

IISc THESES ABSTRACTS

Thesis Abstract (Ph.D.)

Polymer and ion-exchange waveguides for integrated optics: some studies by K. V. Avudainayagam.

Research supervisors: A. Selvarajan and M. Ramakrishna Rao.

Department: Physics.

1. Introduction

Integrated Optics (IO) as the name implies deals with the fabrication of optical components in thin films on monolithic substrates and the integration of several such components to form compact optical circuits and systems¹. The potential of this field to aid optical communications and to serve the medical and industrial field through the development of various optical sensors and optical instrumentation is very promising. The key element of IO is the optical waveguide. A study of the design, the fabrication and the characterisation of different waveguides using polymers and ion exchange technique was undertaken. First, planar waveguides were formed using polymers and by silver ion exchange in soda-lime glass substrates. These were characterised by using prism couplers. Some of the interesting optical properties of the polymers and the ion exchange process were then investigated. The results were used to make channel waveguides in the form of branching circuits that could act as power dividers or as star couplers in fiber optic communication systems.

2. Fabrication

The waveguides studied were generally of the planar type in which a material of higher index is deposited on a substrate of lower index. Commercially available microscope glass slides were used as substrates. Extreme care was taken to clean the substrates to ensure the removal of all kinds of impurities before the formation of waveguides.

To form polymer waveguides, several solution deposition techniques were tried. Spin coating method was found to offer good control of thickness and uniformity of films. While forming the films of polystyrene, the waveguides were found to be highly scattering when the spinning duration was long. This was due to the rapid evaporation of benzene (used as solvent) leading to the formation of strains in the films. By making the spinning time short, these strains were avoided. Similarly, in the case of Epotek epoxy films, it was found to be necessary to form the waveguides only after a few hours from preparing the solution. Otherwise, the solution did not stick to the substrate and formed a number of droplets on the surface. Thus, for a successful realisation of low-loss waveguides using polymers, the fabrication processes are to be carefully studied and controlled. To form ion-exchange waveguides, the inside of a stainless steel vessel was fully covered with a pure, thin aluminium sheet and the salts of silver nitrate and sodium

nitrate were taken in it in the required proportion. The vessel was kept in a temperature-controlled furnace. The substrates were cleaned and tied with thin copper wires. These substrates were pre-heated almost to the same temperature as that of the melt before introducing them into the melt. After being kept in the melt for the required time substrates were taken out, cooled quickly and cleaned to remove the salt sticking to their surfaces.

3. Characterisation

The important parameters that characterise an optical waveguide are its thickness, refractive index and the light propagation loss in it. Prism couplers offer the most simple and efficient method of measurement of optical properties of thin film waveguides². Besides being non-destructive, they require only angular measurement to determine the modal properties of waveguides.

In the present study, a symmetric prism coupler was used for the measurement of mode angles in terms of effective indices of refraction. During this study, an observation of back-scattered m -lines was made use of for improved angular measurements³. An input-output prism coupler combination was used for the measurement of light propagation loss in the waveguides. From the observed effective indices, to calculate the refractive index and thickness of the film, the dispersion relation as given by P. K. Tien was made use of². This relation being transcendental in nature it has to be solved by numerical computational methods. For most of the practical applications wherein the optical confinement is strong, one may make use of Marcatili's analytical approximation, which avoids the use of computer and is given as,

$$t = \frac{(m+1)\pi}{2\pi n_f \cos\theta_f} - \frac{1}{k(n_f^2 - n_s^2)^{1/2}} - \frac{1}{k(n_f^2 - n_c^2)^{1/2}} \quad (1)$$

The polymer materials studied here had refractive indices around 1.560 and these were coated on glass substrates of index 1.513. The Marcatili's approximation was found to hold good for such films. The result of modal analysis carried out on an Araldite film with index 1.552 thus formed is given in fig. 1. The continuous lines in fig. 1 show the exact solutions and the discrete points correspond to the solutions obtained using relation (1). It can be seen that there is an excellent agreement of the two results except near the cut-off region. The plot in fig. 1 is very useful in choosing the waveguiding properties of films for any given application.

