PHOTOFADING AND PHOTODECOMPOSITION STUDIES OF SOME INDIGOID DYES

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Graduate Studies
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IN

Partial Fulfilment of the Requirements
for the Degree of Master of Science in
Chemistry

by

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DEDICATION

I dedicate this work to Dr. Berehanu Abegaz and Dr. Fisseha H.Meskal; whose demands for perfection and staunch belief in hard work had been a constant reminder, that I could attain my goal, yet.

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ABSTRACT

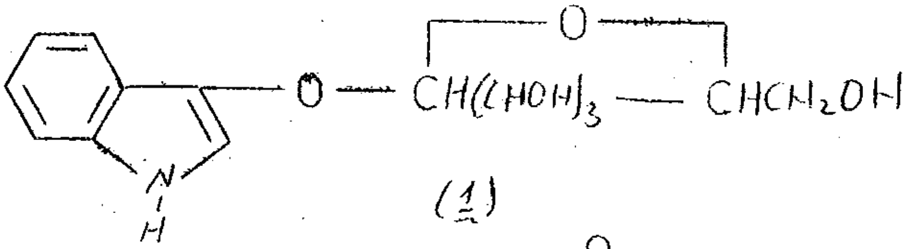
The light fastness of five indigoid dyes in benzene is examined. Of the five dyes; indigo showed the least resistance to fading and thioindigoscarlet, the highest. The photofading of indigo is examined under air, oxygen and nitrogen. The fading was fastest in oxygen and slowest under nitrogen. N, N'-diacetlindigo showed similar variation in fading under different atmospheres. The photofading of indigo and N,N'-diacetylindigo showed little variation when exposed as solutions in polar or non-polar solvents. Photodecomposition of indigo is affected to some extent when different solvents are used. The effect of oxygen is significant in outcompeting other photochemical reactions other than photooxidation to isatin. The absence of oxygen from the dye solution results in a multicomponent photoproduct. N,N'-diacetylindigo is not affected by change of solvent but is affected by change of atmosphere. In all cases it shows less numbers of fragmentation products. The photofading and photodecomposition studies show that as previously suspected; oxygen is a major factor for the fast photofading indigo and N,N'-diacetylindigo. The photodecomposition products of indigo were isolated as six components. One of these is identified as a -lactam by available means. Its formation from the photodecomposition of isatin is an additional evidence. One photodecomposition product from N,N'-diacetylindigo has also been assigned a most probable structure of an N-acetyl -lactam analogue of the one found from the photodecomposition of indigo.

I. INTRODUCTION

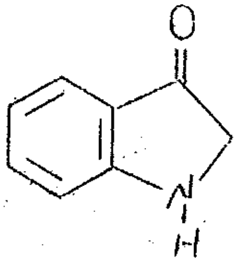
1. HISTORICAL

Indigo is one of the oldest dyes used by man. Many historical evidences, including a 5000 years old mummy cloth dyed with indigo, show that it was known and used in India, China and Egypt thousands of years ago[1]. The Romans are supposed to have learnt of it from Egypt and later introduced it to the rest of Europe[2]. Natural indigo is extracted from *Indigofera tinctoria*, of the leguminasea family; a shrub ranging from 4 to 6 feet in height and growing wild in South East Asia[3].

The dye is contained in indican(1), a glucoside of indoxyl (2) which is present to the extent of 0.2-0.8% in the leaves and stems of various plants such as *Isatis tinctoria*, *Indigofera tinctoria*[4].



(1)



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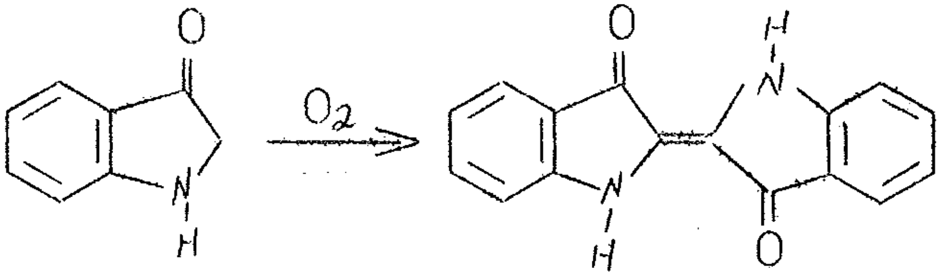
Recently, the species *Indigofera arrecta*, *Indigofera rochstetteria* and *Indigoferra articulata*; that contain indican have been found to be indigenous to Ethiopia[5]. The extract of the plant which does not contain indigo but *Indican*; can be hydrolysed by hydrochloric acid or by enzymes which occur in the crushed plant juice; is coverted into Indoxyl. The indoxyl on oxidation by atmospheric oxygen gives indigotin[6] (3).



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2. PHYSICAL AND CHEMICAL PROPERTIES

Indigo (also known as; Indigotin; 2,2'-bisindoleindigo;▽2,2'-indoleenindigo; CI Vat Blue 1:73,000) occurs as deep blue crystals with a copper -red metallic sheen. It melts at 390-392°C and sublimes without decomposition to form copper-red prisms. It is insoluble in water, alkalies or dilute acids. It is very slightly soluble in benzene, toluene, cyclohexane and other organic solvents. It has been established by X-ray crystallography that indigo exists as a Hydrogen bonded polymer in the solid state[7] as shown in fig 1. Recently, a new crystalline phase of indigo has been reported[8].

Reduction of indigo in the presence of alkali,with zinc dust, iron (II) hydroxide, dithionite, or by fermentation yields the pale-yellow leuco compound indigo white(4) or CI Reduced Vat Blue 1:73,001[9].

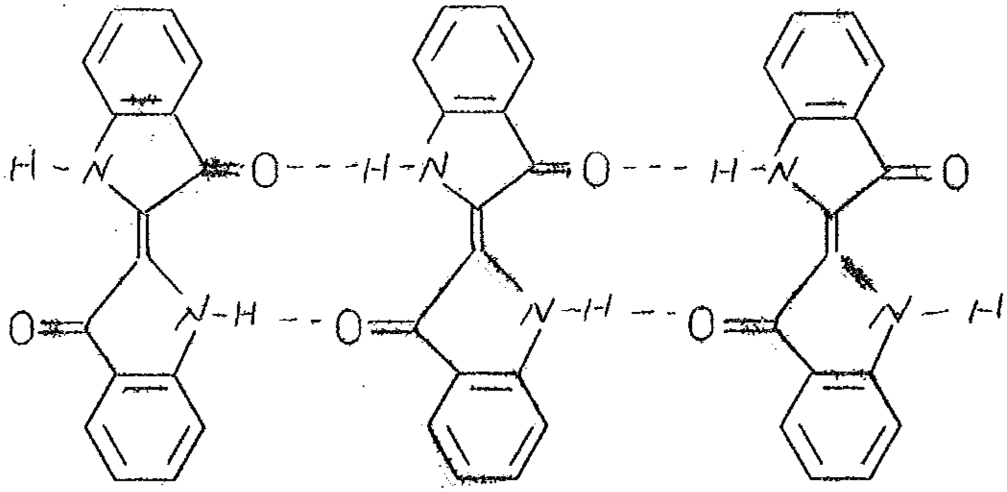
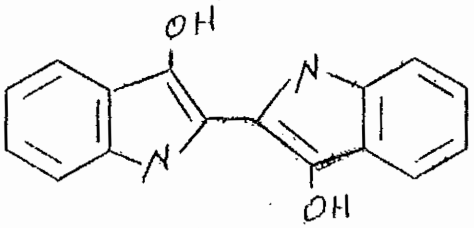


fig. 1. Hydrogen-bonded indigo polymer in the Solid State.

It can also be reduced by using sodium hydrosulfite in aqueous ammonia[10-12], forming the monosodium salt of the leuco form. Mild oxidation with lead (IV) oxide gives dehydroindigo (5)[13-15].



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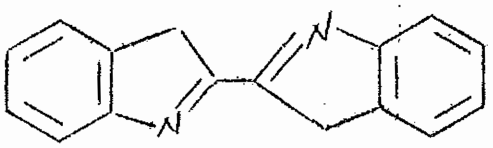

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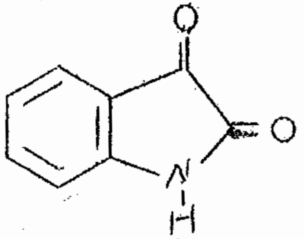
Oxidation with chromic acid, sulfuric or nitric acids produces isatin (6) in high yields [16-18].



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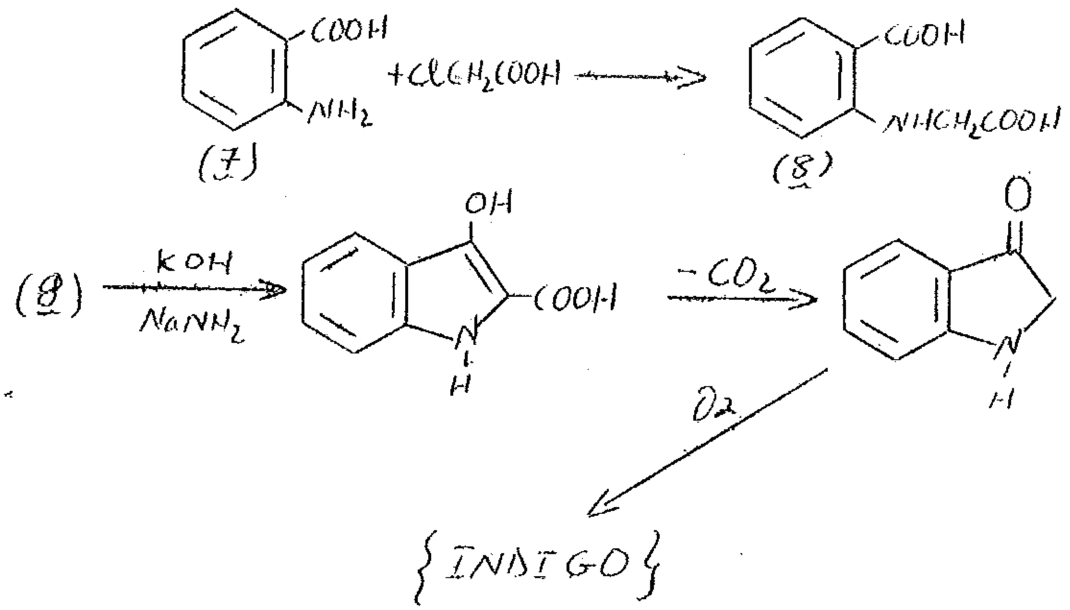
Depending on reaction conditions, sulfonation yields indigo-5-monosulfonic acid[19], indigo 5,5'-disulfonic acid[20], or indigo-5,5',7-trisufonic acid[21]. Nitration in acetic acid yields mono-,di-, and trinitoroindigo. The nitro groups occupy the 5,5' and 7 positions successively[22].

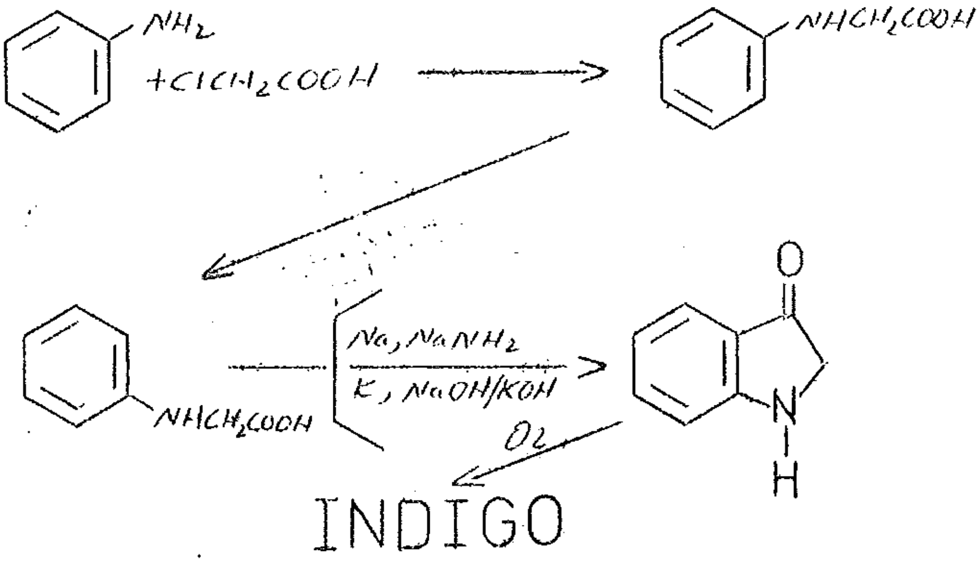
3. SYNTHESIS AND MANUFACTURE

Indigo was one of the first naturally occuring dyes whose structure was elucidated[23]. It was first syntesized by Baeyer in 1870[24] via the chlorination and reduction of isatin(6). This was followed in 1880 by his preparation of the dye from (0-nitrophenyl) -propionic acid and glucose in alkaline solution[25]. In 1883, Baeyer published the structural formula in the cis-form of the presently accepted trans structure of indigo which later was established through X-ray spectrography by Reis and Schneider in 1928[26].

Indigo is the first dye whose synthesis on a technical scale could be accomplished[27]. Heumann was responsible for the first commercial synthesis of indigo at BASF, Germany[28]. Anthranilic acid(7) is heated with chloroacetic acid and the product, phenylglycine 0-carboxylic acid(8) is heated with a mixture of potassium hydroxide and sodamide. Indoxylic acid(9) is thereby produced, and this decarboxylates into indoxyl which on exposure to atmospheric oxygen is oxidized to indigotin. This was essentially Heuman's synthetic route proposed in 1896.



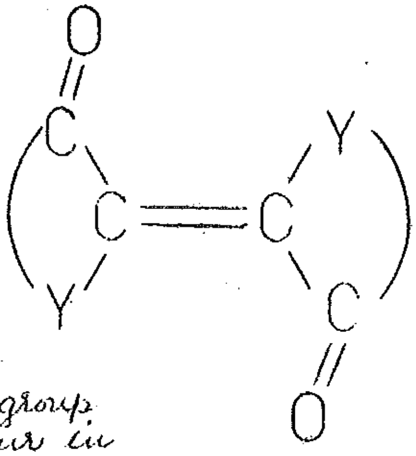
In 1901, Pfleger found that good yields of indoxyl could be obtained from the more readily available phenylglycine by using sodamide in alkali melt[29,30]. Aniline is first heated with chloroacetic acid, the product phenylglycine converted into a mixture of its sodium and potassium salts. These are fused with sodamide and potassium hydroxides at 220-240°C. Indoxyl which is thereby obtained is converted into indigo by atmospheric oxygen.



This process proved to be the most useful for the purpose of manufacture[31].

Other methods of manufacturing indigo were devised by Sandmeyer starting from diphenylthiourea[32] or isonitroacetanilide[33]. The problem of synthesis of indigo had remained a popular undertaking by many chemists. Upto the middle of 1960, well over thirty syntheses for indigo have been reported[34]. The syntheses attempts have not stopped yet as it can be shown that as late as 1980, several new syntheses and manufacturing process have been reported[35-38].

Indigoid dyes are characterized by the following general structure(fig 2).



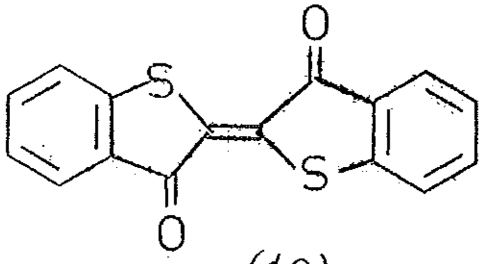
Y = imino group or sulfur in thioindigos.

fig. 2. General structure of indigoid dyes

Indigoid dyes are either symmetrical or unsymmetrical depending on whether the two portions of the molecule connected by the double bond are identical or different. Derivatives of indigo which have relevance in this work are briefly reviewed.

3.1 THIOINDIGO

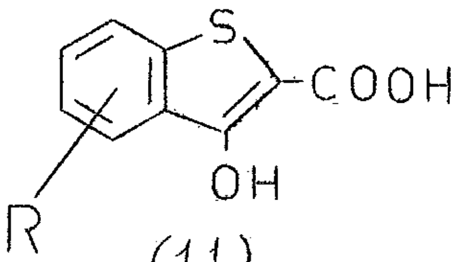
Thioindigo (2,2'-bisthionaphthene indigo)(10) was first synthesized in 1906 by Friedlaender[39] via the oxidation of O-acetylthiophenol. Unlike indigo, it is not found in nature[40]. It is a brown red crystal and has a metallic luster.



(10)

It is used principally for printing cellulosic materials and for dyeing wool; it has limited affinity for cotton. Pure thioindigo imparts a brilliant flourescent bluis red color to certain plastic materials.

Important intermediates for synthesis of thioindigo and its derivatives are the thioindoxy-2-carbonic acids (11) which are synthesized via phenylthioglycolic-0-carbonic acids (12)



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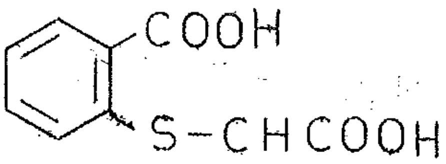

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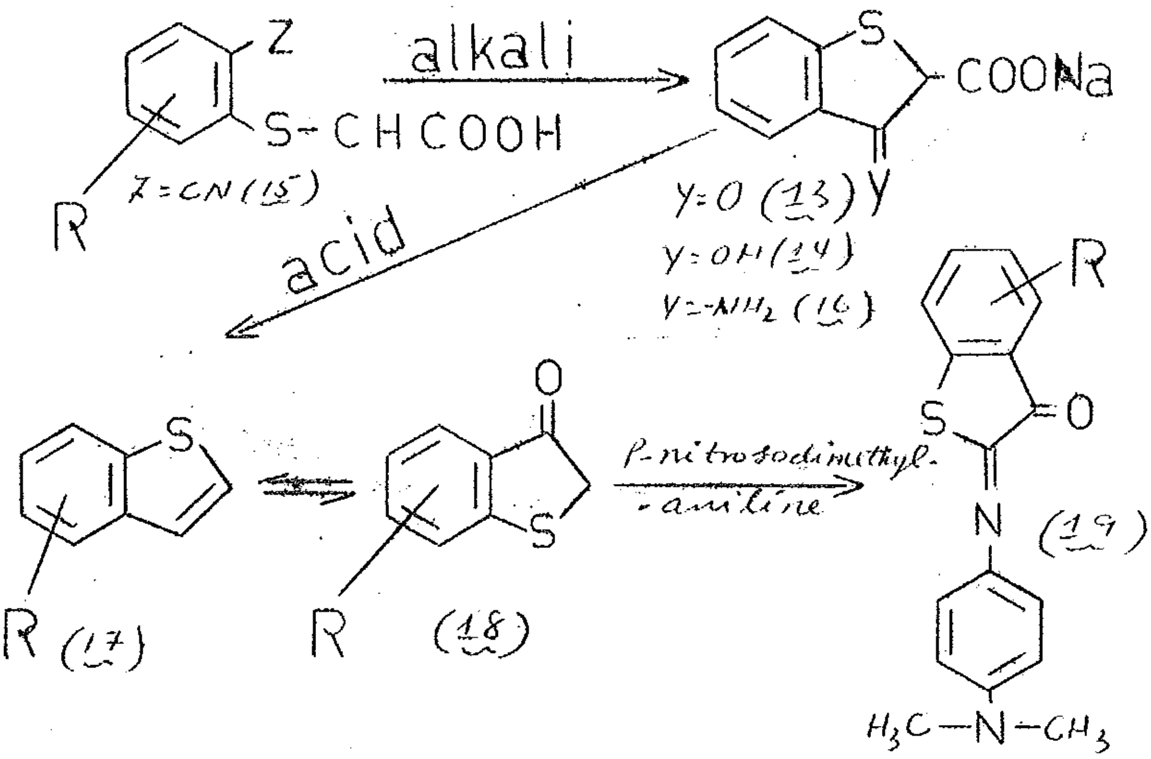
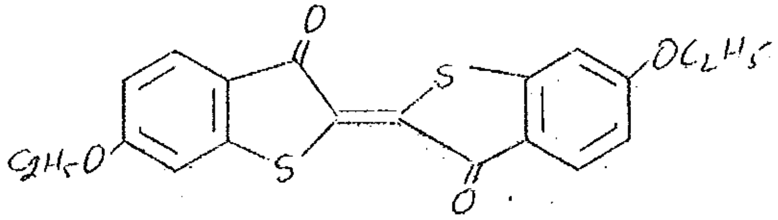
Treatment of (12) with alkali[41,42] yields the corresponding sodium salt of thioindoxyl-2 carbonic acid (13). Treatment of (14) with alkali gives (15)[43].



