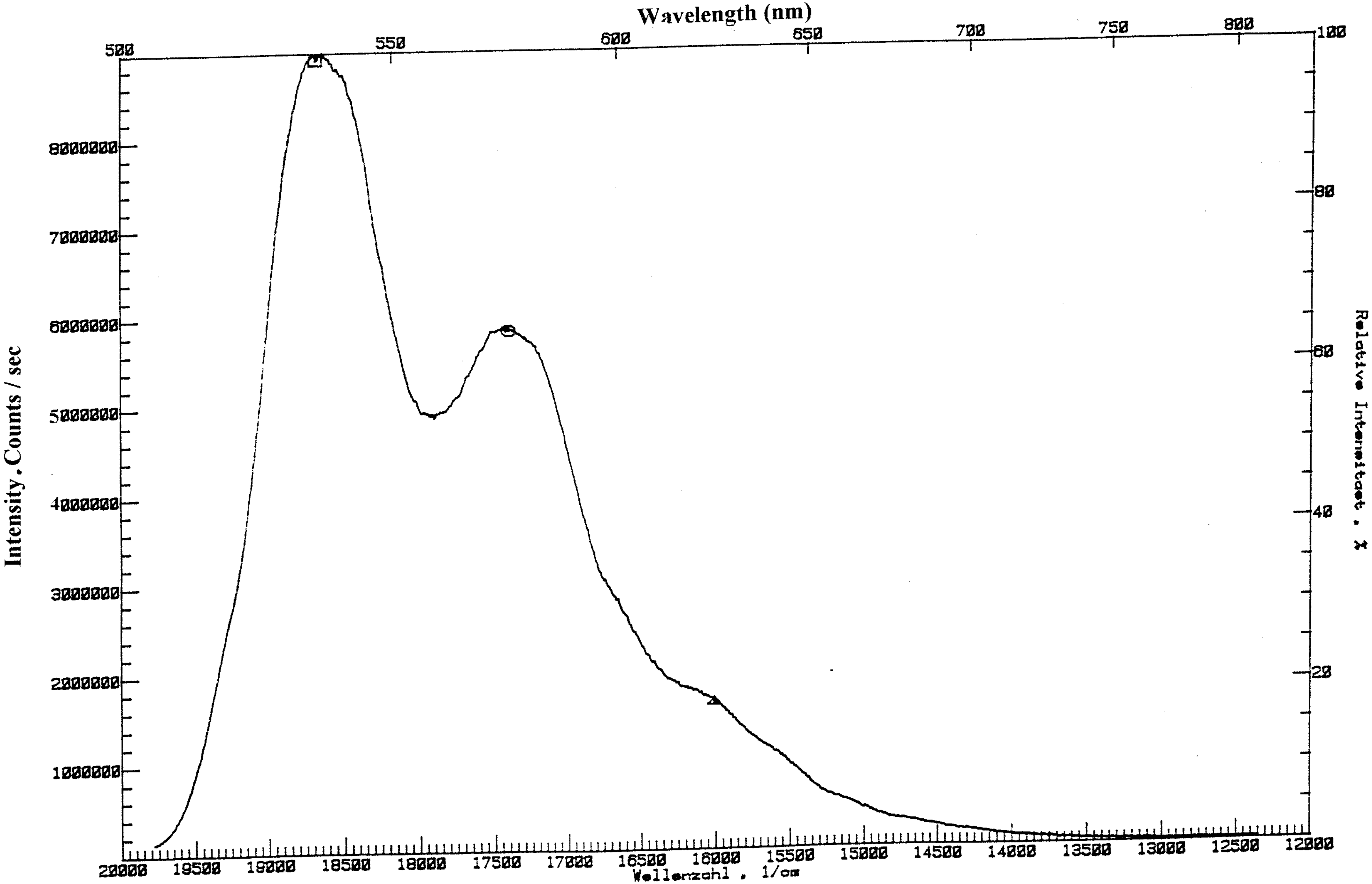


Fig IV.6 Emission Spectrum of 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10 - imide, in DMF