4. Waveguides

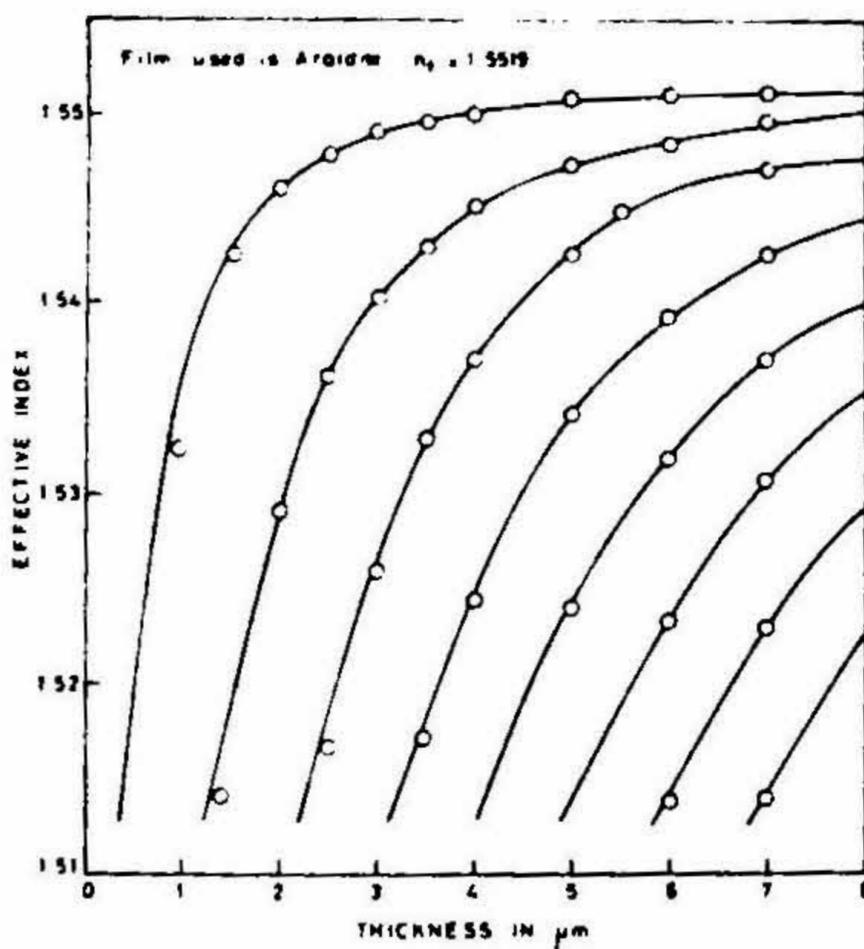
4.1 Polymer waveguides

In modern science and technology, polymers play a key role. Their optical properties are yet to be fully exploited. It is particularly promising in the field of IO. In this study, waveguides were formed using polymers like polystyrene, polycarbonate, polyester, polyurethane, and epoxy resins of Araldite, Dobekot and Epotek. These were characterised using prism couplers and the results are presented in Table I. Then birefringence was checked in them by measuring their indices of refraction for TE and TM modes. Only polystyrene films showed large stress birefringence which was removed on heating. Quite often it may be necessary to have a waveguide of specified refractive index. A material with the required index or refraction may not be readily available. In such cases, a mixture of two different materials having higher and lower indices can be used.

Table I
Properties of the polymer films studied

Film	Solvent	Thickness ± 1 in μm	No. of modes	Index $\pm .0005$	Loss dB/CM
Polystyrene	Benzene	1.6366	2	1.5887	4.4
Polycarbonate	Methylene chloride	1.2300	2	1.5770	5.6
Polyurethane	-do-	1.2550	2	1.5575	High
Epotek-epoxy	-do-	4.780	6	1.5745	1.6
Araldite	Methyl- ethyl- ketone	3.3831	4	1.5517	2.8
Dobekot	-do-	3.7220	5	1.5661	2.0
Polyester	Benzene	1.525	2	1.5670	High

With this in view, a study was made on the variation of the refractive index of a mixture of PMMA and polystyrene using benzene as solvent. The index of the resulting film was found to vary proportional to the ratio of the weights of the polymers. To realise waveguiding patterns in thin films, selective photo polymerisation is normally made use of. In this method, a polymer doped with a monomer and a photosensitiser. Using this mixture film is cast. A selective region is then exposed to UV radiation. This causes the monomer to polymerise in the exposed region only. Then the monomer is removed from the unexposed region. This leaves the film doped with the monomer in selective regions. The presence of monomer affects the index of the film. In the present study selective photopolymerisation was found to be effective when the matrix solution of Epotek-epoxy resin methyl acrylate monomer and benzoin ethylether was used to cast films. This was useful since the Epotek epoxy showed best loss among the films studied. The Araldite PZ820 resin was found to polymerise without the addition of hardener. This resin has a physical consistency which is very suitable to form fibers. This property is lost when it is mixed with the



Curves are exact solution of characteristic equations. Points are solutions after Marcatili's analytical approximation.