Alkaline Oxidation of (13)and(15) produces the symmetrical thioindigos. Mild oxidation in acid medium causes decarboxylation and gives the thioindoxyls (16,17) which condense with P-nitrosodimethylaniline to give the corresponding anils (18)[44]. Although cyclization of phenylthioglycolic acid does not occur in alkali, it proceeds readily with chlorousulfonic acid[45] or aluminum chloride[46]. The Herz reaction[47,48] provides a convenient synthesis for thiophenols, which are important precursors for thioindigos.

Due to the low reactivity of the thioindigo molecule, direct substitution is not used for commercial processes; therefore, substituents must be present in the starting material. Although thioindigo is stable to most reagents, very strong alkali cleaves it at high temperature, to give thiosalicylic acid and 3-hydroxy -1- thionaphthene -2- aldehyde. This cleavage is typical of all indigoids.[49-53] Oxidative cleavage with ozone gives thioisatin[54,55] and degredation with nitric acid gives O-sulfobenzoic acid[56,57].

3.2 6,6'-diethoxy Thioindigo (20)



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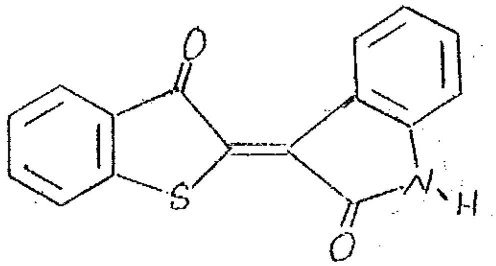
3.3 Thioindigoscarlet (21)



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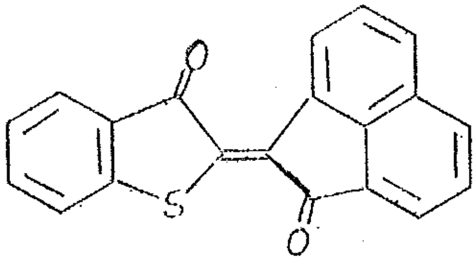
3:4 Acenaphthene Thioindigo(22)



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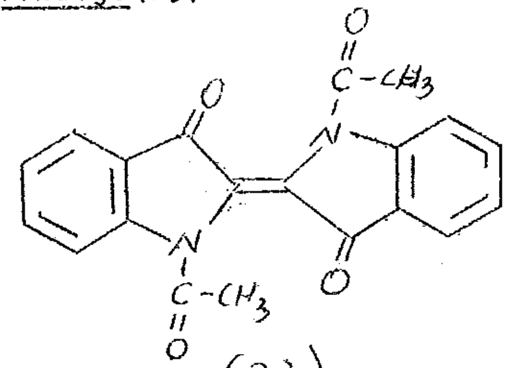
3:5. N,N'-diacetylindigo(23)



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II. COLOR THEORY

1. COLOR

When white light (750nm-400nm) falls on a substance, the light may be totally reflected or totally absorbed. In the former cases the substance appears white, in the later . black. If a certain portion of the light is absorbed and the rest reflected, the substance has the color of the reflected light. If only a single band is absorbed the substance absorbs all visible light except one band, which it reflects the substance will have the color of that reflected light. Thus a substance can appear green because it absorbs the pruple portion of the spectrum only; or because it absorbs all the visible spectrum except the green. The shades however will be different. No dye gives a pure shade.

Witt in 1876 was the first to show that color usually appeared in a compound when it contained a group with multiple bonds[58]. These groups were called chromophores, eg. NO_2, NO, etc.

of the appropriate energy is absorbed. The molecule is now in an excited state, and the wavelength of the photon absorbed depends on the energy difference between the excited and ground states, the smaller the difference, the longer being the wavelength.

Ethylene can be considered as an example. According to the V.B.Theory, ethylene can be regarded as the resonance hybride of (24) and (25)

$$CH_2{=}CH_2 \qquad\qquad \overset{+}{C}H_2-\overset{-}{C}H_2$$

(24) (25)

The ground state is represented predominantly by (24) and the excited state by (25). The energy difference between the two is quiet large and so the energy of the photon required to excited ethylene is very high; i.e. its wavelength is very short. This is the general situation for short molecules, and it has been shown that: (i) Resonance among charged structures lowers the energies of both ground and excited states; (ii) charged structures contribute more to the excited state than to the ground state.(iii) The larger number of electrons involved in resonance, the smaller is the energy difference. Hence, the more extended the conjugation in a molecule and the greater the contribution of

The molecular orbital theory treats conjugated compounds with a quantum-mechanical method called the free electron model[59]. The free electron model (FEM) presumes that electrons in compounds with conjugated π systems are mobile and little restricted to specific nuclei.

The FEM makes use of this property by assuming that there is a region in which the electron is free to move without this restriction, and that this region extends over the entire π-electron system. With this assumption, the problem of the behavious of the electrons becomes the well known problem of the particle or electron in a box[60].

In the region with the one-dimensional box, it is therefore assumed, that the potential energy is constant and equal to zero. The wave equation[61]

$$-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} = E\Psi(0 \leq x \leq a) \ldots\ldots\ldots (1.1)$$

the solution for which is

$$\psi n = \sqrt{2/a}\ \sin\left[\frac{\pi n}{a}\right] x \quad (0 \leq x \leq a) \ldots (1.2)$$

where a is the length of the potential well or box, x is the distance along the well and the quantum number n is a positive whole number, 1,2,3,.... To each ψn there corresponds an energy:

$$E_n = \frac{n^2h^2}{8ma^2} \qquad \ldots\ldots\ldots\ldots\ldots\,(1.3)$$

Where a and n have the meanings defined above, h is planck's constant and m is the mass of the electron.

In applying equation (1.3) the choice of a proper value for a, the length of the potential well is critical. In the case of conjugated polyene, the average distance between the carbon atoms is 1.39 Å.

The pi electrons of the system are distributed in such a way that each state is occupied by a maximum of two electrons. The transition from the highest occupied state (HOMO) to the lowest unoccupied state (LUMO) corresponds to the long wavelength absorption band. The model predicts a linear dependence of the wavelength of the long wavelength absorption band on the number of pi electrons.

$$\lambda = k(N+1) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\,(1.4)$$

N= number of π electrons

k= constant.

An analogous dependence is predicted by a simple Huckel molecular orbital model (HMO).The corresponding energy level diagram is shown in fig (3).

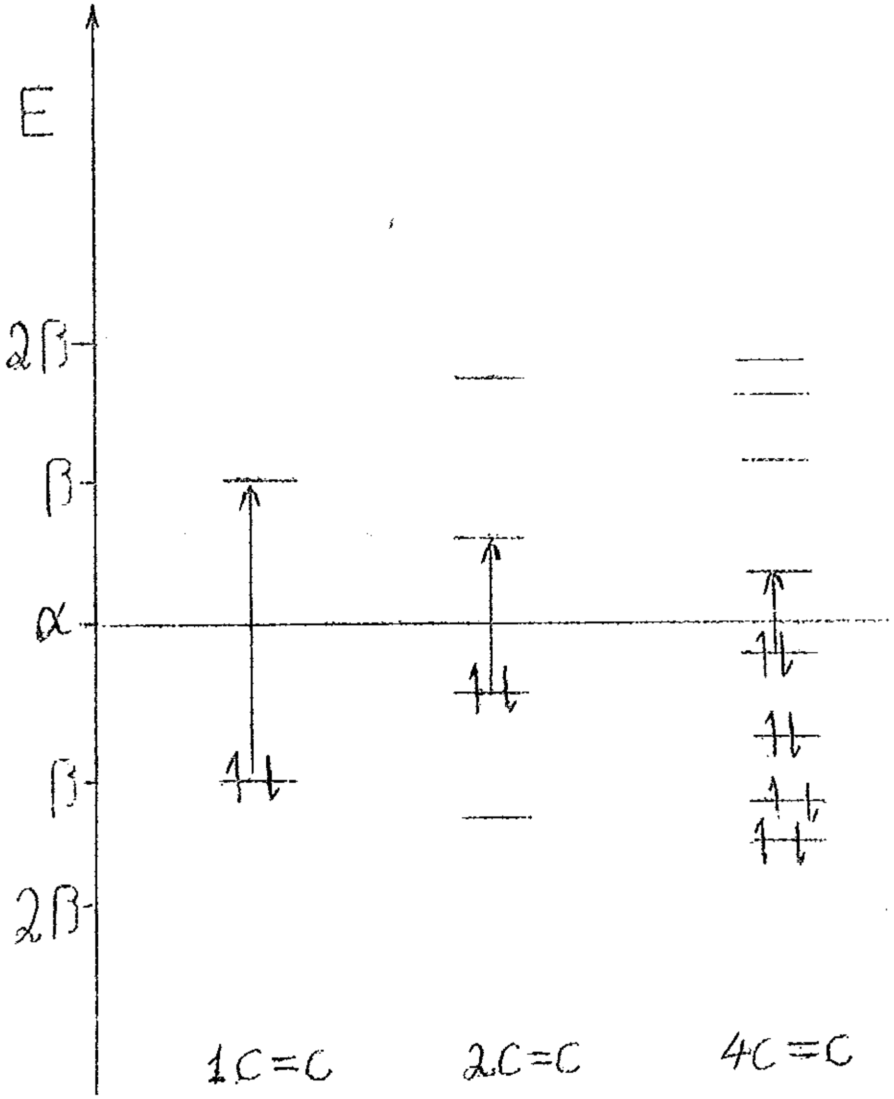


fig. 4. Energy level diagramme according to a simple Hückel MO orbital

The position of the long wavelength absorption band of a number of linear polyenes is listed in table(3). A plot of the wavelength against the number of $\bar{\mu}$ electrons $(\lambda = f(N)$ does not show a linear dependance but a square one.

$$\lambda = a\sqrt{N} + b\ldots\ldots\ldots\ldots\ldots\ldots(1.5)$$

a,b = constants.

However, if one considers the polymethine dyes,

$$R_2\overset{+}{N} = CH\ (CH=CH)_2-\bar{N}R_2$$

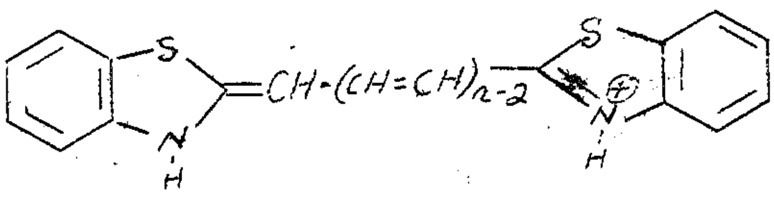
The agreement between the observed data and the calculated value is very satisfactory (table 4). The disagreement in the case of polyynes between the observed and calculated value can be explained in terms of incomplete delocalization of the π electrons. A distortion in this delocalization should give rise to a hypsochromic or blue shift. Another problem is when the actual color of the compound occurs at a longer wavelength than predicted by assuming maximum delocalization. In such cases it is necessary to take into account the fact that, in general, the electronic excitation energy Δ i-k is not equal to the difference between the orbital evergies, Ek-Ei. Thus

$$E_{i-k} = E_k - I_{ik}\ldots\ldots\ldots\ldots(1.6)$$

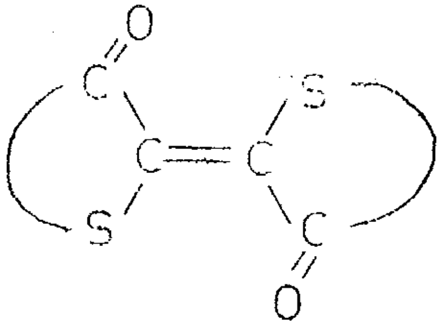
n in $H(CH=CH)_nH$	λmax(nm)		color
	calculated from Eq. 1.3	Observed	
1	204	162	Colorless
2	328	217	Colorless
3	454	258	Colorless
4	586	296	Colorless
5	706	335	Pale yellow
8	870	415	orange
(β-Carotene) 11	1469	470	red
15	1978	547	violet

Table 3. Long wavelength absorption of Some linear polyenes.

Table 4. Calculated and observed wave lengths of some polymethine dyes.

COMPOUND	Wavelength in nm			
	n = 2	3	4	5
	3C	5C	7C	9C
$R_2\overset{\ominus}{N}-(CH=CH)_{n-1}CH=\overset{\oplus}{N}R_2$	313	416	519	625
$\overset{\ominus}{O}-(CH=CH)_{n-1}CH=O$	268	368	455	548
	422	560	648	765
Calculated from Eq. 1.3	328	454	580	706

observed a long wavelength absorption. On the otherhand the charge-transfer transition from S to CO seems plansible. This is further supported by the drastic hypsochromic shift compound (27) exhibted when the conjugation between the S and CO is interrupted. A similar effect occurs if the structural unit (



Is forced to be no longer planar compound (27) the hypsochromic Shift for the compounds (29) & (28) (.) can be explained by a decrease of the electron donor strength (and thereby the extent of charge transfer) through the special arrangement of the NH group. Thus it can be concluded that the chromophoric part of the indigo dyes are the planar, cross-conjugated donor-acceptor groups.

2. LIGHT-FASTNESS

When a dye is exposed to light of frequency that it absorbs, it undergoes changes in two ways; phototropism and fading. Phototropism is a reversible change in shade shown by some dyes on short exposure to light. The original shade is restored however, on storage of the fabric or the dye it self in the dark. The exact nature of such a change is not completely known but it is assume to involve a trans-cis rearrangement[62].

Fading however is an irreversible change induced by light. On absorption of light the dye molecule undergoes electronic transition and is converted into an excited state involving either a singlet or a triplet state. There is ample evidence to show that the excited state in its brief existence ($\leqslant 10^{-8}$ sec) is much more reactive than one in the ground state and reacts either with the substrate and/or environmental elements such as oxygen or moisture in the atmosphere[64].

During the early development of the dye industry, the relation between the structures and fastness of dyes was not well understood. Therefore a large number of dyes were synthesized, and only a few with satisfactory fastness were marketed as commercial dyes inspite of their difficiencies in one or two properties. Later however, attention has been given to this relationship and a systematic investigation of the same is being carried out in numerous industrial and technological laboratories of the world.

The light-fastness of indigoid dyes on fabrics had been studied by a number of researchers in the first half of this century. Haller in 1923 investigated the effect of metallic hydroxides on the fastness of fabrics dyed with indigo[65]. Pieces of indigo dyed cotton fabric were printed with a thickened solution of various metallic salts passed though sodium hydroxide solution, washed and dried. Portions of the printed and unprinted material were exposed to direct sunlight during July and August. Haller found out that resistance to fading increased by the presence of the precipitated hydroxides of Fe,Mn,Ni,Co,Cu in that order. Apple and

Smith (1928) studied the effect of filtering direct sunlight with various types of glass and quartz on the fading characterstics of twenty indigoid dyes[66]. Noguchi and Ishikawa have reported that the color of cotton cloth dyed with natural indigo was found to be more fast against repeated washing and sunlight than that dyed with synthethic indigo[67]. A reason for the difference was considered to be the presence of some impurities in the natural indigo which prevented the sublimation of the dye molecule itself to the surface of the cloth.

III. A REVIEW OF THE PHOTOCHEMISTRY OF INDIGOID DYES

1. THEORY

The absorption of energy by molecules or atoms, which normally exist in a state of minimum electronic energy or ground state, raises them to a less stable state of higher electronic energy or excited state. In most photochemical reactions except those involving ions or radicals; only two half vacant orbitals are associated with a molecule in the excited state. The presence of only these two orbitals (the orbital from which the transition takes place and the anti-bonding orbital to which the electron is promoted) sets only two values for the multiplicity, one and three. The first is the singlet state and the second the triplet state. The various modes of deactivation open to excited states may be divided into radiative and non-radiative processes. These conversions are succintly represented by the well known "Jablonski diagramme".

There are two types of radiative deactivation processes. The excited singlet ground state singlet emission known as flourescence and the excited triplet ground state singlet emission known as phosphorescence. Both the excited singlet and triplet states posses a great deal of excess energy (in the range of 40-200 k.cal/mole) and are therefore labile. If the energy is is not dissipated by radiative (flourescence or phosphorescence) means, it is often enough to overcome activation barriers so that chemical processes can take place.

Other than radiative or direct photochemical reactions, excited states may be deactivated by energy transfer in the form of vibrational energy to the surrounding solvent or to molecules of the same species by processes that must involve collisions. The availability of such energy that can be used to excite another species electronically is the besis for sensitization. The important feature in sensitized reactions is the incident light need only be of the wavelength absorbed by the sensitizer; the acceptor can be entirely transparent. Because triplet states are longer lived (10^{-5} to 10^{-3} sec) as against singlets (10^{-9} to 10^{-5} sec); sensitization involving triplets are more favorable than those involving singlets. The most effective sensitizers are those involving singlets. The most effective sensitizers are those that have very efficient intersystem crossing, that absorb preferrably at longer wavelength than the acceptor but have a higher triplet energy than the acceptor, and that are photochemically unreactive[68]. One of the most frequently used sensitizers is benzophenone with a triplet energy of 68.5Kcal/mole and 100% efficiency in intersystem crossing when excited at 3665A°.

2. CIS-TRANS ISOMERISATION

One of the earlier photochemical processes to be observed was the cis-trans isomerisation of olefines. This isomerisation can be effected by direct irraciation of the olefins, or by irradiation in the presence of a sensitizer or a catalyst. The study of this phenomenon is still persued extensively[69-71].