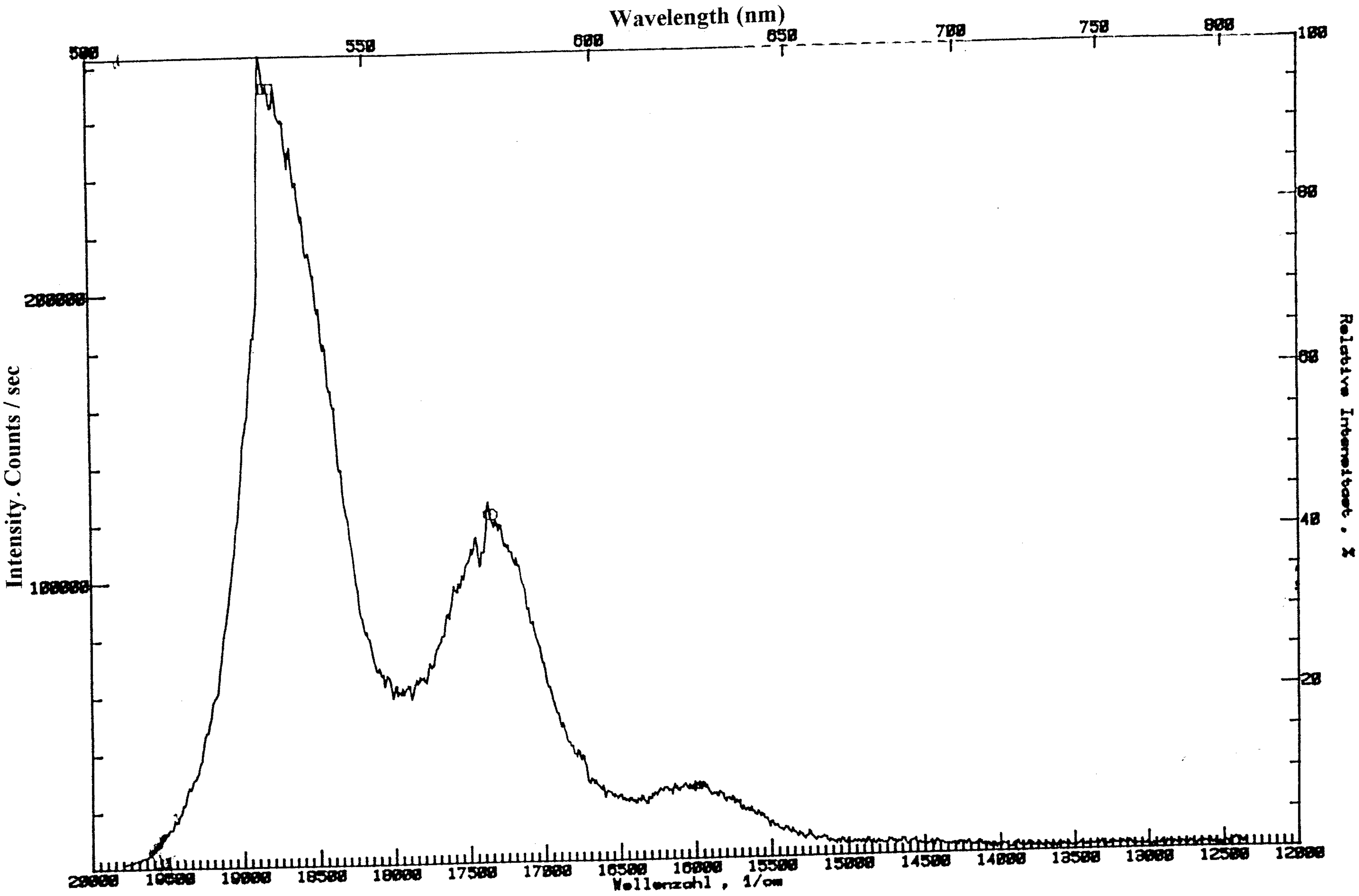


Fig IV.7 Emission Spectrum of N–octadecyl – 3,4,9,10 - perylene tetracarboxy diimide, in chloroform