FIG 1. Characteristics of planar waveguide (verification of marcatilis approximation).

hardener. Making use of this property, some of the fiber branching waveguide patterns were formed on glass substrates which seem to form a very useful component for fiber optic applications.

4.2 Ion-exchange waveguides

One of the simplest and most versatile methods of forming optical waveguides and components for IO is the ion-exchange method⁴. This method offers a variety of means to control the index distribution of the waveguide. In order to establish the formation of silver-ion-exchange waveguides in locally available microscope glass substrates, waveguides were formed in dilute melts of AgNO_3 in NaNO_3 . Three sets of several samples were prepared varying the melt concentration and diffusion time. Then the effective indices of the samples were measured using prism couplers. The index distribution in each of these samples was shown to follow a second order polynomial distribution (fig. 2). The continuous lines in this figure correspond to the theoretical values obtained assuming a second order polynomial index distribution and the discrete points indicate the values obtained from experimental conditions and observations. The agreement between these values is excellent except for lowest order modes. Using this plot, for any diffusion time and temperature, one could have a clear idea of how many modes will be supported and the corresponding effective indices that determine the propagation characteristics of any waveguide formed by this method.

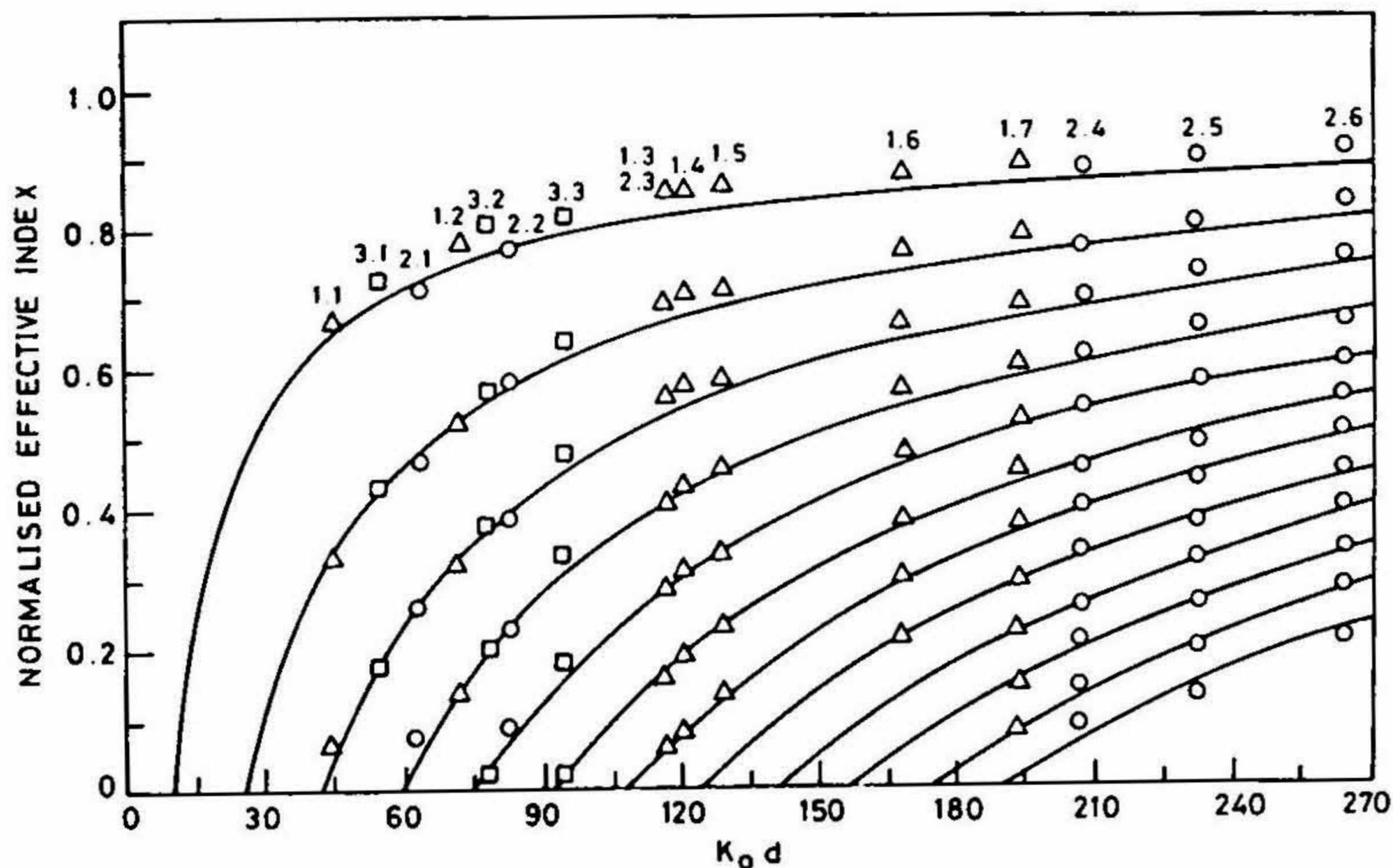


FIG 2. Characteristics of waveguide with second order polynomial index distribution.

4.3 Branching optical waveguides

Using strip loading by ion exchange, ridge formation in an ion-exchange waveguide, and polymer fibers, three types of novel branching waveguides that have some advantage over their conventional counterparts were formed and studied. In the strip-loading waveguide, loading was achieved by making use of ion exchange underlay. This enables one to store the guiding patterns in the substrate and replenish the planar waveguiding overlay any time. Ridge waveguides were formed by masking the branching pattern and etching the rest of the region of an ion-exchanged substrate slowly in a controlled manner using very dilute HF acid. In waveguides thus formed, the optical confinement will be strong due to the presence of silver ions in the ridge region. Fiber waveguides formed using Araldite PZ 820 resin, offers one of the simplest ways of forming branching channel waveguides having low loss. They form natural junctions by their physical property, which are very smooth and could be used to distribute optical power efficiently between different fibers and thus can be used as couplers.