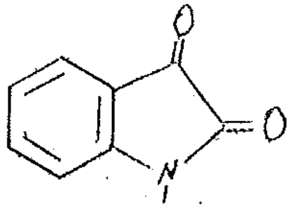
Electronic excitation of cis and trans olefins leads to two distinct excited states, the trans-excited state usually being of lower energy than the cis-excited state. Furthermore the molar extinction coefficient of a cis-olefin is generally lower than that of the trans-isomer, so that any given time more of the later than the former is being excited. Thus the trans-excited state is more heavily populated be it by direct excitation or through sensitization. Photochemical processes lead to conversion into the cis-isomer by virtue of the fact that a small but definite percentage of the trans-excited psecies is continually being converted to the cis-isomer, which is considerably less reactive photochemically.

If it is possible to irradiate a sample only at the absorptionwavelength of one of the isomeers, complete conversion to the other isomer would occur, because once formed, it would not be able to undergo further excitation. Such a process in which one can obtain a less stable, high energy product merely because it is transparent to the incident light is sometimes referred to as "optical pumping". Continued irradiation with light absorbed by both isomers leads to a point where the ratio cis:trans in the mixture is no longer altered, because a constant ratio of the excited species is being generated, leading to a constant ratio of isomers on decay. Such a situation referred to as a "photostationary state", is reached regardless of the isomer or mixture of isomers with which one starts[72].

The photoisomerization of indigos and thioindigos has been studied extensively. In their investigation of the photochemical behaviour of indigoid dyes; Wyman et al[73-75] had proposed a singlet mechansim for the direct photochemical trans cis isomerization. Later they have concluded from the quenching of the trans cis isomerization by oxygen and flash photolytic measurements that this reaction occurs in the triplet state[76-78] Kasstens et.al. then discounted the possibility of a tiplet mechanism[79]. Later Grellman and Hentzschell presented finding which are assumed to agree with the idea of a common tiplet state responsible for the trans-cis isomerization[80]. The latest investigations into the mechanism of trans-cis photoisomerization however favours a singlet rather than a triplet state at least for thioindigos[81,82].

3. PHOTODECOMPOSITION OF INDIGO

As early as 1927, Hibbert showed that the destruction of color in calico dyed with direct colors like indigo occurered quiet independently of any reducing action by cellulose in the presence of light[84]. This photodecomposition of indigo on cotton gave isatin (30) as oxidation product.



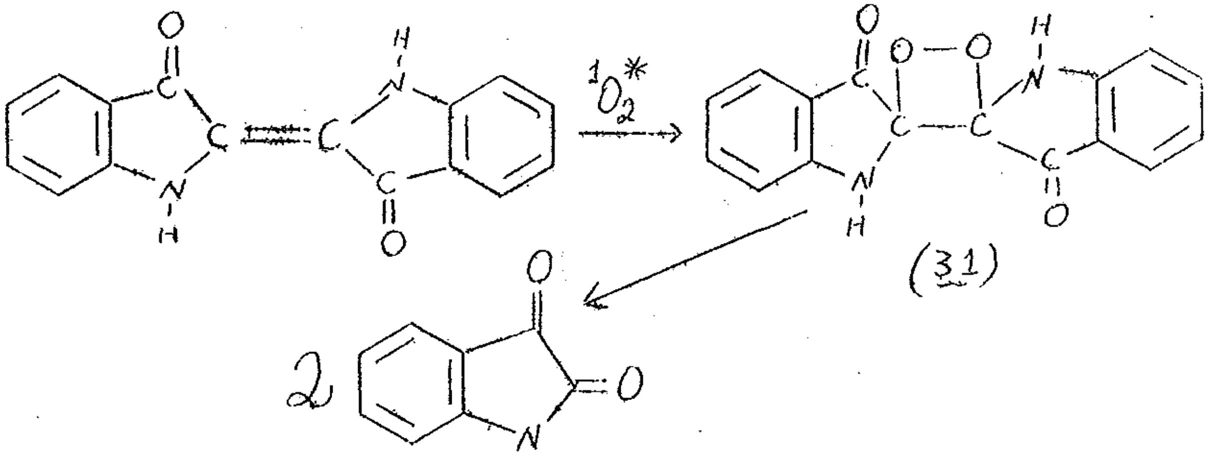
(30)

It is possible to obtain isatin from indigo dyed cotton by oxidizing the color on the fiber with potassium permanganate in 7.5% H_2SO_4. Similarly Haller etal, have identified isatin on indigo dyed fabric which has been taded by exposure to sunlight under glass[85]. This photooxidation to isatin sets indigo apart from other vat colors, like indanthrene yellow which normally under goes reduction.

Although the photooxidation of indigo to isatin was an established fact, no firm chemical evidence and explanation had been obtained fro the process. In recent years the contribution of singlet oxygen to the photofading of some dyes has been examined. For example Griffth and Hawkins had reported on the photochemical oxidation of 4-arylazo -1-naphthols-and their analogs[86]. Kuramoto and Kitao have then showed that 1-arylazo-2-naphthols undergo the self sensitized or dye sensitized photooxidation in solution giving the arenediagonium salts and 1,2,-napnthoqninones via a hydroperoxide intermediate by "ene' reaction[87]. The same authors also reported the role of singlet oxygen in the p photfading 2-(2-quinolyl) indan-1,3-dione and indigo itself[88,89].

In their work, kuramoto and Kitao irradiated solutions of indigo in dichloromethane, chloroform acetone or ethanol under oxygen with filtered (>390) radiation. Uniform decomposition of indigo occurred and isatin was isolated and isatin was isolated as tbe main product. It was found that singlet oxygen sensitizers like main product. It was found that singlet oxygen sensitizers like methylene blue, or Rose Bengal, accelerated the photofading of indigo. The intermediacy of singlet oxygen was also indicated by the efficient quenching of the reaction with carotene, 1,4-diazobicyclo (2.2.0) octane (DABCO) or nickel dimethyl dithiocarbamate (NMC). From the results of their own work and other related photooxidation investigations [90-95]; the authors have suggested a mechanism for the photofading of indigo in solution via the presence of singlet oxygen formed by self-sensitization.

The authors proposed that attack of singlet oxygen on indigo should lead to the unstable dioxetane intermediate which could produce isatin by fission of the carbon-carbon bond. The presence of the dioxetane intermediate in the reaction is assumed by analogy with the known reactions of simple olefins, which have no allylic hydrogen with singlet oxygen[96-97].



III. STATEMENT OF THE PROBLEM

The concepts of colors, dyes and their interaction with light have always been intimately interrelated. Fading, an irreversible change induced by light; is the result of photochemical changes ocuuring on the dye molecule. Although the process of fading itself has been a subject of numberous investigations; the exact nature of the phenomenon has yet to be fully elucidated.

Although there are several studies made on the comparative light fastness of indigoid dyes on cotton fabrics, there have not been reported in the literature similar investigations done on solutions of the dyes in appropriate solvents such as benzene, toluene and others. Exposing such dye solutions to sunlight exclude the effect of the fabric and other factors that make it difficult to understand the process of fading. Such a study can therefore give some insight into the photochemical processes responsible thereof. In the first part of this work, the comparative light fastness of five indigoid dyes; indigo, Thioindigo 6,6'-diethoxythioindigo, thioindigoscarlet, acenaphthen Thioindigo are compared. Further more, indigo and N,N-diacetyl indigo are separately compared for their light fastness under different conditions (atmospheric, oxygen and nitrogen); and solvents (benzene, toluene, cyclohexane, chloroform).

As shown earlier, the fading of indigo is known to b be due to the photooxidation of the indigo molecule. The presence of singlet oxygen is also accepted to be an essential feature of this photofading. The exposure to sunlight of a solution of indigo in a nitrogen atmosphere however would be an interesting investigation either as an additional evidence for or against the recently suggested mechanism for the photofading of indigo or as an uninvestigated, therefore unknown photochemical behaviour of indigo. When photodecomposition under nitrogen occurs, it would probably be analogous to fragmentations that occur at the electron impact site of a mass spectrometer. The mass spectra of indigo thionaphthene indigo and their derivatives have been studied by Puchkou and Bezoborodov[98] in USSR and Yamada[99] etal in Japan. Will the photodecomposition products of indigo under an inert atmosphere, nitrogen, show similarities to the fragmentation patter that occurrs at the electron impact of the mass spectrometer? N,N'-diacetyl indigo will also be investigated, the result of which would shed light on the manner of photolysis that occur in both dyes when exposed to sunlight. The second part of this work will deal with the isolation and identification of the major photodecomposition products of indigo and its derivative N,N'-diacetylindigo.

V. RESULTS AND DISCUSSION

A. COMPARATIVE FADING STUDIES OF SOME INDIGOID DYES

When light of the suitable frequency is absorbed by a dye, it undergoes changes in two ways; phototropism and fading[59]. Phototropism is a reversible change in shade shown by some dyes on short exposure to light. The original shade is restored however, on storage of the fabric or the dye itself in the dark[60]. Fading is an irreversible change induced by light. On absorption of light, the dye molecule undergoes electronic transition and is converted into an excited state involving either a singlet or triplet state.

The light fastness of indigoid dyes on fabrics had been studied earlier by Haller[65], and Apple & smith[66], later by Noguchi & Ishikawa. However, the comparative light fastness of the dyes as solutions in organic solvents had not been studied. In part A of this study, the light fastness or fading of some indigoid dyes at different conditions is investigated.

1. Comparative Fading Studies of Five Indigoid Dyes Under Normal Atmosphere.

Five indigoid dyes were used for this study. These were: (i) Indigo (ii) Thioindigo (iii) Thioindigo-scarlet (iv) 6,6'-diethoxythioindigo and (v) Acenapnthenethioindigo. The exposure of the five dyes in benzene solution were done in the months of October, November and December. In each case enough dye was dissolved to produce approximately equal intensity of absorbance when measured in a UV-Vis spectrophotometer (fig 5-fig 9). The solutions were exposed in heremetically sealed flasks under normal atmosphere. The comparative fading rate determinations show that:

(i) The least resistance to fading was shown by indigo. After only four hours of exposure to unfiltered sunlight, it showed no absorbance at its previous absorbing frequency (fig 5)

(ii) The highest resistance was shown by thioindigo scarlet. After 96 hors of continuous (only daylight hours; arbitrarily fixed from 6.00AM to 6.00PM were recorded) exposure, it still showed a 0.19 absorbance on the spectrophotometer when all others showed zero absorbance. It faded completely only after 120 hours of continous exposure. (fig 6).

(iii) 6,6'-diethoxythioindigo which completely faded in 50 hours showed a different spectral characterstic than the other dyes. Prior to any exposure, it had an absorbance peak at 523nm and a shoulder at 534nm. After four hours of exposure to sunlight the absorbance at 523nm decreased and the shoulder at 534nm began to be prominent and