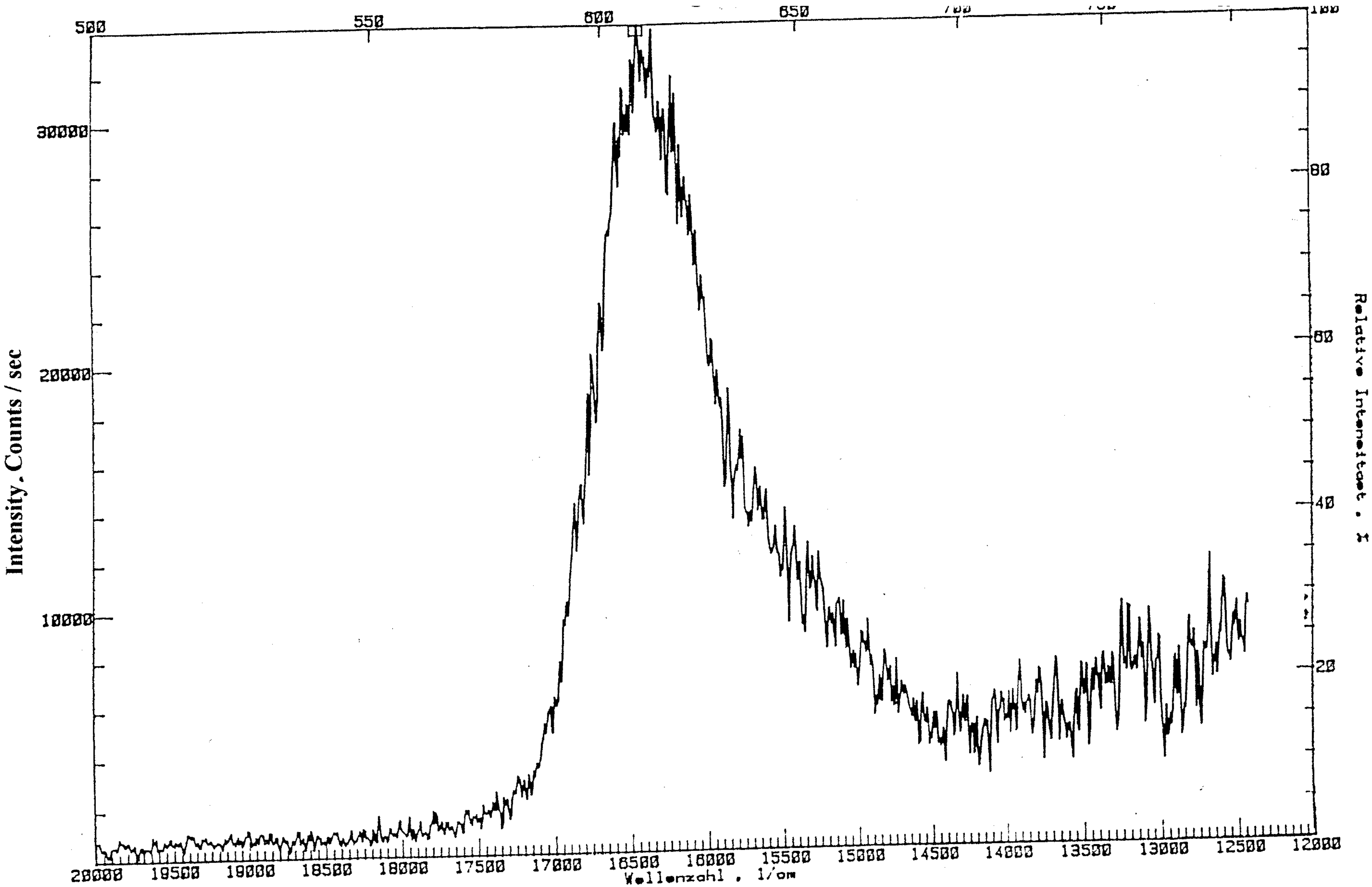


Fig IV.8 Emission Spectrum of RHD101 at 485 nm for N,N′- dioctadecyl- 3,4,9,10 - perylene bis(dicarboximide), in chloroform