5. Conclusion

The study clearly shows that ion-exchange process and polymers play a key role in IO and they are worthy of further investigations. The performance of devices developed in this study is promising. Besides the polymer and ion exchange waveguides reported above, simple methods were developed to fabricate geodesic lens, channel waveguide and a star coupler during this study. However, these methods reported in the appendix need further in-depth study.

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Thesis Abstract (Ph.D.)

Intramolecular interactions in porphyrin systems by G. Bhaskar Maiya.

Research supervisor: V. Krishnan

Department: Inorganic and Physical Chemistry

1. Introduction

The light reactions in photosynthesis involve a primary donor and an acceptor to accomplish ultra-fast photoinduced electron-transfer. Many intramolecular systems comprising of a porphyrin donor covalently attached to organic π -acceptors have been reported¹. Model systems that describe the redox and spectral features of the primary donor unit (the "special pair" chlorophyll)

in photosynthetic systems have also been studied². The present study is taken up with a view to develop a comprehensive understanding of the intramolecular photochemical electron-transfer and elucidate the possible nature of the primary donor in photosynthesis through model systems. These investigations include studies on novel model Schiff-base porphyrins to duplicate the spectral behaviour of the *in vivo* chlorophylls.

2. Experimental programme

Synthesis of diverse intramolecular donor-acceptor systems has been accomplished by condensing together 5(hydroxyphenyl) 10, 15, 20 triphenyl porphyrin and chloroderivatives of nitroaromatic π -acceptors in DMF (fig. 1). The preparation of *meso*-tetrakis (benzo-15-crown-5) porphyrin (TCP) and its metalloderivatives has been carried out using reported procedures³. The Ni(II)/Cu(II)TPP aldehydes were condensed with various mono- and di- amines to obtain Schiff-base porphyrins. The spectroscopic (optical absorption/emission, ¹H NMR and EPR) and electrochemical techniques have been used to characterize these compounds. On line irradiation of Zn(II) derivatives of donor-acceptor porphyrins has been carried out on ~0.1 mM solutions of porphyrins in an EPR cavity using a Xenon arc lamp as the light source.