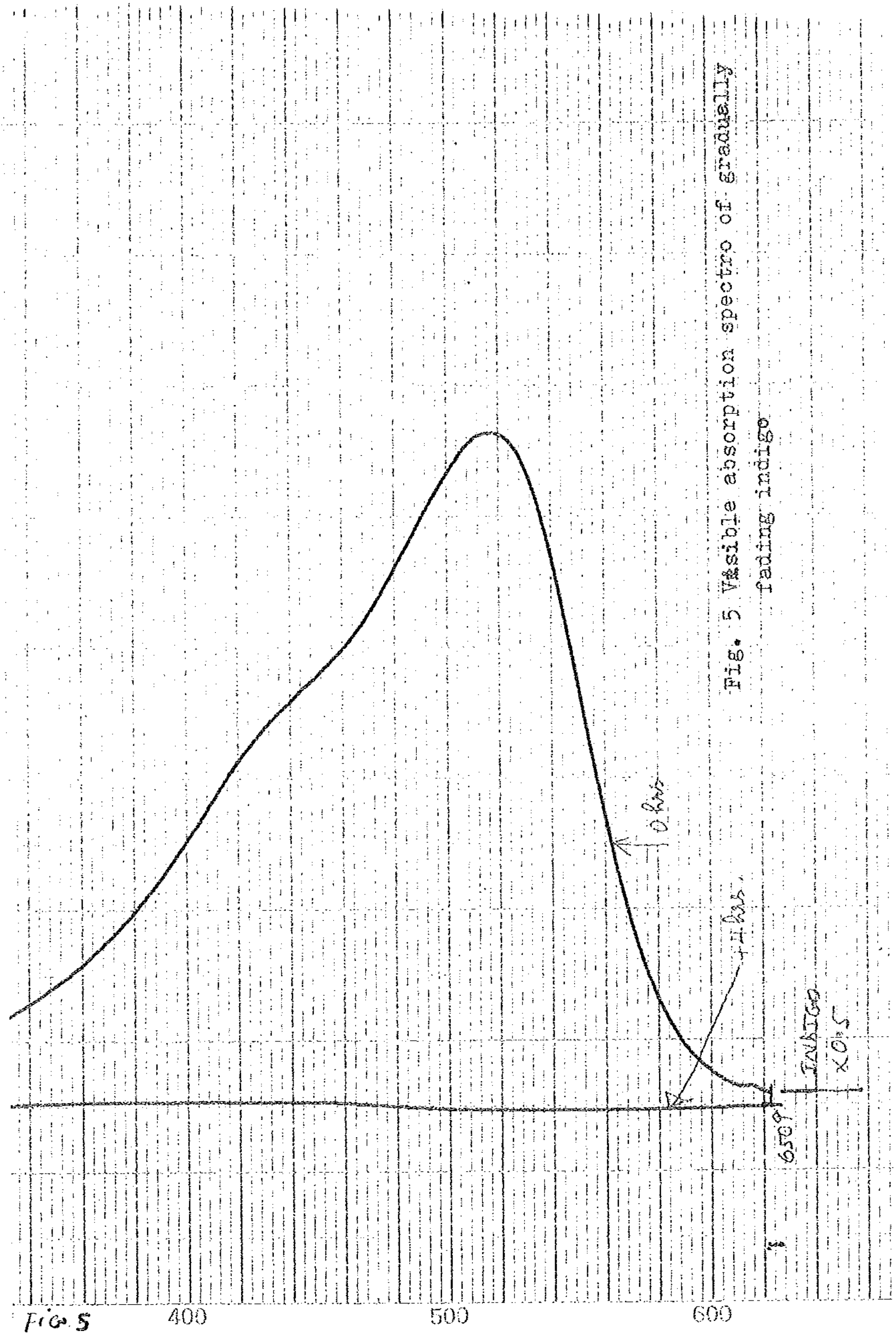


Fig. 5 Visible absorption spectro of gradually fading indigo

FIG. 5

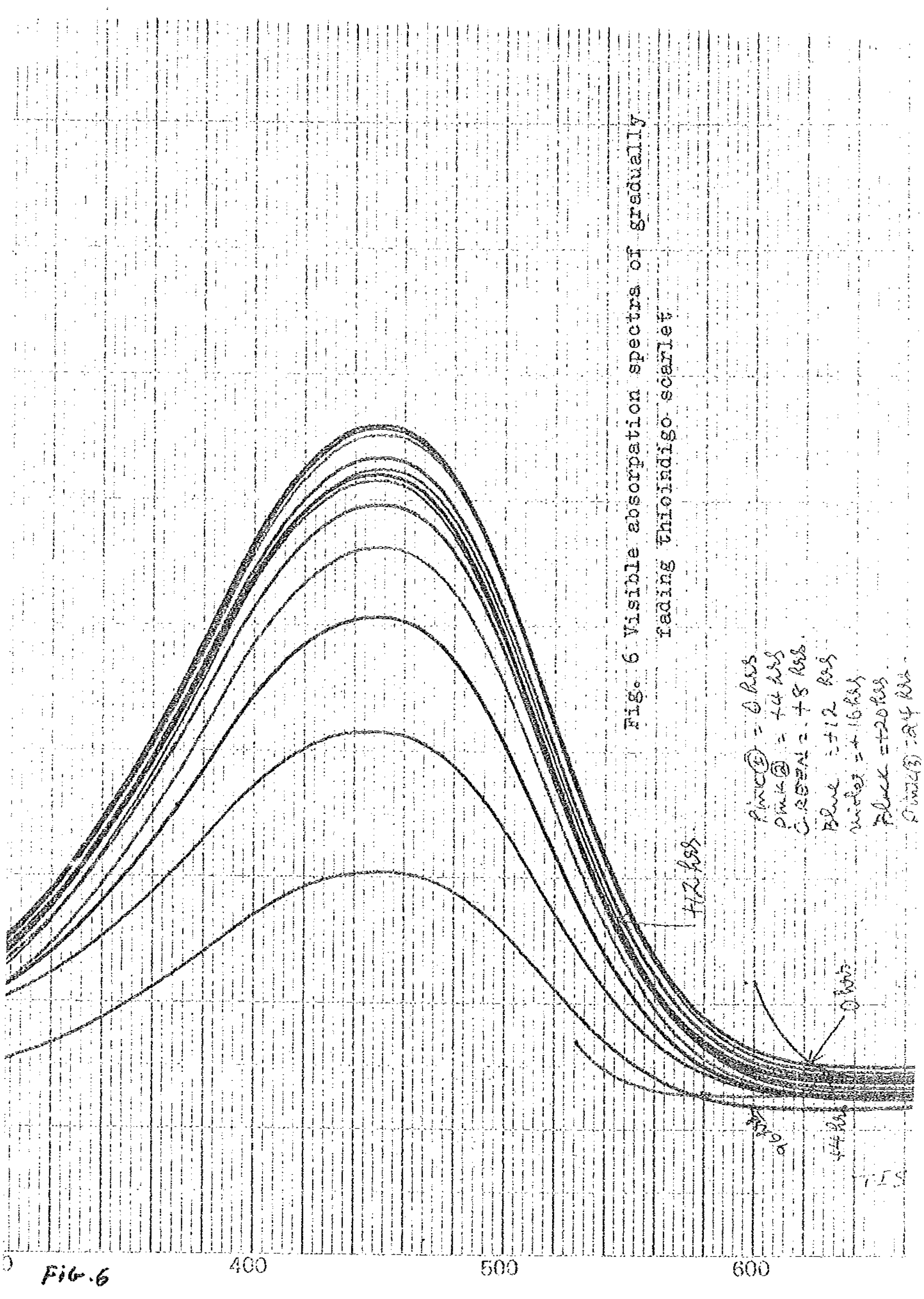


Fig. 6 Visible absorption spectra of gradually fading thioindigo scarlet

Fig. 6

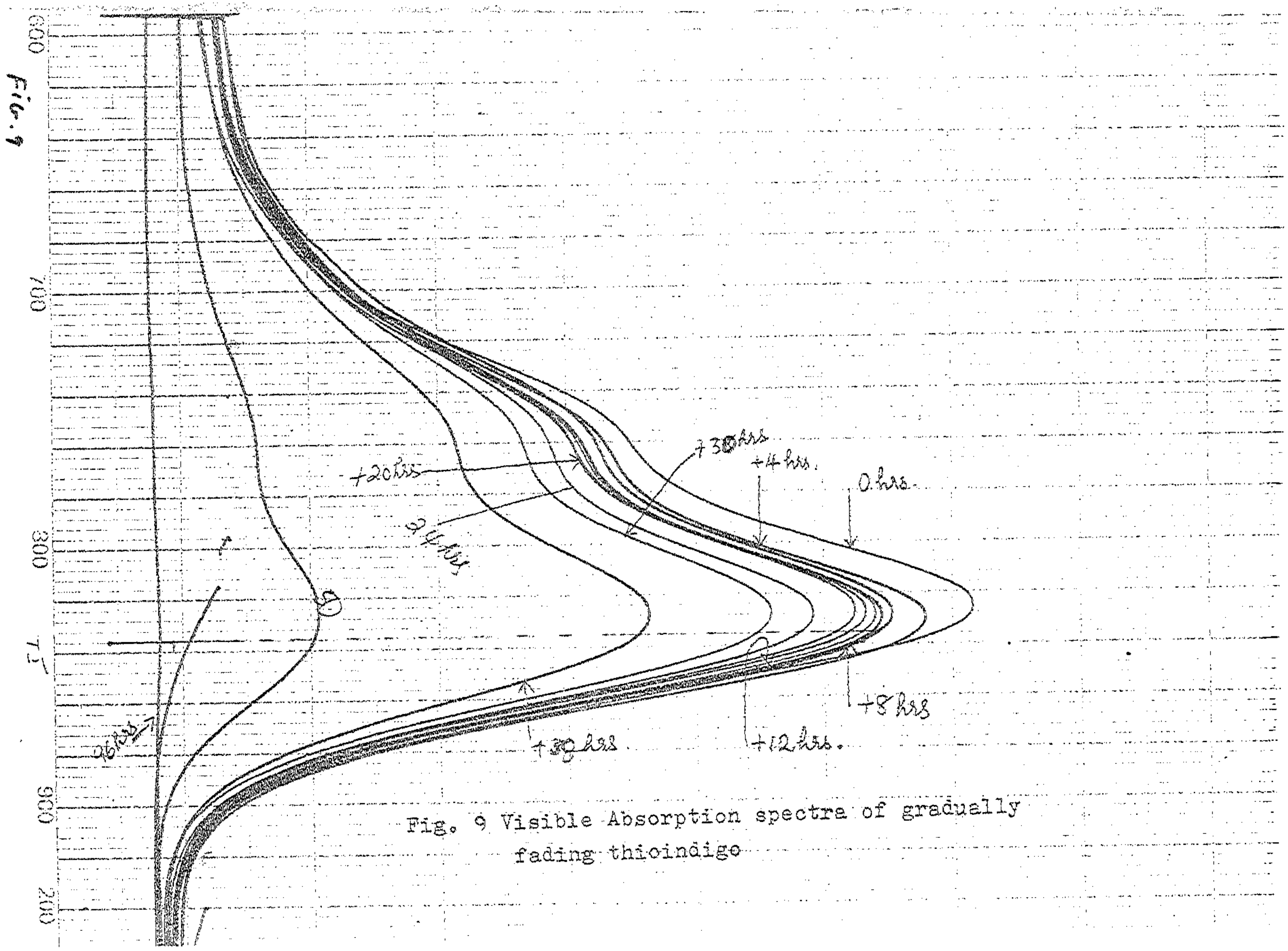


Fig. 9

Fig. 9 Visible Absorption spectra of gradually fading thioindigo

Fig. 8

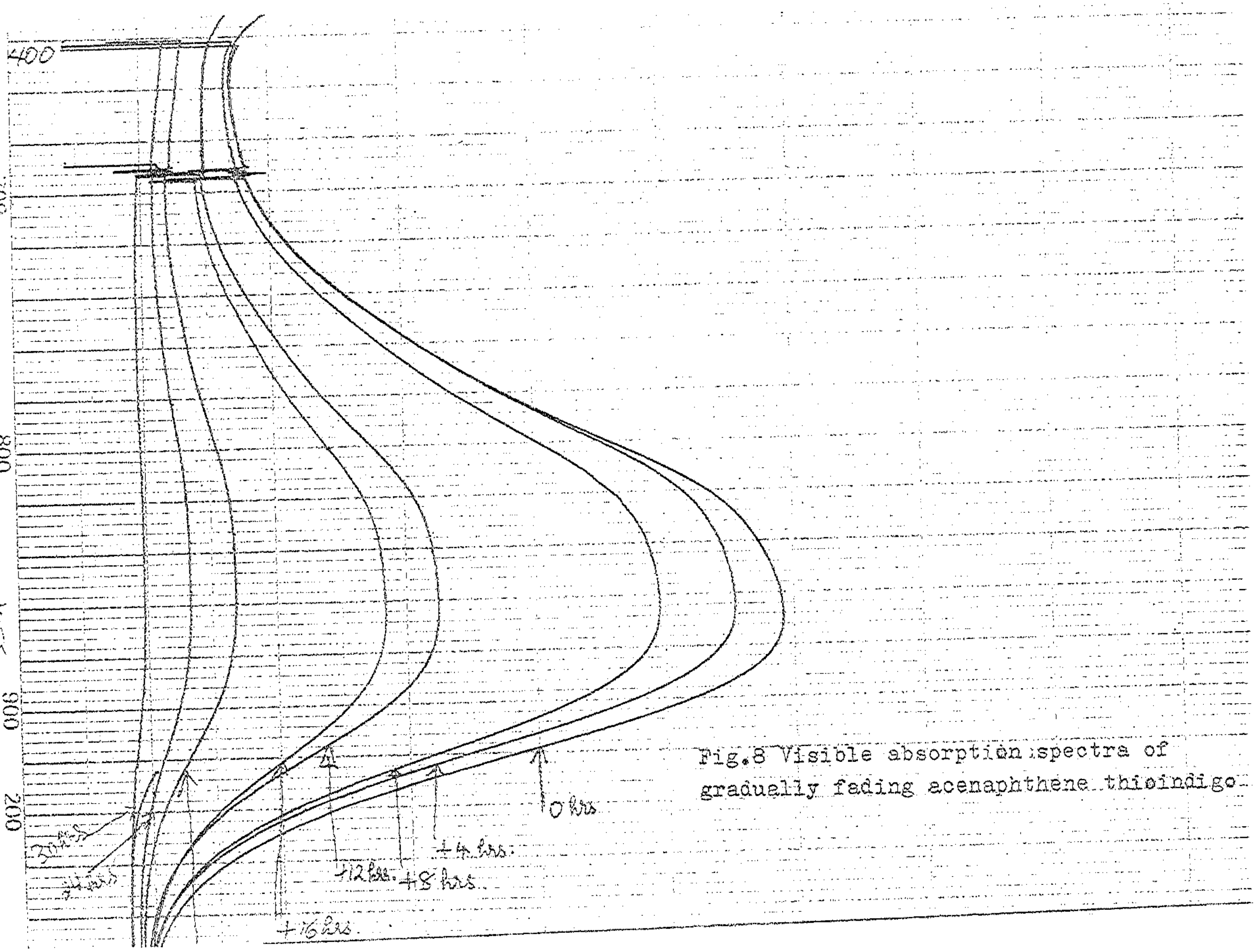


Fig.8 Visible absorption spectra of gradually fading acenaphthene thioindigo.

FIG. 7

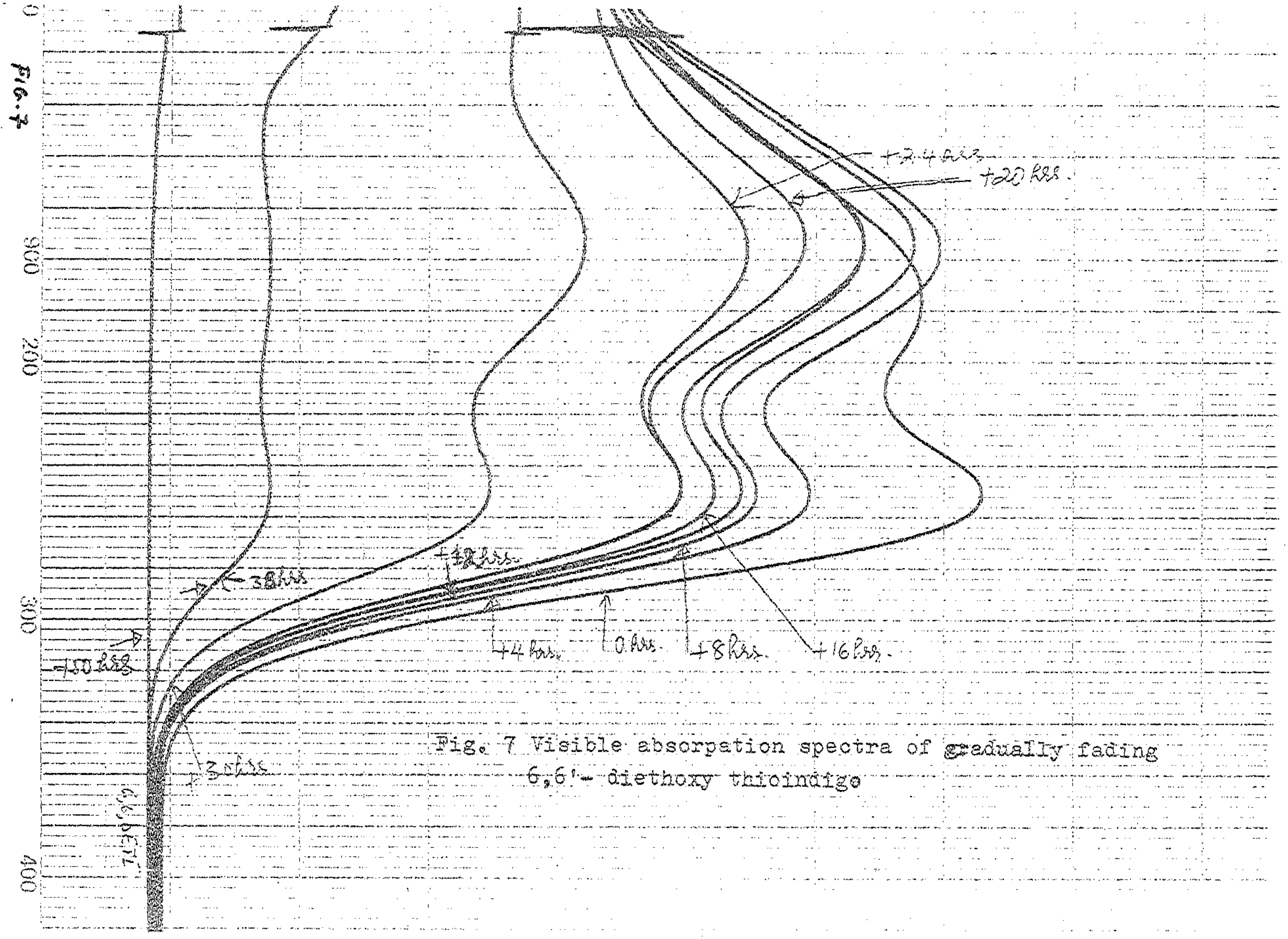


Fig. 7 Visible absorpation spectra of gradually fading 6,6'- diethoxy thioindigo

	DYE	TIME
1	INDIGO	4 hrs.
2	AcenaphtheneT.I	30 hrs
3	6,6'-diethoxyTI.	50 hrs
4	Thioindigo	96 hrs
5	Thioindigoscarlet	120 hrs

Table 7 - Light fastness of five indigo dyes.

2. The Fading Rate of Indigo Solutions of Benzene Under Normal Atmosphere, Oxygen and Nitrogen.

Three equal concentrations of indigo dissolved in benzene were exposed to unfiltered sunlight. One was heremetically sealed under ordinary atmosphere; the second was sealed after bubbling oxygen gas for thirty minutes into the solution. The third flask was purged with nitrogen for thirty minutes and seald under nitrogen atmosphere. The indigo solution exposed to sunlight under oxygen completely faded in less than two hours. The indigo sealed under ordinary atmosphere faded next after six hours of continuous exposure to sunlight. The indigo solution which was purged and sealed under nitrogen atmosphere took the longest to fade (24 hrs) showing a fading rate many times less than that for indigo under oxygen.

The results show that the photofading of indigo is fastest in the presence of oxygen than when it is not present. The photooxidation of indigo via a dioxetan intermediate as proposed by Kuramoto and Kitao[96,97] therefore appears to be a relatively facile process. On the other hand the fact that completed fading of indigo under inert nitrogen atmosphere and in the absence of oxygen occurrs; also indicate the presence of other photofragmentation or decomposition of the indigo molecule. It is also possible to deduce from the results that these other decomposition photochemical processes are not significant or competing when oxygen is present during the photofading of indigo. Finally, in the fading of benzene solutions of indigo, the most important factor for fading is found out to be oxygen.

3. Comparative Fading Rate of Indigo and N,N'-diacetylindigo Under Different Conditions

The fading rates of benzene solutions of indigo and N,N'-diacetyl indigo were compared under (i) inert nitrogen atmosphere; (ii) oxygen and (iii)air. In all three cases indigo faded faster than N,N'-diacetylindigo. The increased rate of the photofading of indigo observed when exposed to sunlight under oxygen atmosphere was also seen here not only for indigo but also for the N,N'-diacetylindigo. The increased photofading of N,N'-diacetylindigo when exposed to sunlight under oxygen atmosphere suggests that photooxidation is also a preferred photochemical process by which the dye is faded.

4. The Fading Rate of N,N'-diacetylindigo Under Different Atmospheres.

Equal quantities of N,N'-diacetylindigo were dissolved in benzene closed in (i) air (ii) nitrogen and (iii) oxygen were sealed and exposed to sunlight. The fading rates at the three different conditions followed closely the variation shown by indigo. The solution containing oxygen faded the fastest, then the one in air and finally the solution closed under nitrogen atmosphere. The results show that as for indigo, photooxidation is also an important sunlight induced pathway by which the dye, N,N'-diacetylindigo is faded when exposed to unfiltered sunlight as a benzene solution. The fact that complete fading occurred even under inert atmosphere and in the absence of oxygen; indicates similarly to to indigo that other photodecomposition processes are taking place when the dye is exposed to sunlight. However, the very slow fading rate of the dye when exposed under nitrogen shows that these decomposition processes are not facile and probably involve and require high energetic conditions inorder to proceed rapidly.

B. PHOTODECOMPOSITION STUDIES ON INDIGO AND N,N'-DIACETYLINDIGO

When light of appropriate frequency is abosorbed by a dye molecule, it will undergo an electronic transition being converted into an excited state. Having acquired now the necessary energy, it is ready to proceed to photochemical processes which will finally result in the formation of completely novel molecules which are of course related to the parent molecule. The indigo molecule for example under oxygen atmosphere is photooxidized and then fragments into two isatin molecules. The photodecomposition patterns of indigo and the closely related diacetyl derivative; N,N'-diacetylindigo are investigated under different conditions for a clear understanding of the photochemical processes that take place when the dyes are exposed to sunlight.

1. Solvent Effects On the Photodecomposition of Indigo

Four organic solvents; benzene, toluene, cyclohexane and chloroform, were chosen for this study. Approximately equal quantities of indigo were dissolved in each of the solvents, purged and heremetically sealed under inert nitrogen atmosphere. Oxygen was avoided inorder to remove its already confirmed active role in photooxidation of the dyes and make the study of the solvent effects easier.

After the indigo had completely faded and decomposition was complete, the solvents were removed and the photodecomposition products studied by thin layer chromotography.

The results show (i) that there are two major products that appear in all cases; (ii) that the photoproduct from the benzene consist the larger number of components(six).

2. Solvent Effects on The Photodecomposition of N,N'-diacetylindigo.

About equal quantities of N,N'-diacetyl indigo were dissolved in four different solvents; benzene, toluene, cyclohexane and chloroform. The solutions were purged and sealed under nitrogen. The four solutions were then exposed to unfiltered sunlight until the deep red color completely changed to a golden color. The decomposition was then assumed to be complete. The solvents were removed and the photoproducts analysed by thin layer chromotography.

The t.l.ç. Secondly it was found out that all four cases contained a single major product with an Rf value of (0.36). However the decomposition product from the benzene solution also contained two other products in significant quantities with Rf values of (0.29) and (0.55) respectively.

This difference in the photodecomposition products of the dye indicate that the solvent itself(benzene)plays and active role during the photodecomposition of the molecule. There are two possible ways by which benzene can take part in the photodecomposition reaction of the dye. One is by reacting with a highly active photoproduct which had been created in the initial stages of the photodecomposition process. This is a rather common occurrence as seen for example in the photoaddition to aromatic compounds. It is an established fact that 1,2, 1,3, or 1,4 photoadditions to the benzene ring can occurr.

The second possibility is for benzene itself to be excited and undergo certain photochemical reactions. As is known, benzene is not completely inactive photochemically. Since the finding of Blair and Bryce-Smith[101] that irradiation of benzene under a nitrogen atmosphere and 50°C will produce some fulvene; ther have been numerous other examples (102-105) that show the photochemical activity of benzene. However, this second possibility seems unlikely since benzene absorbs in the ultraviolet and there would probably be too little UV radiation reaching the solution through the flask to effect the photochemical excitation necessary before benzene undergoes any type of reaction.

Finally the difference that has arisen from using different solvents is in accordance with the property of carbonyl compounds whose photochemical reactions greatly depend on the choice of solvent in which the reaction is conducted[106].

3. The Effect of Different Atmospheres on the Photodecomposition of Indigo

Three equal quantities of Indigo were each dissolved in benzene. The first flask containing the benzene solution of indigo was thoroughly purged and sealed under nitrogen. A similar procedure using oxygen gas was followed for the second flask. The third flask was sealed as it is; under air. The three flasks were then exposed to unfiltered sunlight until decomposition was complete. The solvent was then removed under reduced pressure and the photo products analyzed by t.l.c. using 0.25mm thick silica gel plates. Visualization was done by UV light; comparison with an authentic sample shows that isatin is produced as a photdecomposition product of indigo under oxygen atmosp-ere. It is also produced during the photodecomposition under air. The yield as expected is larger when decomposition occurs under oxygen than decomposition under air. The result agree with the one published by kuramoto et al[96,97]. There are five distinct (and possible six) products from the photodecomposition product of indigo under nitrogen atmospheere. The components from the other two are three and four respectively. This result suggests that minor fragmentation photochemical reactions which were overshadowed by the photooxidation of indigo to isatin grow prominent in the absence of oxygen. Isatin may also have been present in the third product, but the large number of components make it difficult to be certain.

4. The Effect of Different Atmospheres on the photodecomposition of N,N'-diacetylindigo

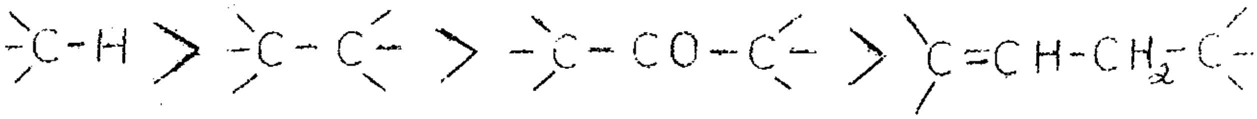
Three equal quantities of N,N'-diacetylindigo were each dissolved in benzene. The first flask containing the benzene solution of indigo was thoroughly purged and sealed under nitrogen. The second was bubbled with and sealed under oxygen gas. The last one was sealed while it is under normal atmosphere. The three N,N'-diacetylindigo solutions were then exposed to unfiltered sunlight until decomposition was complete. The solvent was then removed and the photoproducts analysed by t.l.c. on 0.25mm silica gel plates impregnated with a flourescent indicator for visualization at 254mm. A benzen-chloroform (1:1) solvent system was used for developing the chromotograms.