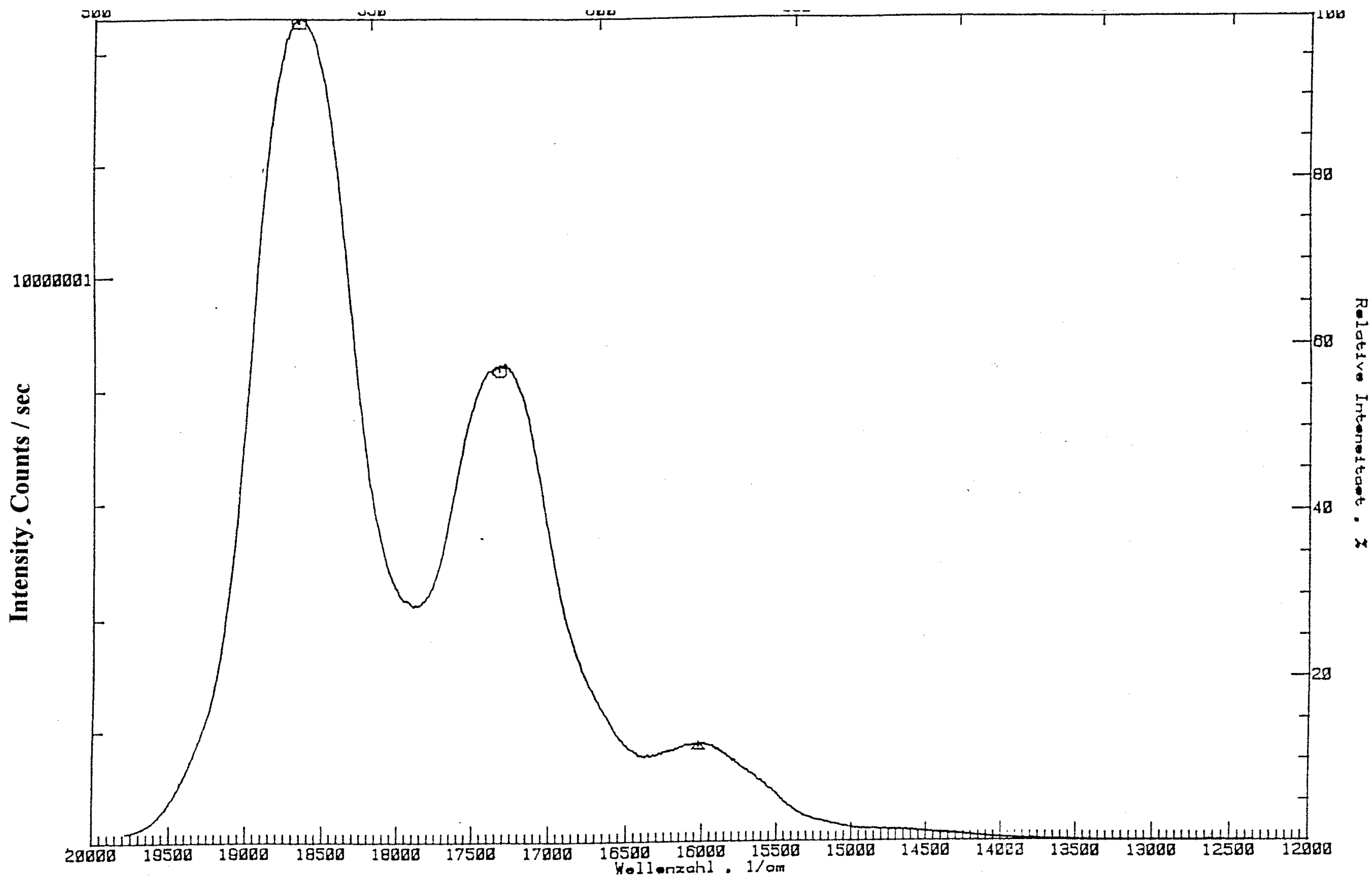


Fig IV.9 Emission Spectrum of DOD at 485 nm, for 3,4,9,10 - perylene tetracarboxylic-3,4-anhydride-9,10 - imide, in chloroform

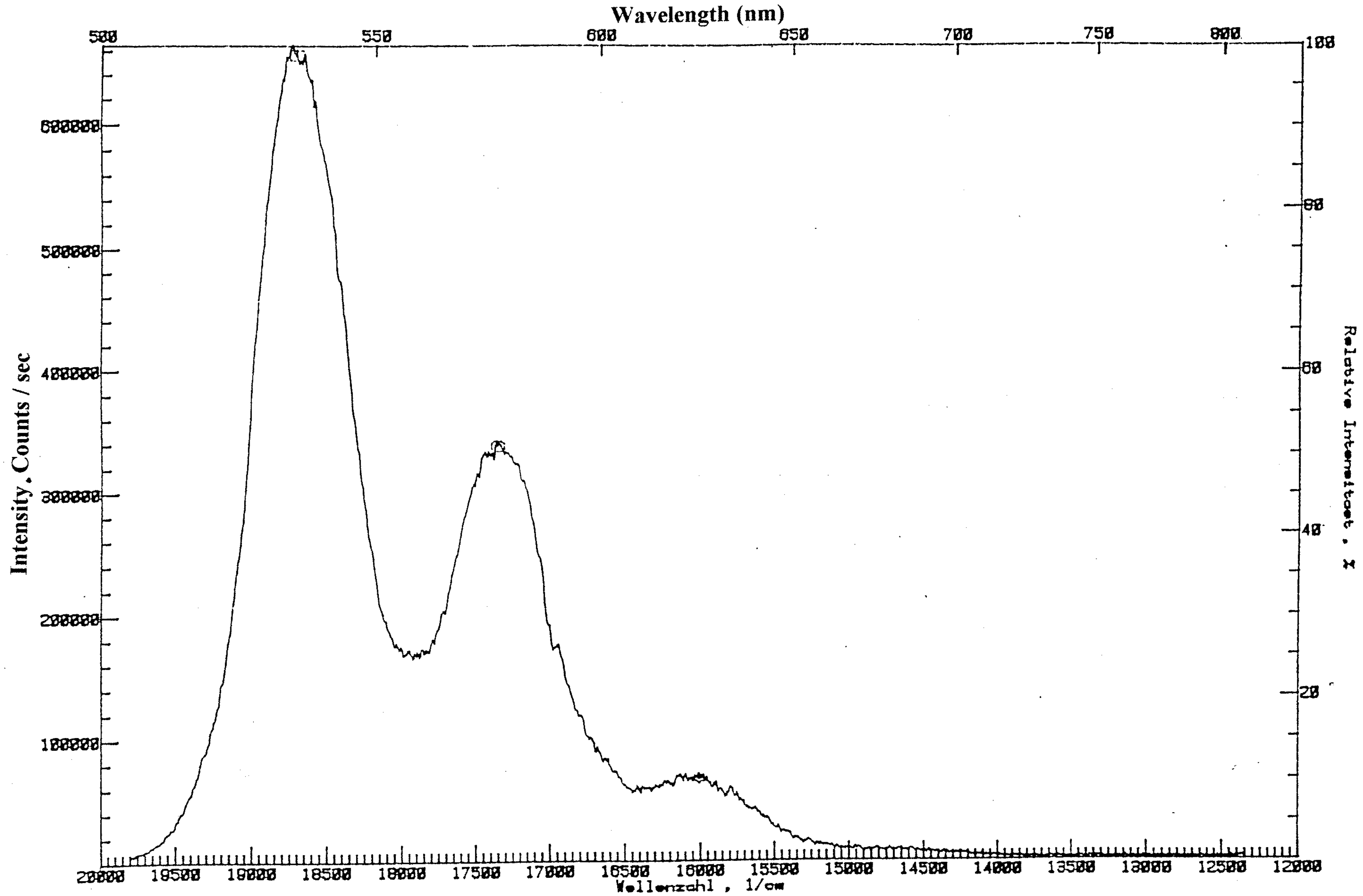


Fig IV.10 Emission Spectrum of DOD at 485 nm for N–octadecyl –3,4,9,10-Perylene tetracarboxy diimide, in chloroform