The t.l.c. of all three photoproducts shwo no difference at all in the number and type of products formed during the photodecomposition of diacetylindigo. Three distinct products with appro.ximately comparable yield are observed in the photopro.duct.

C. ISOLATION AND IDENTIFICATION OF THE MAJOR PHOTODECOMPOSITION PRODUCTS OF INDIGO AND N,N'-DIACETYLINDIGO UNDER NITROGEN ATMOSPHERE.

It has been sufficiently described that the major photochemical change that occurs when indigo is exposed to sunlight under oxygen, is the photooxidation of the indigo molecule to form isatin. However when this photooxidation is excluded by conducting the experiment under inert nitrogen atmosphere, then non -oxidative photochemical processes assume greater significance and their endproducts actually become major products instead of isatin.

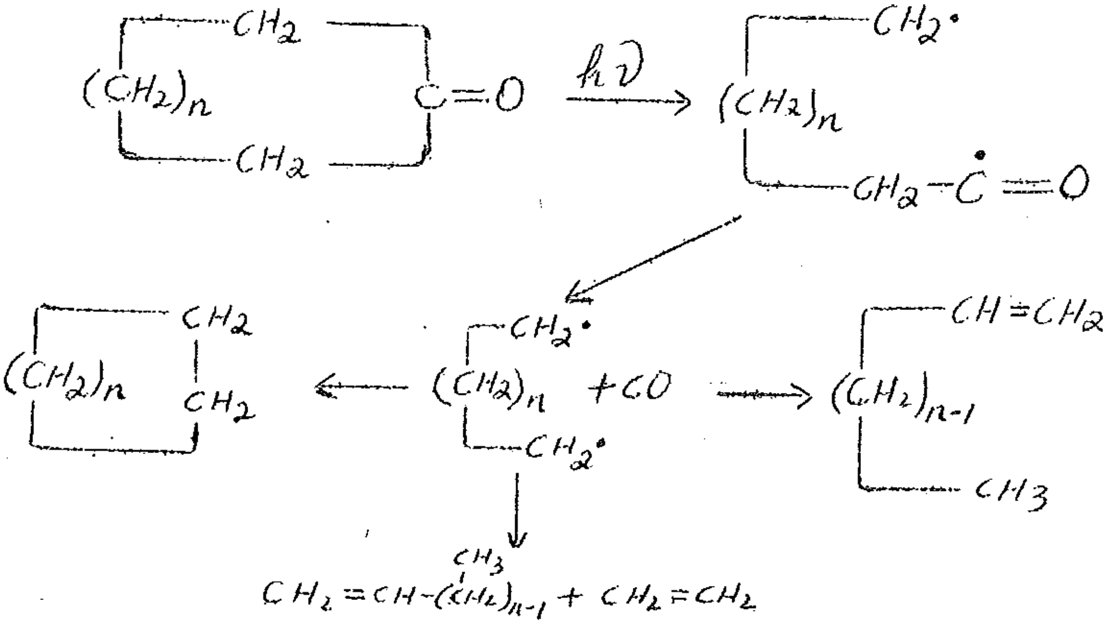
It is generally believed that in photochemical reactions the magnitude of excitation energies being comparable to that of bond energies, bond dissociations can occur without much difficulty. Where homolytic fissions are concerned, the stability of the radicals to be formed and the relative bond dissociation energies will play a role in determining which bonds undergo breakage. When one considers the magnitude of bond-dissociation energies which fall in the order



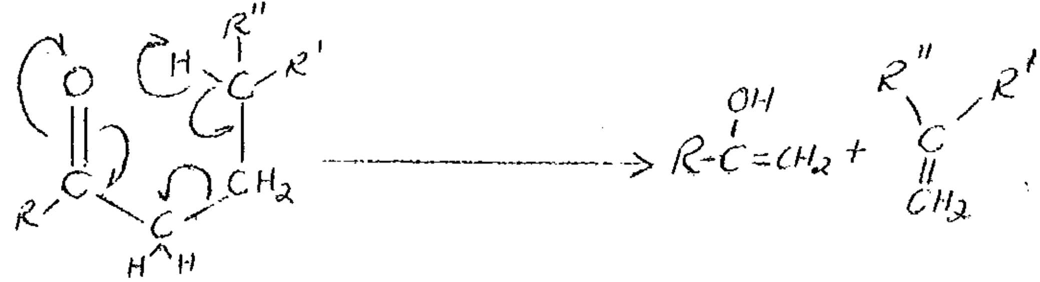
it can be seen that C-C bonds adjacent to carbonyl groups and allylic to olefinic bonds are prone to dissociate in photochemical reactions. The fragmentation patterns are rather similar to those observed in mass spectrometry.

The course that the photochemical reactions of carbonyl compounds take greatly depends on the reaction phase employed. When the photolyses are conducted in the liquid phase, the choice of solvent is critical. Two main routes are generally followed in the photolysis of aldehydes and ketones.

The first, referred to as Norrish type I process, can be formally represented by the cleavage of bond followed by decarbonylation of the resulting acyl radial formed. The radicals formed after the decarbonylation step may recombine, abstract hydrogen, or undergo secondary fission reactions to yield hydrocarbons and olefins:

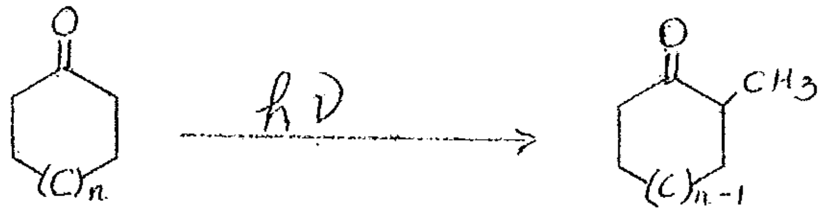


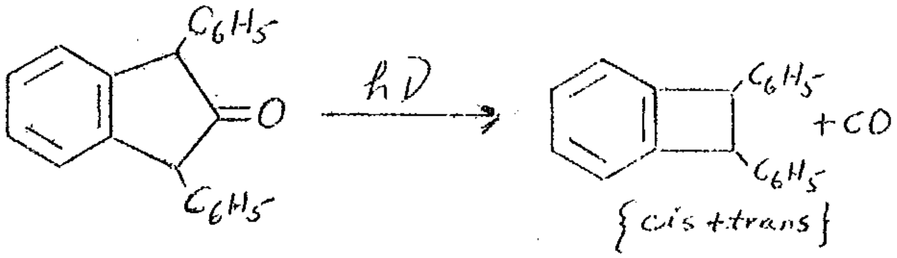
The second route is the Norrish type II reaction. It is characterized by a hydrogen transfer to the carbonyl groups; in many cases studied such transfer apparently occurs through a six-membered transition state. In saturated ketones, the bond to the carbonyl group often broken, so that olefins and methyl carbonyl derivatives may result.



Both types of processes may occur simulteneously. The type I process is especially prominent in gas-phase photolysis, while in the liquid phase the loss of carbon monoxide is observed only with small-or intermediate-sized ring compounds[103]. On the other hand reactions of type II can be observed in both gas and liquid-phase photolyses, but the formation of a ketone is observed only in the presence of a nucleophilic solvent capable of adding to it. Furthermore, there apparently exists a relationship between the ring size, the number of conjugated double bonds, and the type of process taking place on the photolysis of conjugated unsaturated ketones.

Since both indigo and N,N'-diacetylindigo are both cyclic ketones, it would be relevant to summarise some important characterstic photochemical reactions they undergo. One of these is the ring contraction observed during decarbonylation. Thus cyclohexanon yields 6% of 2-methylcyclopentanone, cycloheptanone yields 0.2% of 2-methylcyclohexanone, and cycloctanone yields traces of 2-methylcycloheptanone as well as about 1.2% of 2-n-propylcyclopentanone.





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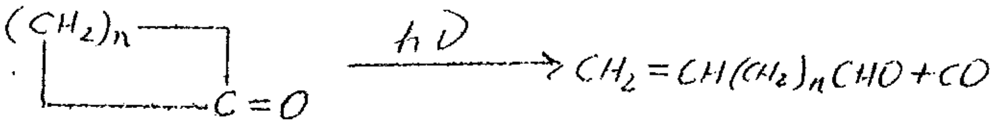
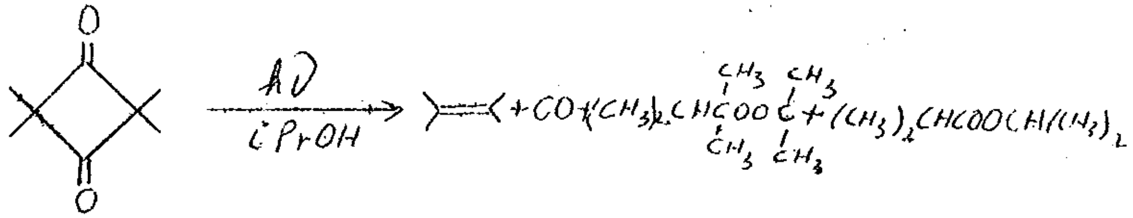
Ring opening, resulting in formation of an unsaturated aldehyde, is also common to all cyclic ketones



In solution, the behaviour of ketones varies markedly with the solvent. In hydrogen-donor solvents such as alcohols and some hydrocarbons, photo reduction generally occurs, whereas in aqueous media, carboxylic acids, indicative of ketone intermediates; are the major products. Only in chemically inert solvents such as aromatic hydrocarbons is photodecarbonylation an important reactions[110]. Cyclic diketones mostly behave either as isolated keto easomophores or as enols. In the gas phase, the photochemical behaviour diketones is virtually uninvestigated. In solution, both decarbonylation and other decomposition pathways have been observed. Decarbonylation of cyclic diketones is one of the most efficient solution phase decarbonylation reactions. The most popular example is the loss of 1 mole of carbon monoxide from cyclobutane-1,3-diones leading the formation of cyclo propanones[111-113]. Photolysis of tetramethyl cyclobutanedione-1,3 under an argon atmosphere in methanol or isopropylalcohol causes a rapid evolution of carbon monoxide and formation of two esters.



After this brief summary of the photolysis of carbonyl compounds, the isolation and identification attempts of the major photo decomposition products of indigo and N,N'-diacetyl indigo in benzene and under inert nitrogen atmosphere will be discussed.

1. <u>Compound ST-1A</u>

This is a light yellow oil which eluted as one of th the first fraction during the column chromotographic separation of the photodecomposition product of indigo. It is soluble in most non-polar solvents. Several repeated t.l.c trials show that it is a pure compound. The yield was small, 2.9%.

IR. The strong absorption at 1740cm^{-1} is assigned to C=0.
(fig.10) That this carbonyl is that of an aromatic ester is indicated by the absorption at 1286cm^{-1}. The higher absorption frequency of C=0 (1740cm^{-1}) is characteristic of esters as compared to ketones.

The absence of any absorbance >3100cm^{-1} rules out the presence of N-H stretching vibrations for secondary amines which show weak absorbance at >3100 cm^{-1}.

NO. 007-1494

PERKIN-ELMER

CONCENTRATION ____
THICKNESS ____
PHASE ____
REMARKS V. Small amts of $CHCl_3$

SCAN MODE ACCY. ☐ HI ENERGY ☐ RESOLUTION ☒ SURVEY ☐ CAL. ☐
OPERATOR Solomon T. DATE 1/5/82

SPECTRUM NO. ____
SAMPLE ST-1A
ORIGIN INNIGO

Slight shift to the left in 5µm

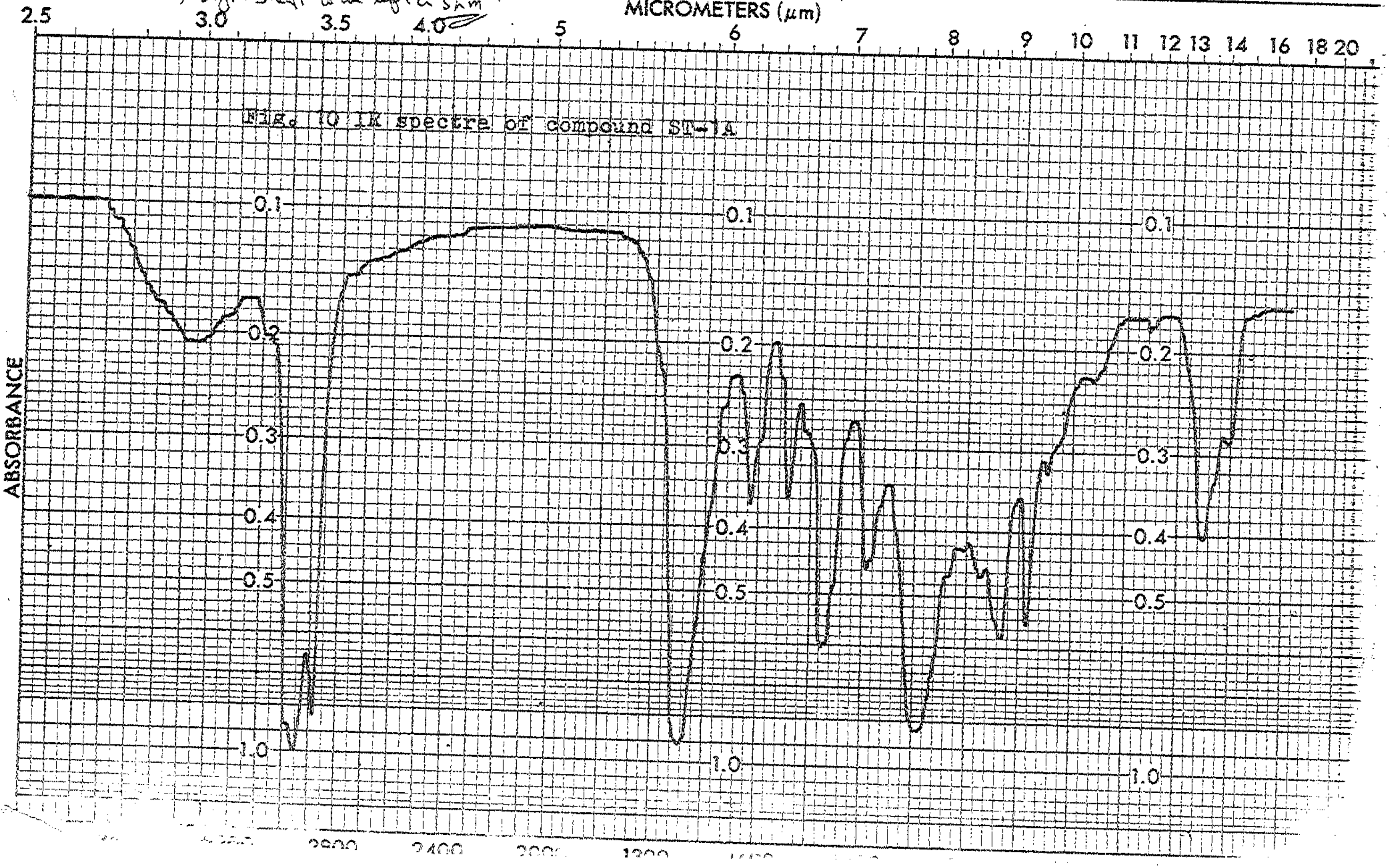


Fig. 10 IR spectre of compound ST-1A

The intense peaks between $2870 cm^{-1}$ and 2960 indicate the presence of aliphatic C-H stretching vibrations. The intensity suggests an aliphatic chain $-CH_2-CH_2-CH_3$.

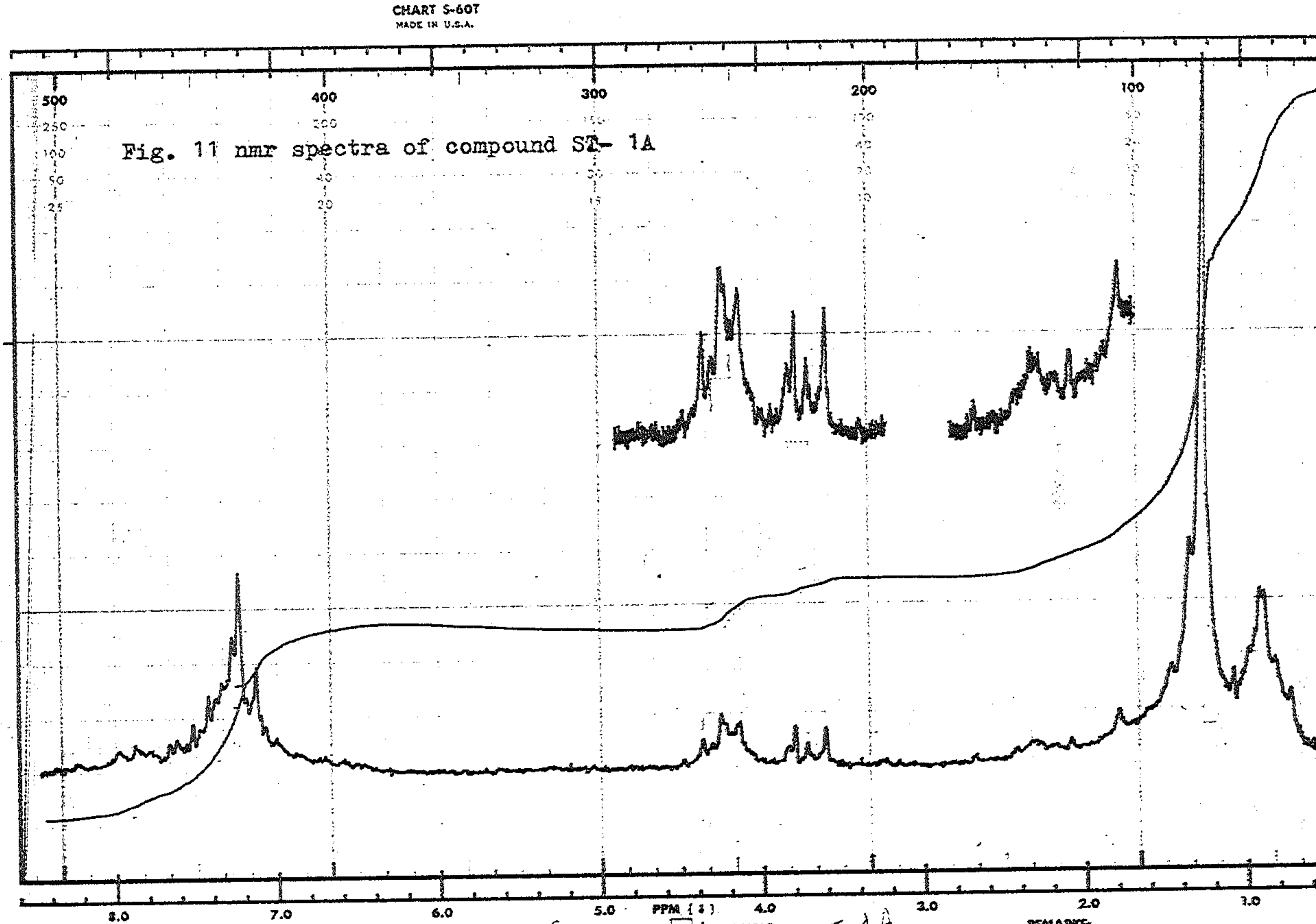
NMR. (fig 11)

The nmr clearly shows the presence of aromatic hydrogens (δ = 7.3ppm) fig(8). The protons at (δ =4.2ppm and δ =3.6) indicate protons in the vicinity of a heteroatom, oxygn agireins with the $-O-CH_2-$presence in the ir spectra. Large numbers of aliphatic protons are shown in the nmr by the signal at (δ =1.2ppm).