V. DISCUSSION

V.1 Synthesis; Analysis and IR Spectra

The insolubility of high molecular weight symmetrical or unsymmetrical perylene diimides have limited the methods of analysis of synthesized compounds. Proton and carbon NMR spectra could not be taken due to poor solubility in all organic solvents. Mass spectra of 3,4,9,10-perylene Tetracarboxylic-3,4-anhydride-9,10-imide, N-octadecyl-3,4,9,10-perylenetetracarboxy diimide and N,N'-dioctadecyl-3,4,9,10-perylenebis(dicarboximide) have been taken successfully.

Elemental analyses of 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10-imide, N-octadecyl-3,4,9,10-perylenetetracarboxy diimide and N,N'-dioctadecyl-3,4,9,10-perylenebis(dicarboximide) have shown clearly the purities. The structural characteristics are checked in solid state IR spectra displayed in Figures III.1, 2, 3, 4.

The IR spectra of unsymmetrical perylene diimide (N-octadecyl-3,4,9,10-perylenetetracarboxy diimide) (P3) showed the bands at 3450 cm^{-1} (N-H stretching), 2919 and 2849 cm^{-1} (aliphatic C-H stretching), 1695-1677 and 1656-1595 cm^{-1} (C=O of imide). Symmetrical perylene diimide (N,N'–dioctadecyl–3,4,9,10- perylenebis (dicarboximide))(P4) showed the bands at 2922.6 and 2848.4 cm^{-1} (aliphatic C-H stretching),1696.7-1656.4 and 1593.9-1578 cm^{-1} (C=O of imide). As can be seen the four carbonyl groups of imides are not identical. The fingerprints region of both the symmetrical and unsymmetrical diimide are very similar. The IR spectrum of monopotassium carboxylate of 3,4,9,10-perylenetetracarboxylic acid (P1) showed the bands at 3437 cm^{-1} (carboxylic OH stretching), 1770 cm^{-1} (C=O of anhydride), 1727 (C=O of acid), 1593 (C=O of carboxylic acid salt). The IR spectrum of 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10-imide(P2) showed the bands at 3449 cm^{-1} (N-H stretching), 1781-1757 cm^{-1} (C=O of anhydride), 1687-1595 cm^{-1} (C=O of imide).

The characteristic IR absorptions are given in Table V.1.

V.2 UV Spectra

The UV spectra of monopotassium carboxylate of 3,4,9,10-perylenetetracarboxylic acid, 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10-imide, N-octadecyl-3,4,9,10-perylenetetracarboxy diimide and N,N'-dioctadecyl-3,4,9,10-perylenebis(dicarboximide) are seen in figures IV.1, 2, 3, 4. The UV maximum absorption wavelength and extinction coefficients are given in the table V.2 for all the products.

The absorption intensities of three bands are declining in the order of λ_1- λ_2 - λ_3 as in agreement with literature data[29,30,31]. Highest absorption was observed for the 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10-imide, ε_{max}= 139600. As can be followed from the table the unsymmetrical perylene diimides showed little hypsochromic shift. Absorption bands at λ_4 is due to aggregation.

The UV absorption data of all products in chloroform are listed in Table V.2.

V.3 MS Spectra

The high purity and characteristic fragmentation are detected from the mass spectra. The mass spectrum of 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10-imide showed the molecular peak at 392 m/e (M+1). Base peak has been seen at 341 m/e.

On the MS spectrum of N-octadecyl-3,4,9,10-perylenetetracarboxy diimide molecular peak is shown at 643.3 m/e (M+1). Base peak was seen at 341.2 m/e. On the MS spectrum of N,N'-dioctadecyl-3,4,9,10-perylenebis(dicarboximide) molecular ion peak is at 895 m/e (M+1) as base peak. Good volatility of products enables us to have MS spectra to prove the structure.

The mass spectra of the products are seen in the figures III.5, 6, 7.

V.4 Analysis of Emission Spectra and Fluorescence Quantum Yields

The emission spectra of the product in chloroform are seen in figures IV. 5, 6, 7, 8, 9, 10. All the emission spectra are recorded at 485 nm excitation wavelength. All the three products, 3,4,9,10-perylene tetracarboxylic-3,4-anhydride-9,10-imide, N-octadecyl-3,4,9,10-perylenetetracarboxy diimide, N,N'-dioctadecyl-3,4,9,10-perylenebis(dicarboximide) show three bands between 535-625 nm from singlet excited states.The fluorescence emission wavelengths are shown in the Table V.3. Emission spectra, which correspond to fluorescence emission, are mirror images of absorption spectra as expected. No excimer emission was observed. Unsymmetrical perylene diimide (N-octadecyl-3,4,9,10-perylenetetracarboxy diimide) shows weak fluorescence in contrast with the symmetrical one (N,N'-dioctadecyl-3,4,9,10-perylenebis(dicarboximide)) due to the aggregation in unsymmetrical one. The aggregation cause to reduce the fluorescence.

V.5 Fluorescence Quantum Yields

Table V.4, lists the calculated fluorescence quantum yields of the products in chloroform at 485 nm excitation. Unsymmetrical perylene dye tends to aggregate even at a concentration of 1 x 10^{-6} mol L^{-1} (see figure IV.4). It is apparent that the fluorescence weakness, reduction in fluorescence quantum yield in unsymmetrical perylene diimide is all due to increasing tendency to aggregrate. No aggregation is detected for the symmetrical perylene dye. On the other hand the chain length of the N-terminal substituents are made sufficiently long for the exclusion of aggregation in homogeneous solutions (see the increasing quantum yields from unsymmetrical to symmetrical as a result of decreasing tendency to aggregrate). These results show a parallelism with the literature.

V.6 Conclusion

Overall our results indicate that in UV absorption wavelengths a hypsochromic shift exist in unsymmetrical perylene dye comparing to the symmetrical one. For both of them absorption bands due to aggregation are observed. The emission spectra of the symmetrical and unsymmetrical diimides are nearly same. But emission intensity of the unsymmetrical one is very weak comparing the other. Also the fluorescence quantum yield is reduced from 0.80 to 0.37. We know that these differences are coming from higher tendency to aggregation in unsymmetrical perylene diimides. We believe also that on our symmetrical perylene diimide the long chain length of the N-terminal excludes the aggregation in homogeneous solution.

The colors of symmetrical and unsymmetrical dyes are very close. Symmetrical is dark brown and the other is reddish brown. Both of them have similar melting point, higher than 500 °C.

It is of interest to search new unsymmetrical and symmetrical perylene diimides for practical applications. In future we will continue to search the properties of these dyes.

TABLE V.1 Characteristic IR absorptions of P4 and P3

Perylene	**C=O imide I**[a]	**C=O imide II**[a]
P3	1695-1677	1656-1595
P4	1696.7-1656.4	1593.9-1578

[a]Wavenumber, cm^{-1}

TABLE V.2 The UV absorption data of all products in chloroform.[a]

Perylene	λ_1[b]	ε_1[c]	λ_2[b]	ε_2[c]	λ_3[b]	ε_3[c]	λ_4[b]	ε_4[c]
P1	452.5	11400	481	26000	518	37800	-	-
P2	-	-	480	139600	517	138300	558.5	54600
P3	457	57700	484	70900	524	79300	604	54900
P4	458	18580	489	52850	525	86100	582	12500

[a] At concentration of 1×10^{-5} M [b] λ (nm) [c] ($M^{-1}cm^{-1}$)

TABLE V.3 Fluorescence emission wavelength (max.) of P2, P3 and P4, at excitation wavelength of 485 nm in chloroform

COMPOUND		λ_{max} **(nm)**	
P4	535.95	575.57	624.48
P2	535.02	574.50	624.68
P3	531.32	576.11	624.68

TABLE V.4 Fluorescence quantum yields of perylene diimides in chloroform[a]

Perylene	**Q_f**
P4	0.8
P2	0.81
P3	0.37

[a] At concentrations of $1x10^{-6}$ mol.L^{-1}

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