Integeration also suggests a high aliphatic protons to aromatic protons ratio again in agreement with the intense aliphatic stretching vibration frequencies shown in the ir spectra.

The results are not completely sufficient to ellucidate the structure of the compound. A tentative assignment can be made however to a compound which is a benzoic acid ester group connected to a long aliphatic chain. ([illegible] it may also be possible

Fig. 11 nmr spectra of compound ST- 1A



MANUAL

SWEEP OFFSET (Hz):

SPECTRUM AMPLITUDE: 10X1

INTEGRAL AMPLITUDE: 4

SPINNING RATE (RPS): 30

SWEEP TIME (SEC): 50 250 (250)

SWEEP WIDTH (Hz): 25 50 100 250 500 (500)

FILTER: 1 2 3 4 5 6 7 8 (2)

RF POWER LEVEL: (.05)

AUTO ☐

SAMPLE: ST-1A

SOLVENT: CDCl₃

REMARKS:

varian
analytical instrument division

DATE:

OPERATOR:

60 MHz NMR
SPECTRUM NO.

[illegible]

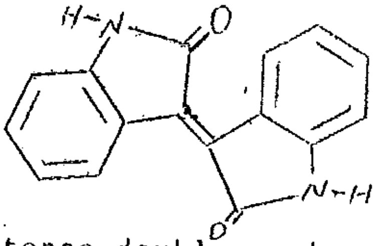
Starting from a photo fragmentation of indigo, it is difficult to account for the presence of such a compound with large aliphatic character. The solvent used, benzene and the indigo molecule are both aromatic, Although decomposition could result in the presence of small aliphatic chain, it still is not sufficient to account for the presence of such large numbers of aliphatic hydrogens which would require several bond making steps. The small amount of the yield is also an additional evidence for suspecting this compound not to be a primary or even secondary photodecomposition product of indigo. It may well have been formed from a reaction between a benzoic acid group (a more probable photodecomposition product) and a saturated hydrocarbon contaminant.

2. Compound PIC-6

This is a reddish brown solid isolated from the sixth fraction during the column chromatographic separation of the crude photochemical decomposition of indigo. It is insoluble in non-polar solvents but moderately soluble in chloroform, acetone and in ethanol in that order. The compound melts with decomposition at 225-227°C.

IR. (fig .)

The multiple absorbance shown by the spectra 3100cm^{-1} is assigned to an N-H stretching vibration. Although normally the N-H stretching vibrations give a single peak; combination could develop due to C=O and NH coupling if there is a β -carbonyl-group. This is seen for example in the ir spectra of isoindigo (12).



The intense double peaks at 1765cm^{-1} and 1728cm^{-1} are assigned to C=O which is strongly coupled to N-H. The C=O stretching vibrations of lactams with six-membered rings or larger is near 1650cm^{-1}. Five membered rings(β -lactams) absorb in the 1750-1700cm^{-1}. Unfused β -lactams absorb at 1760-1730cm^{-1}. This clearly indicates that increased strain of the lactam to another ring generally increases the frequency by 20-50cm^{-1}(117).

Another strong peak at 760cm^{-1} could be assigned to an out of plane wagging of N-H in agreement with the same phenomena being seen in β -lactams between 800-700cm^{-1}.

The sharp peak at 680cm^{-1} is indicative of a 1,2, [illegible] ring, [illegible]

[illegible] of the [illegible]

NO. 007-1494

PERKIN-ELMER

CONCENTRATION ______
THICKNESS ______
PHASE KBr
REMARKS ______

SCAN MODE ACCY. ☐ SURVEY ☐
HI ENERGY ☐ CAL. ☐
RESOLUTION ☒
OPERATOR ______ DATE ______

SPECTRUM NO. ______
SAMPLE PIC 6
(lowest concentration)
ORIGIN ______

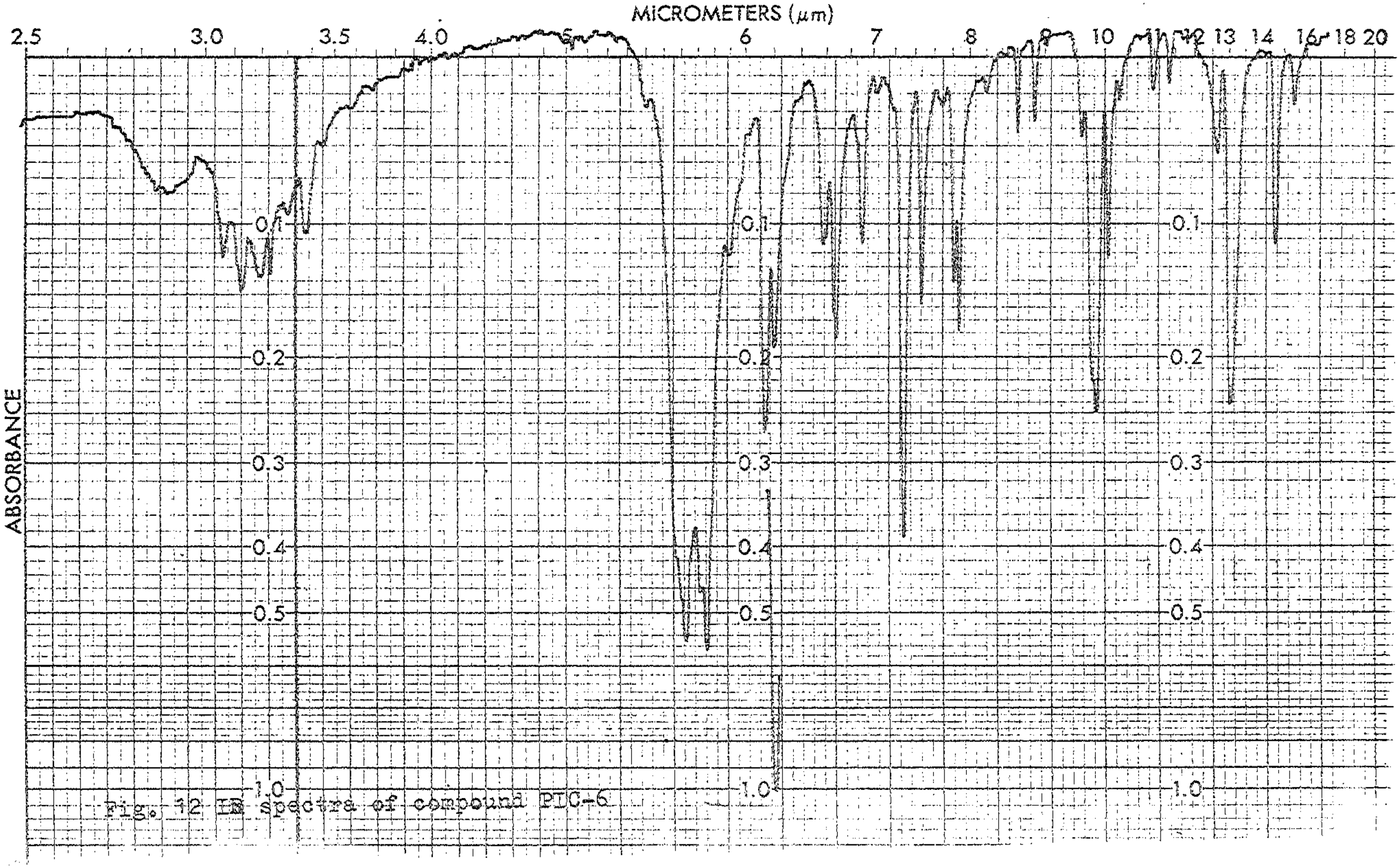


Fig. 12 IR spectra of compound PIC-6

NO. 007-1494

PERKIN-ELMER

CONCENTRATION
THICKNESS
PHASE KBr
REMARKS

SCAN MODE
ACCY. ☐
SURVEY ☐
HI ENERGY ☐
CAL. ☐
RESOLUTION ☒
OPERATOR Han
DATE 13/5/81

SPECTRUM NO. ①
SAMPLE Isoindigo
ORIGIN

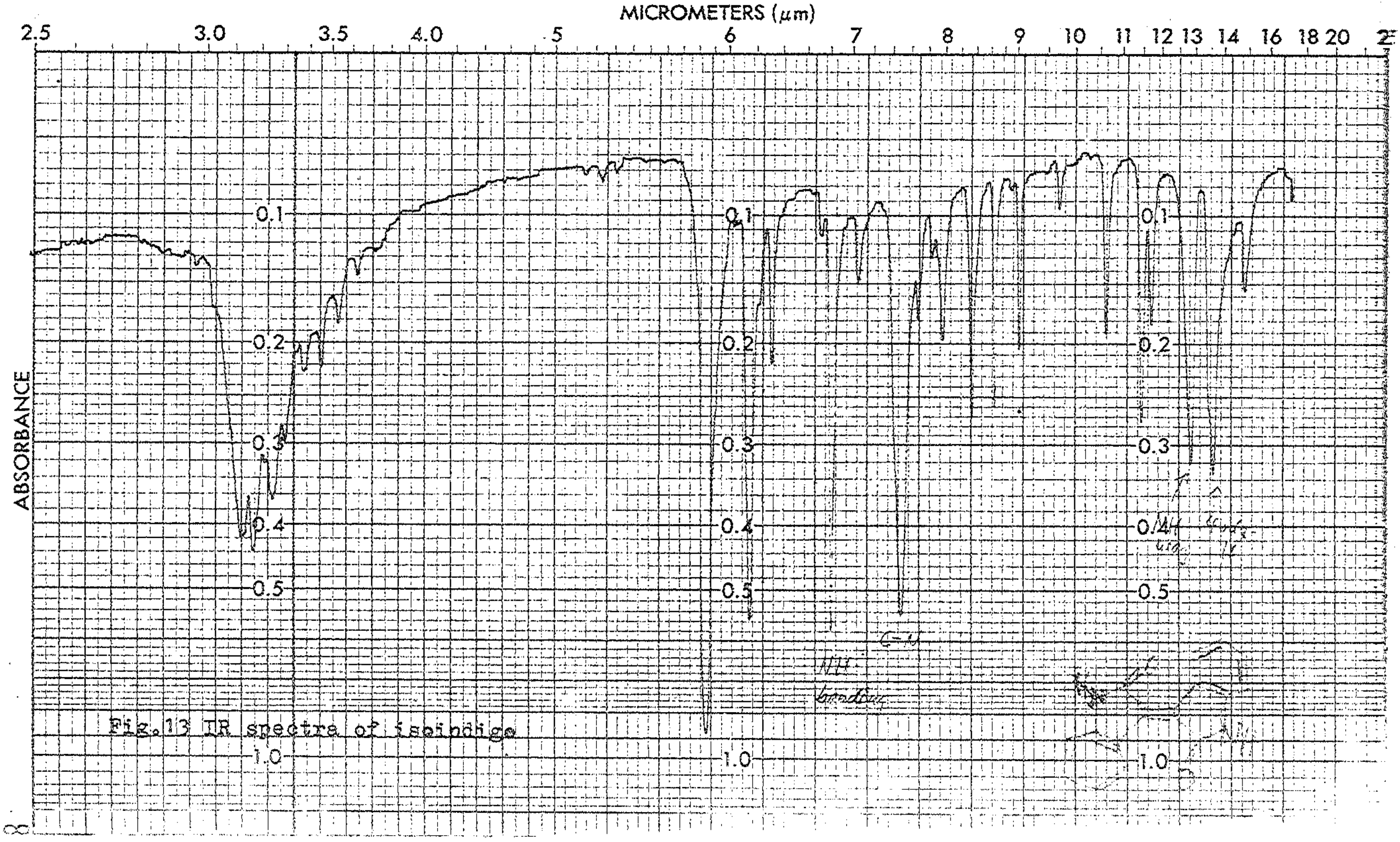


Fig.13 IR spectra of isoindigo

disubstuted benzene ring, originating from out of plane bending of the C-H bonds.

The peak at 1620 cm^{-1} is assigned to the skeletal vibrations of benzene. Finally although it is weak (the spectra is done in low concentration) the peak at 3010cm^{-1} could be assigned to an aromatic C-H stretching frequency. Note is also made here that there is no aliphatic C-H stretching vibrations seen in the spectra.

<u>NMR</u> fig(14)

The compound is not very soluble in chloroform. Therefore deuterated acetone was used to run the nmr. The signals at ($\delta \simeq 1.00$ppm) is a side band. And the quinted at ($\delta \simeq 2.0$ppm) is due the presence of CD_3COCD_2H in the solvent it self. This was confirmed by running the nmr of the solvent alone (fig 15).

The nmr shows no non-aromatic protons. The signals between ($\delta \simeq 7.0$ppm - $\delta \simeq 8.0$ppm) are assigned to aromatic protons. The pattern of the aromatic proton signals suggests a 1,2, substitution of the benzene ring. This is in good agreement with ir spectral data.

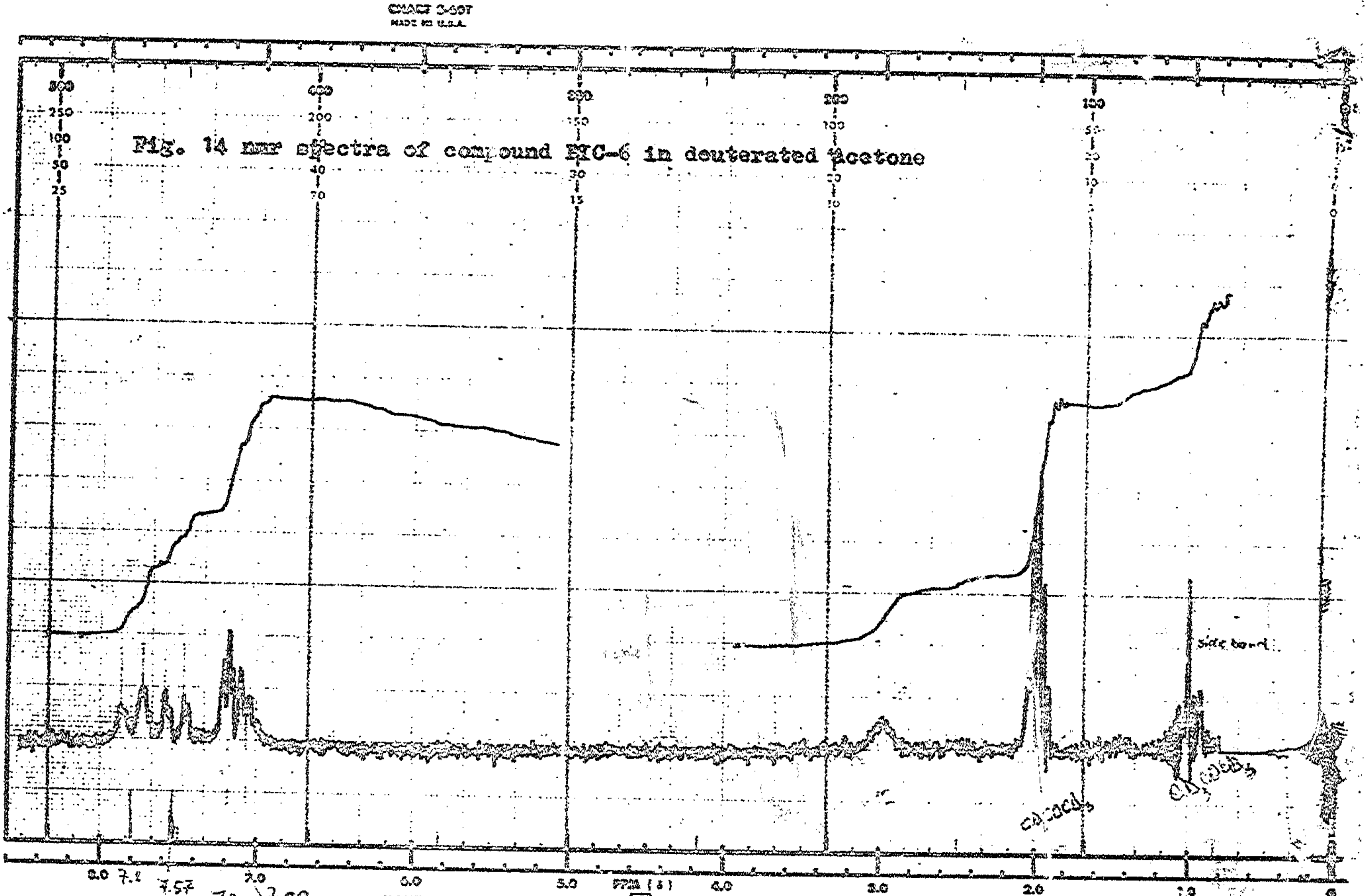


Fig. 14 nmr spectra of compound PIC-6 in deuterated acetone

SWEEP OFFSET (Hz):
SPECTRUM AMPLITUDE: 40×2.5
INTEGRAL AMPLITUDE: 4
SPINNING RATE (RPS): 30

MANUAL

SWEEP TIME (SEC): 50 | 100 | 250
SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500
FILTER: 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8
RF POWER LEVEL: 0.05

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: PIC-6

SOLVENT: CD3COCD3

REMARKS:

Varian

DATE: 10/5/82

OPERATOR: W. Manuel

60 MHz NMR
SPECTRUM NO.

CHART S-60T
MADE IN U.S.A.

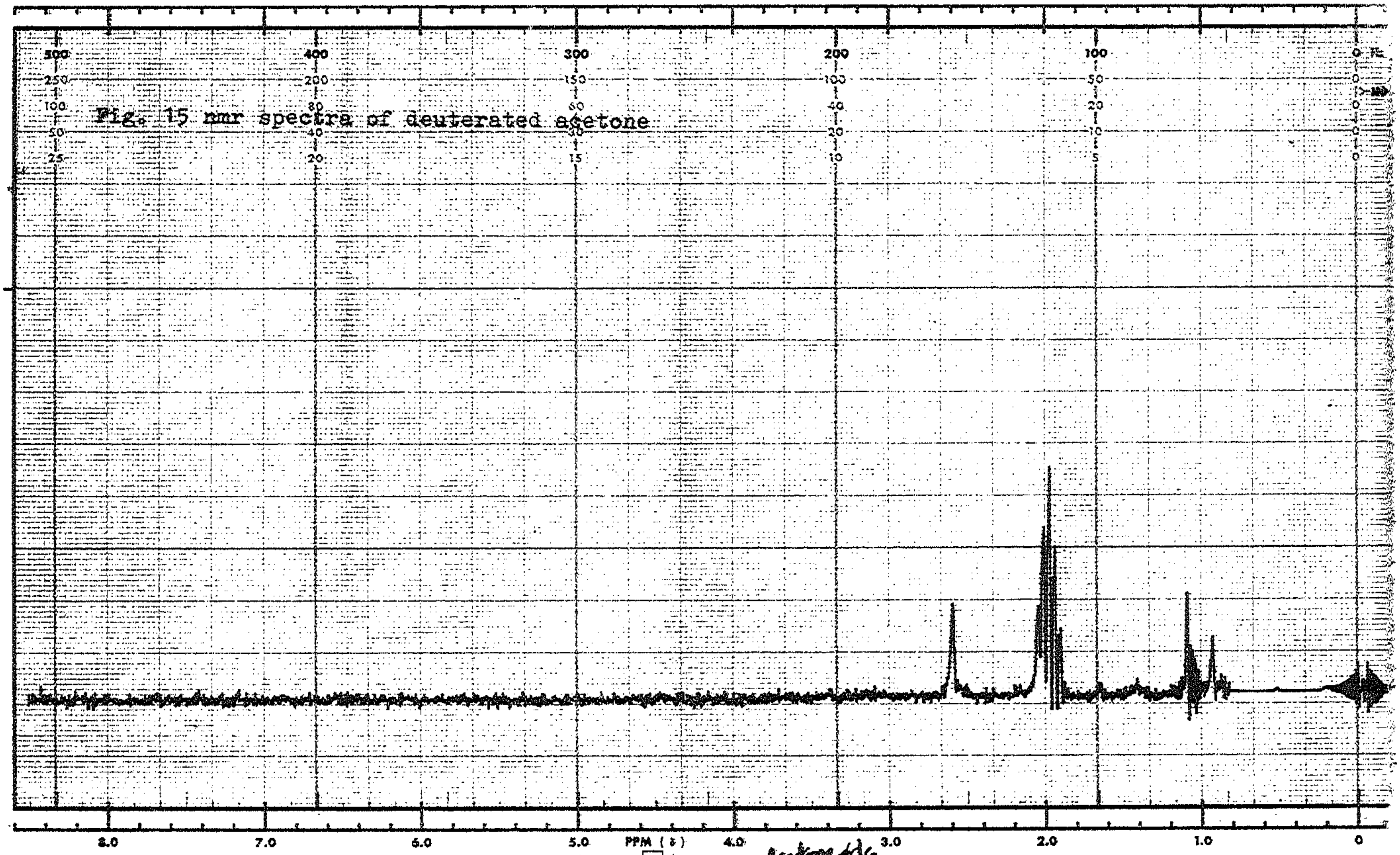


Fig. 15 nmr spectra of deuterated acetone

MANUAL

AUTO ☐

SWEEP OFFSET (Hz): 10X2.0
SPECTRUM AMPLITUDE:
INTEGRAL AMPLITUDE:
SPINNING RATE (RPS): 52

SWEEP TIME (SEC): 50 [✓ 250] (250)
SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500] (500)
FILTER: [✓ 1] 2 3 4 5 6 7 8 (2)
RF POWER LEVEL: .05 (.05)

SAMPLE: Acetone-d_6
SOLVENT: CD_3COCD_3

REMARKS:

varian
analytical instrument division

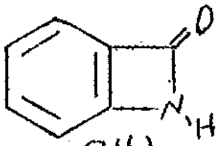
DATE:

OPERATOR:

60 MHz NMR
SPECTRUM NO.

The signal at (δ =3.0ppm) is assigned to an N-H proton. The moderate broadness is characterstic of NH protone which may under go exchange. This is in agreement with the β-lactam fused to benzene ring suggested by the ir spectra. The integration also gives a ratio of 4:1 for the aromatic protons and the proton at (δ =3.0ppm).

The combined results of the ir and nmr data strongly suggest that compound PIC-6 to be a β-lactam of the following structure (34)



(34)

An additional nmr of the sample in the flouro-acetic acid was run to see if the N-H proton will disappear from the (δ =0-10ppm) range. This was actually observed (fig 13). The signal at (δ =2.0ppm) is a side band. This was confirmed by varying the spinning rate and observing the change in the signal. The one at (δ =2.34ppm) is due to a contaminantion with acetone. This was confirmed by running the nmr with added trace amounts of acetone.

Compound PIC-6 with its proposed structure is a member of a gorup of compounds called Anthranils, β-lactams or 2-azetidinones. Although analogous compounds with larger

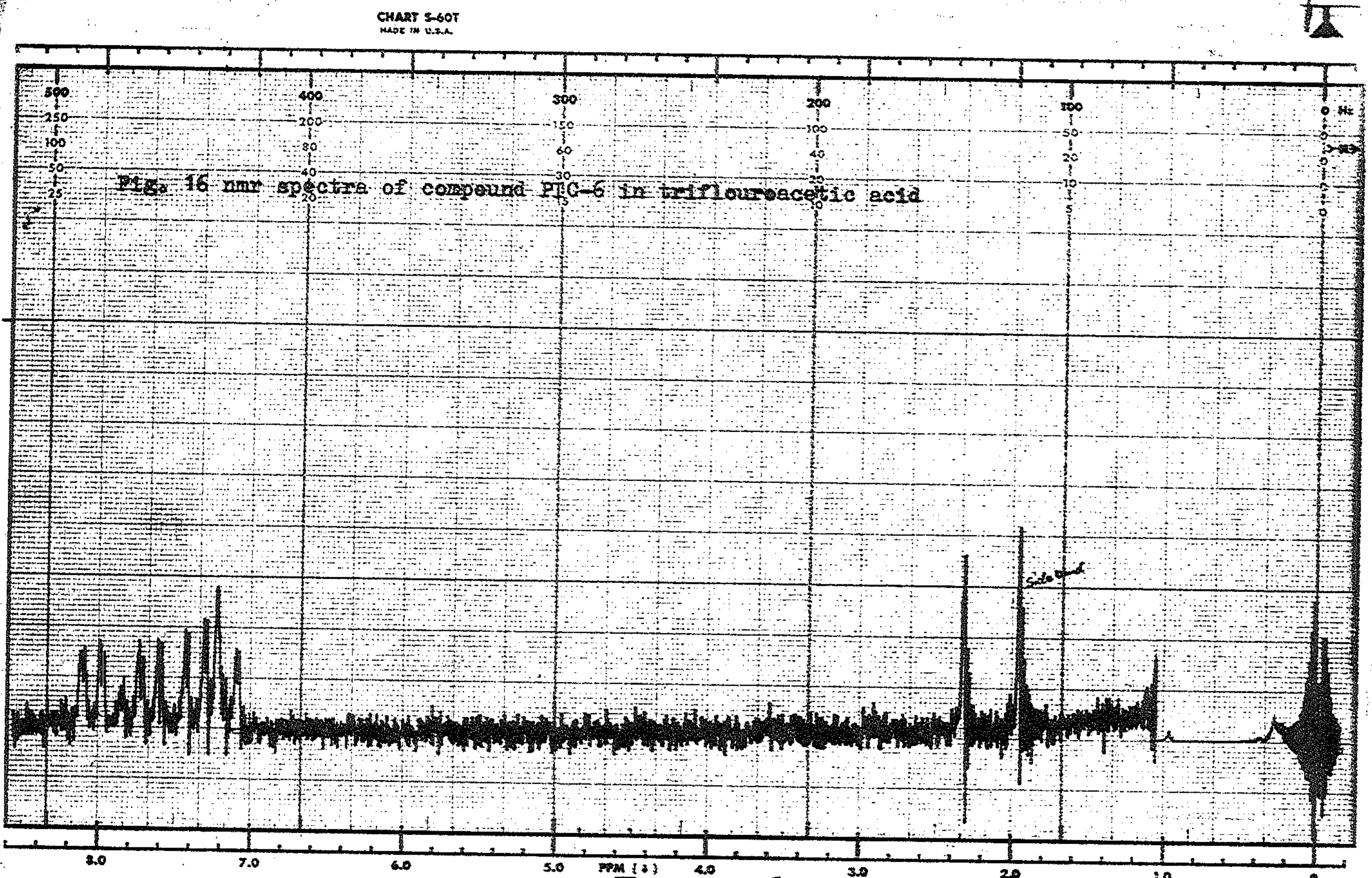


Fig. 16 nmr spectra of compound PIC-6 in trifloureacetic acid

PPM (δ)

MANUAL

SWEEP OFFSET (Hz): -------
SPECTRUM AMPLITUDE: 5X10
INTEGRAL AMPLITUDE: -------
SPINNING RATE (RPS): -------

SWEEP TIME (SEC): 50 [✓ 250]
SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500]
FILTER: [✓ 1] 2 3 4 5 6 7 8
RF POWER LEVEL: 0.01

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: PIC-6

SOLVENT: CF_3COOH

REMARKS:

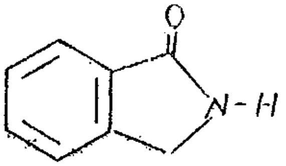
C-H

varian

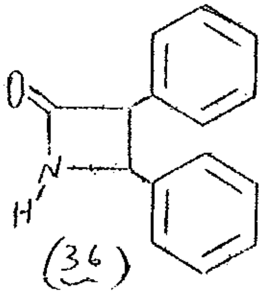
22/6/02

60 MHz NMR

rings (35) or different substition (36) are known;



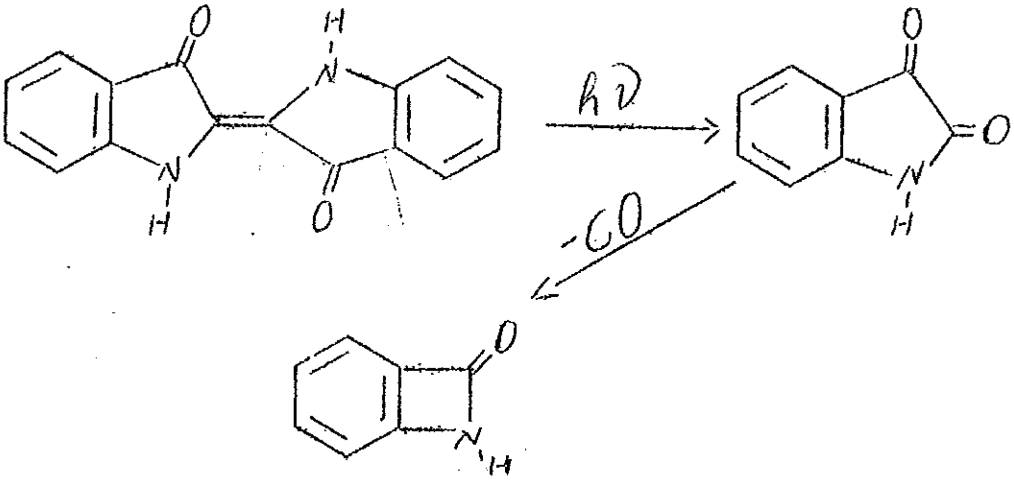
(35)



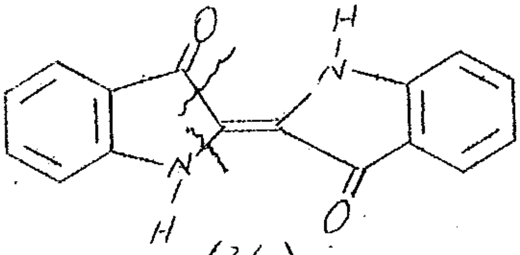
(36)

the compound (34) had proved impossible to synthesize

Even if the synthesis of the compound (34) has proved to be difficult; its probable creation from the decomposition of indigo is rather strong. First the compound could arise as a secondary product from isatin whcih could be formed by the photooxidation of indigo. This is possible if the isatin undergoes decarbonylation, a common feature of the photodecomposition of cyclic ketones.



The above mechanism might not be expected to place as the photodecomposition was done under N_2, and the photooxidation of indigo to isatin therefore being unlikely. The alternative proposal is for bond breaking to occur as shown below (36).



(36)

There are two additional supporting evidence for the possible formation of this compound. First; when isatin was photodecomposed under similar condition, it gave a product containing a compound with the same Rf value as PIC-6. Although additional comparison was not done, the t.l.c. shows isatin to photodecompose giving the compound PIC-6. Secondly, the mass spectra of the photodecomposition product of indigo always show a prominent peak at m/e= 119 which is the same as the molecular weight of the compound. (fig17)

Compound PDA-1

This white fiber like crystal was isolated from the photodecomposition product of N,N'-diacetylinindigo. Its melting point is 229-231°C and does not dissolve in non-polar solvents except moderately in benzene. It is soluble in methanol.

IR. (fig 12)

Th i.r. spectra (fig 12) immediately shows the absence of any N-H stretching vibration indicating that this fragment still contains the acetyl substituent. The carbonyl region (1780cm^{-1}) supports this deduction. The frequency is higher due to the presence of N-acetyl. The N-acetyl itself shows at 1720cm^{-1}. Also the fact that the C=O stretching results in only one peak indicates the absence of any N-H. The peak at 760cm^{-1} is due to an ortho substitution of benzene.

NO. 007-1494

PERKIN-ELMER

CONCENTRATION ______
THICKNESS ______
PHASE ______
REMARKS ______

SCAN MODE ACCY. ☐ SURVEY ☐
HI ENERGY ☐ CAL. ☐
RESOLUTION ☒
OPERATOR ______ DATE ______

SPECTRUM NO. ______
SAMPLE DA - 1.
Photodecomposition Product
ORIGIN of Diacetylindigo

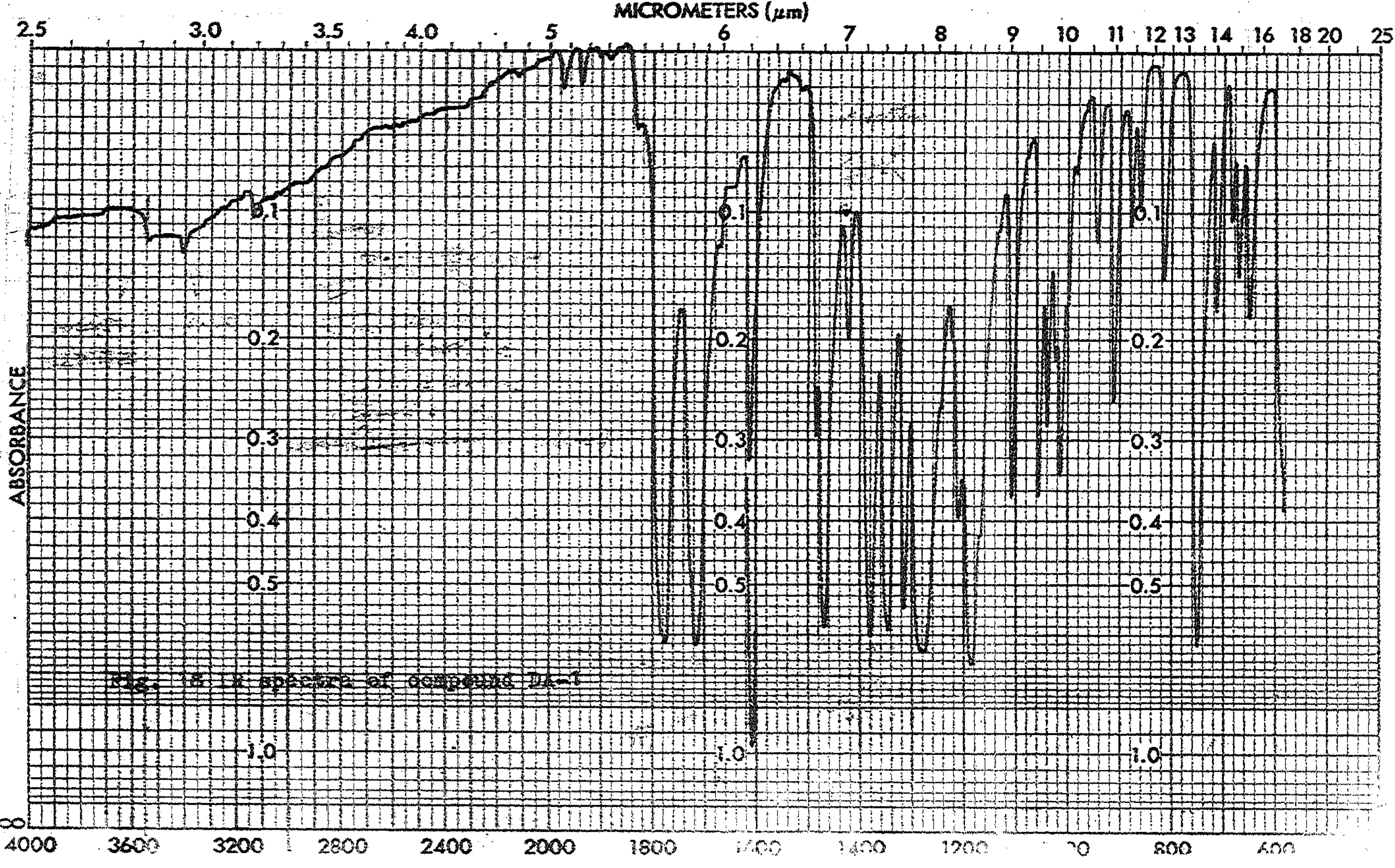


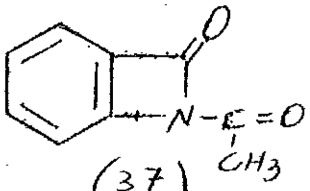
Fig. 18 IR spectra of compound DA-1

NMr. (fig 19)

The nmr shows the presence of aromatic protons a(δ =7.37ppm) .The rest of the signals between (δ =2.0ppm and δ =3.0ppm) indicate methyl protons near a hetroatom.

The available data are not sufficient to identify the compound completely. [illegible]

Although the nmr data alone does not clarify the [illegible]. The nmr and the IR together suggest the compound DA-1 to be an analogous N-acetyl derivative of the β -lactam (37)



(37)

In conclusion, the following findings can be summarized.

(i) Oxygen is the most important factor in the photofading of indigoid dyes.

(ii) Although slow, photofading can occure under inert nitrogen atmosphere.

(iii) Photodecomposition products under oxygen at mosphere are few due to the large yield of isatin but at least half a dozen under nitrogen.

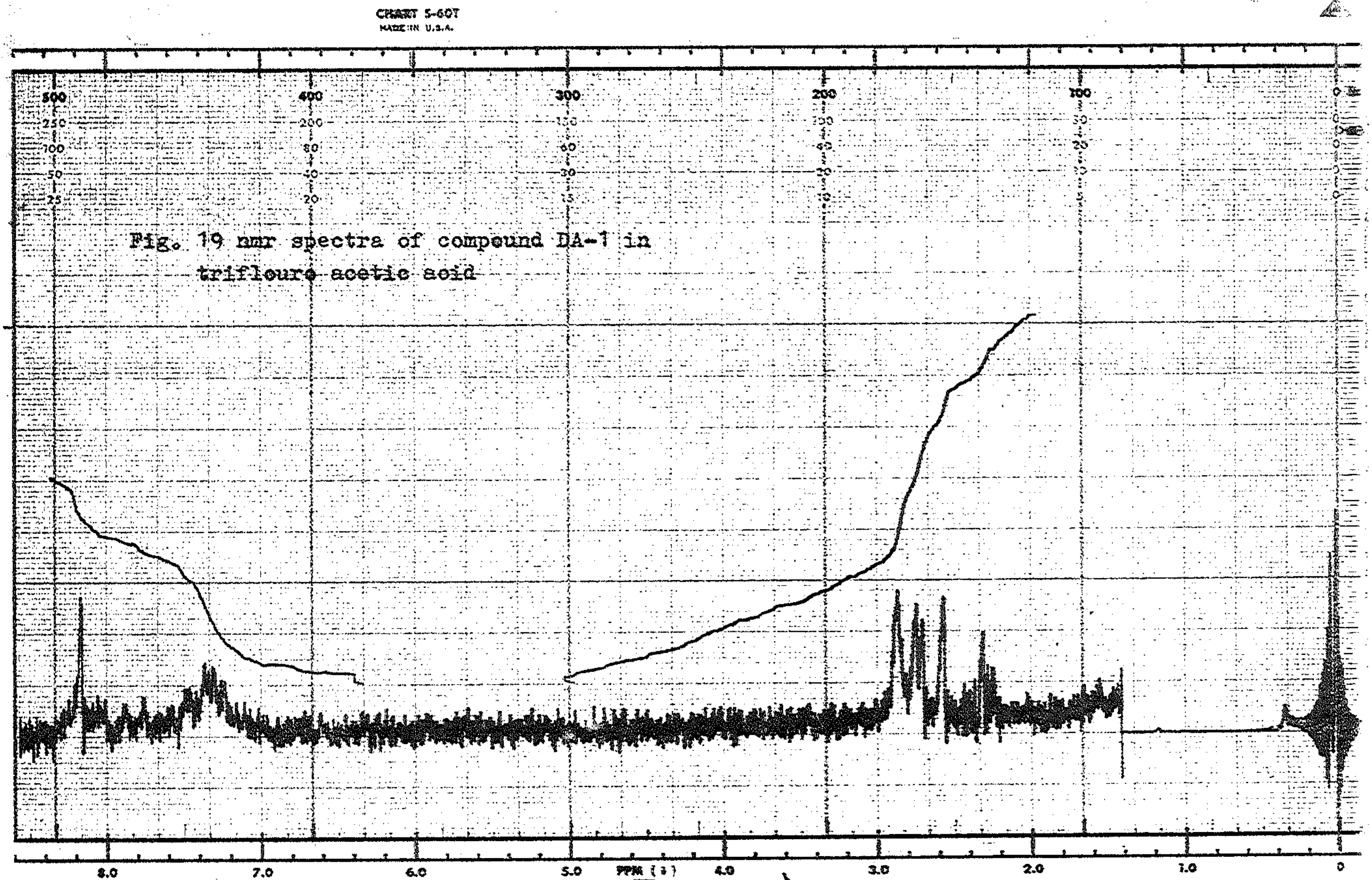


Fig. 19 nmr spectra of compound DA-1 in triflouro acetic acid

MANUAL

SWEEP OFFSET (Hz): ________
SPECTRUM AMPLITUDE: 5X10
INTEGRAL AMPLITUDE: 8
SPINNING RATE (RPS): ________

SWEEP TIME (SEC): 50 [✓ 250]
SWEEP WIDTH (Hz): 25 50 100 250 [✓ 500]
FILTER: [✓ 1] 2 3 4 5 6 7 8
RF POWER LEVEL: 0.05

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: PDA-1
SOLVENT: CF_3COOH

REMARKS:

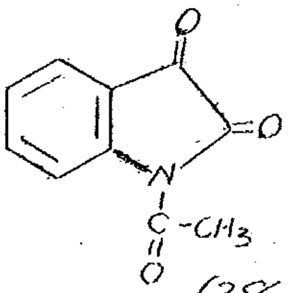
varian
analytical instrument division

DATE: 22/6/82

OPERATOR: U

60 MHz NMR
SPECTRUM NO. ________

If the analogous photooxidation of indigo is adabted here for N,N'-diacetlindigo the product(38) would be expected.



(38)

This product (N-acetyl isatin) would also be expected to be the major product in the diacetyl exposed under oxygen and would consequently be expected to decrease in yield as the environment is changed to air and nitrogen. That this did not happen at all, may be cited as a negative evidence for an indigo like photooxidation by molecular oxygen. Alternatively it may also be possible to conclude that photochemical decompositions such as ring opening, fission and rearrangements are much more facile and energetically favoured than photooxidation by molecular oxygen.

(iv) Photodecomposition of indigo is not severly affected by the choice of solvent.

(v) One of the photodecomposition products of indigo under nitrogen atmosphere is a β-lactam whose analogous component the N-acetyl derivative also being a product of the photodecomposition N,N'-diacetylindigo.

VI. EXPERIMENTAL

1. Purification of Reagents

1.1. Benzene

(a) Large quantities of solvents were required to dissolve sufficient indigo or N,N'-diacetylindigo to get reasonable quantities of photodecomposition product for analysis. A typical weight of photoproduct from 5 1 of benzene solution is about 400 mg. It thus becomes clear why a cheap and available solvent was chosen.

(b) Photochemical reactions are complex and re result in unusual and numberous fragmentation photoproducts. An attempt to find out the major photodecomposition products from a particular molecule could be more complex than desired if the solvent itself is also chemically active. Of the commonly available solvents benzene would be expected to be more or less inert towards the photochemical reactions that occur during exposure to sunlight.

In condensed phase or solution photochemical reactions, the solvent is a very critical factor. In addition, the small amount of photoproduct available from large qunatities of solvent (< 40 mg/l) makes it extremely essential to purify the solvent especially to make sure that it has virtually no residue on evaporation.

Reagent grade benzene filtered over dry calcium chloride using whatman No. 2 filter paper was further purified by distillation. Only the distillate which collected within a ragne of 1°C was taken. Care was also taken to discontinue the distillation when about 100ml of benzene was still left in the distilling flask.

It was also made sure that the solvent did not contain any impurities that may catalyse the photo decomposition of benzene itself during exposure to sunlight. The following procedure was adopted.

250ml of pure redistilled benzene was taken in a well cleaned flask with a ground glass stopper. Prior to exposure to sunlight the absorption spectra of 0.1ml benzene in 100ml pure methanol was recorded using a 1cm cuvette and methanol as reference. After one week of exposure to direct unfiltered sunlight; the spectra was again recorded. This procedure was repeated two more times each after two and three weeks interval respectively. A total of four spectra were recorded over an expsure period of seven weaks (fig 20). All spectra were recorded using a Pye unicam SPS 100 double beam UV-Visible spectrophotometer.

At the end of the 7 weeks exposure period. The purity of the solvent was again ascertained by spotting a 10ml

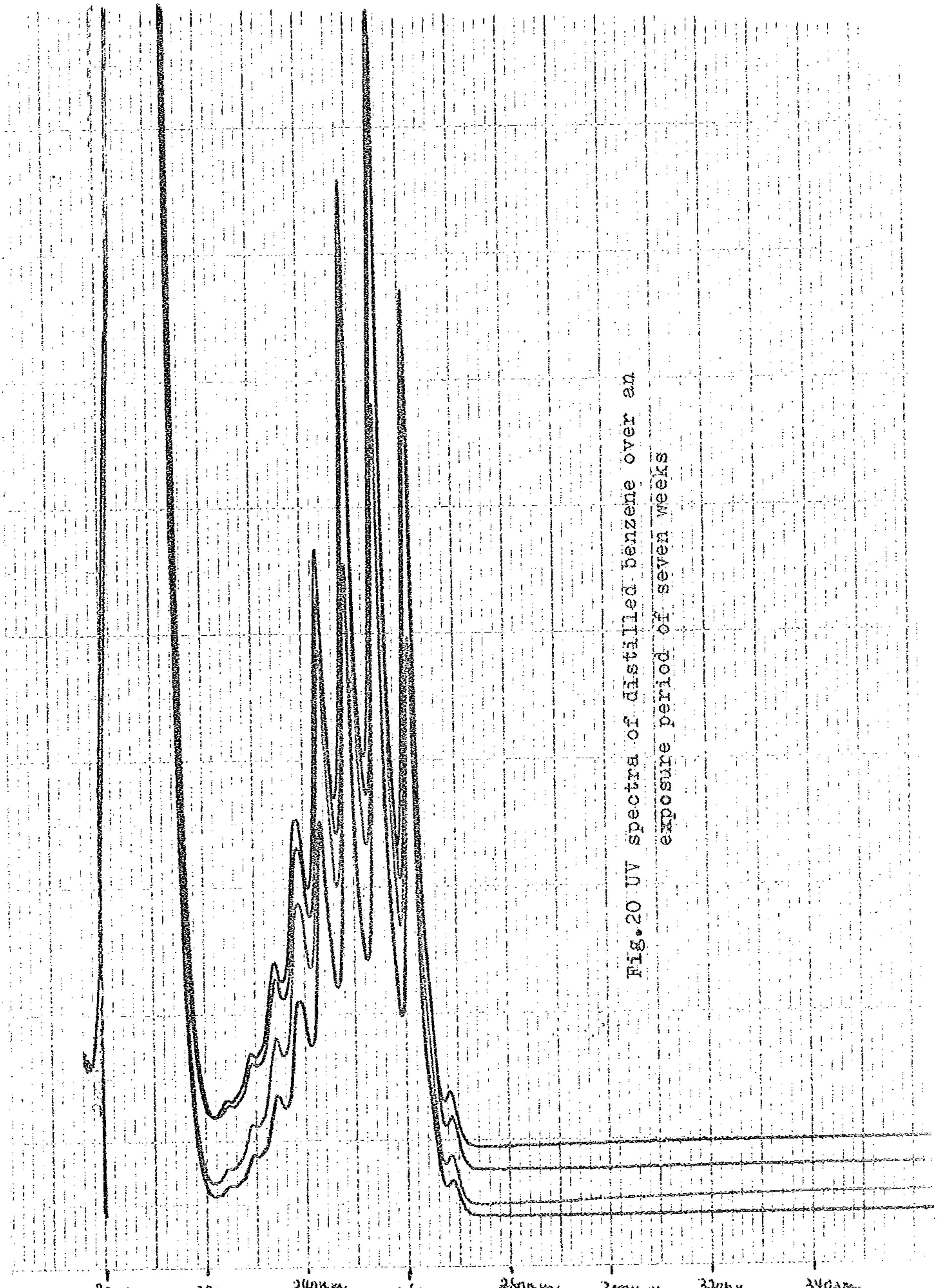


Fig.20.

Fig.20 UV spectra of distilled benzene over an exposure period of seven weeks concentrate of the originally exposed benzene on 0.25mm silica gel H_{254} plates using chloroform as a developing solvent.

Both the absorption spectrophotometric and t.l.c results show that no sunlight induced decomposition of benzene that could be detected by the above two methods occured.

1.2 Dyes.

Four of the dyes; thioindigoscarlet, 6,6'-diethoxy thioindigo; Thioindigo; and acenaphthenthioindigo were acquired in sufficient purity from GDR. Indigo was obtained from the AAU chemical store. It was purified by continuous soxhelet extraction with benzene. N,N'-diacetylindigo was synthesized according to published procedures[114].

A mixture of 5 gm of indigo 25ml of freshly distilled acetylchloride and 40 ml of freshly distilled acetic anhydride was refluxed for 20 hrs until the dark blue color of the indigo changed to deep red. The N,N'-di acetylindigo was isolated from the rst of the reactants and recrystallised from benzene. The purity and homogeneity of the dyes were established by t.l.c and m.p determinations.

2. Preparation of Photofading of Dye Solutions

2.1 Comparative Fading Rates of the Five Dye Solutions

25mg of each of the five dyes; indigo, thioindigo, thionindigo scarlet, 6,6'-diethoxythioindigo and acenaphethen thio indigo were dissolved in enough redistilled benzene. Each of the flasks were tightly closed under normal atmosphere and exposed to sunlight. The absorption spectra of each dye was recorded before the dyes were exposed to sunlight. The second spectra were recorded after 4 hours and was repeated two times every four hours the same day. The exposure recording intervals were gradually lengthened until all the dyes showed no measurable absorbance. The expsures were made over the months of October, November and December, These three months are usually free from any rains in Ethiopia. Only day light hours were counted. The recordings were made on a Pye-Unicam SP8-100 double beam UV-Visible spectrophotometer using a 1cm quartz cuvette and distilled benzene as reference.

2.2 Comparative fading rates of indigo & N,N'-diacetylindigo

The fading rates of indigo and N,N'-diacetylindigo were compared by dissolving 25mg of each dye in redistilled benzene and the usual procedure described in 2.1 was followed. Recording was not made, instead only absorbance was compared.

For comparis on under nitrogen atmosphere; purified nitrogen gas was dubbled into each of the dye solutions at a pressure of 5lb/in^2 for 30 minutes and then the flasks were immediately tightly closed and exposed.

For comparison under oxygen atmosphere purified oxygen gas was bubbled into the solutions at a pressure of 5lb/in^2 for 30 min. and then the flasks were immediately tightly closed and exposed.

In every case during the exposure to sunlight to induce photofading; sufficient space was left in the flasks to ensure as much contact as possible with the atmosphere above the solution in the flask and the dye solution itself.

For comparison of the photofading of the dyes in various solvents, each of the solvents used except benzene was distilled and dried by molecular sieve 5A before use. For benzene the already described purification procedure was employed.

3. Photodecomposition of Indigo and N,N'-Diacetylindigo

3.1 Photodecomposition of Indigo

For comparison of the photodecomposition of indigo; 50 mg of the dye was dissolved in redistilled benzene under normal (air) atmosphere; oxygen and nitrogen before exposure. After decomposition was complete; the solvent was removed by rotavapor under reduced pressure until about 15ml of each solution remained. These were compared with each other by using 0.25mm silcagel plates impregnated with' a fluorescent indicator for visualisation of the component at 254nm. The solvent chosen for development was basic and polar (methanol + ethanol + Ammonia; 10:88:2). The spots were visualised at 243nm and also in iodine vapour.

3.2 Photodeompositlon of N,N'-Diacetylindigo

The photodecomposition of N,N'-Diacetylindigo were made along a similar procedure. The flasks containing the benzene solutions of the dye were sealed under air, oxygen and nitrogen. After photodecomposition was complete; the solvent was removed by a rotovapor at a reduced pressure untill 15ml of each solution remained. These solutions were used for comparison by t.l.c;0.25mm thick sillica gel plate with flourescent indicator was used. The solvent chosen for development was benzen + chloroform (1:1).

3.3 Photodecomposition studies using Different Solvents.

Benzene, toluene, cyclohexane and chloroform were used for dissolving indigo and N,N'-diacetylindigo. The solvents were all purified as described before. The solutions were bubbled with nitrogen gas for 30 min before to sunlight. When the exposure and subsequent decomposition was complete; the solvents were removed by rotavapor under reduced pressure until 15ml of each dye solution remained.

These concentrates were the treated to a similar t.l.c analysis as described in 3.2 .

4. Isolation and Identification of the major photodecomposition Products of Indigo

4.1 Isolation

In order to recover sufficient amounts of the photodecomposition product, several flasks of 51 capacity were used to dissolve the indigo dye in redistilled benzene. Each flask was bubbled with nitrogen gas for 30 min. before exposure to sunlight. All flasks were properely closed and sealed. The exposure of the dye solution were done on a continuous basis to collect as much photoproduct as possible.

The solution was filtered and the solvent was removed on a rotavapor under reduced pressure and a yelloishbrown oily solid obtained. Enough photodecompostion was done until 2.4gms of the photoproduct was obtained. The product has a penetrating and not unpeasant odor.

Preliminary, repeated t.l.c runs show five distinct components and a sixth one that doesnot move from the spot. Solubility tests with non-polar (n-hexane); moderately polar (chloroform); and very polar (methanol) solvent showed that the products contain components with wide solubility differences and could be separated by column chlomatography without undue difficulty.

The two components isolated which were chosen for characterization are ST-1 and PIC-6. These were purified for IR,nmR, and Mass spectrometry by preparative t l.c using 2.0 mm Thick silica gel plates.

4.2 Identification

For the characterization attempts of the three compounds classical and instrumental techniques were used according t› established procedures.

Melting points were determined on a unimelt apparatus; temperatures are uncorrected.

I- spectra was recorded in a Perkin Elmer 727E instrument

nmR spectra was done using a varian T-60A nmR spectrometer at 60 MHZ.

UV-Vis spectra were recorded on a SP8-100 pye Unicam and Perkin Elmer model 727E double beam spectophometers.

Lassinge's Test was done in accordance with published procedures[115].

5. Isolation and Identification attempts of the major Photodecomposition Products of N,N'--Diacetylindigo

5.1 Isolation About 1gm of N,N'-diacetylindigo was dissolved in sufficient purified benzene purged thoroughly with nitrogen and sealed under the same gas. The dye solution was exposed to unfiltered sunlight until decomposition was complete.

The solvent was removed by rotavapour under reduced pressure. A toal of 820 mg of photoproduct was collected. A product insoluble in ethanol was immediately isolated. The product (PDA-1) was a white fibrous solid insoluble in most organic solvent but very slightly soluble in benzene, methanol and ethanol.

T.l.c on 0.25 mm silica,gel H_{254} showed a single component. Even though the photoproduct shows three major component on tlc,the attempt to separate the photoproduct left after the isolation of the product PDA-1 failed due to extensive decomposition of unknown origin. The T.l.c of the left over dark yellow viscous substance showed the presence of at least 13 components visible by ultraviolet light either at 254 nm or 325 nm.

The product PDA-1 gave a total yield of 80 mg. The percentage yield was = 9.7% the melting point was determined with a unimelt apparatus, M.P-229-231°C, temperature is uncorrected.

nmr spectrum could not be recorded as the product PDA-1 could not be dissolved in sufficient quantity either in deuterated acetone, or chloroform and other solvents that could be used for nmr like carbon tetrachloride.

Ir spectrum was taken on a Perkin Elmer IR recording instrument, model 727E; ultra violet spectrum was recorded on a Perkin-Elmer model 555 double beam spectrophotometer.

A column was prepared using sl'ca gel (60-120mesh) specially prepared for column chromeaography. A set of 9 solvents with a gradually increasing polarity were used as eluting solvents. These were; n-hexane, m-hexane + benzene; benzene, benzene + chloroform, chloroform, chloroform + Acetone; Acetone; ethanol, methanol. The separation was continuously followed by t.l.c. A total 40 fractions were collected .

(a) The first component was a colorless substance with an odor faintly similar to DDT. tlc showed one component only 0.25 mm silica gel H_{254}; solvent = n-hexane. totally yield = 6.1 mg; % $\underline{=}$ 0.27%

(b) The first component was a yellow oil (ST-1) showing a single spot with tlc; 0.25mm silica gel H_{254}; solvent benzene totaly.
total yield = 142 mg ; % 6%

(c) The third component (PIC-3) is a brownish Viscous substance tlc showed one component only. 0.25 mm silica gel H_{254}; solvent: chloroform. total yield ≃ 142 mg ; % 6%

(d) The forth component (PIC-6) is a brown solid showing a single component by tlc. 0.25 mm silica gel H_{25} solvent:ethanol total yield ≈ 320mg; % ≈ 10%

(e) The fifth component (PIC-8) a yellowish visco substance is not a single substance tlc showed two very closel- moving spots and a very small amount of a third which was tentatively identified as isatin by t.l.c total yield 438; % 18.2%

(f) The rest of the photoproduct consisted of a dark brown component which did not elute even with methanol

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