3. Main results and conclusions

The distance between the donor and acceptor as well as their relative orientations have been varied in intramolecular donor-acceptor systems by linking the acceptor group at either *o*, *m* or *p* positions of one of the *meso* aryl rings of tetraphenyl-porphyrin. The choice of ether group as a source of covalent linkage is proved to be ideal since they are conformationally mobile and

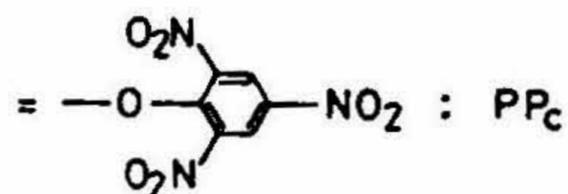
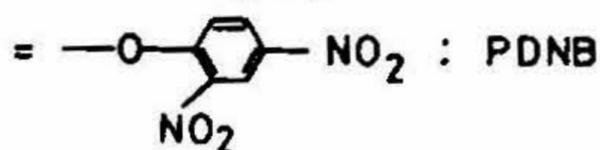
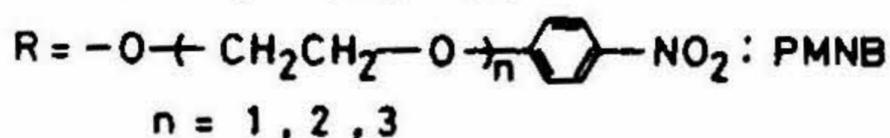
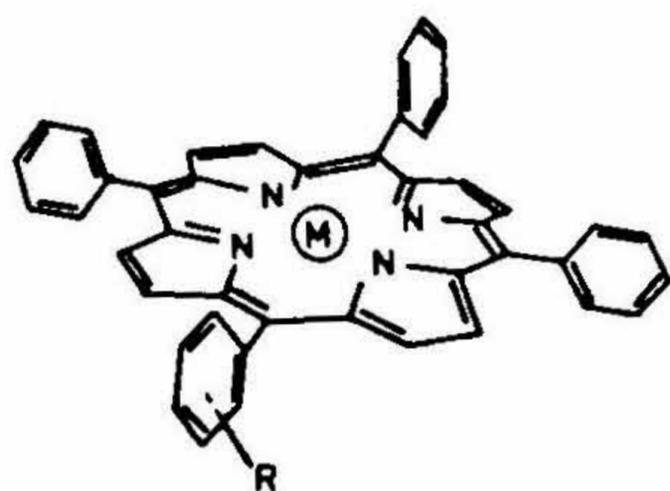


FIG 1. The chemical structures of donor-acceptor systems.

hydrolytically inert. The optical absorption, ^1H NMR and EPR spectroscopic results reveal the presence of π - π interactions in these systems. It is found that the strength of this interaction decreases rapidly with (i) the increasing distance between the donor-acceptor for a given donor-acceptor pair and (ii) the increasing reduction potential of the nitro-aromatic acceptor group (phenoxy > mononitrophenoxy > dinitrophenoxy > trinitrophenoxy), for a fixed donor-acceptor distance and orientation. The spectroscopic results also indicate that the "spacer" ether fragments in these systems are in "folded" conformation in order to facilitate efficient π - π interactions. The centre-to-centre distance between the porphyrin and the acceptor in different donor-acceptor pairs found to vary from ~ 6.0 Å to ~ 13.0 Å depending on the nature of the substituent.

The singlet emission data on free base as well as Zn(II) derivatives of picrylporphyrins (PPc) corroborate with the results of absorption spectroscopy. This indicates the presence of CT interactions in the excited states. The relative fluorescence quantum yields of these donor-acceptor systems decrease with increasing dielectric constant values of the solvents suggesting electron-transfer from the singlet excited state of the donor contributes significantly to the fluorescence quenching process. The results of on-line irradiation of these compounds in EPR cavity substantiate this point of view. Irradiation of ~ 0.1 mM (CH_2Cl_2) solutions of ZnPPc in an EPR cavity results in the generation of signals at $g = 2$ region. Analysis of the EPR spectra suggests that these signals are due to radical pairs ($\text{ZnP}^{+\cdot} \sim \text{Pc}^{-\cdot}$) generated as a consequence of intramolecular excited state electron-transfer in these systems. It is interesting to note that the $t_{1/4}$ values for the decay of the EPR signals and the relative ultimate saturation yields for the production of $\text{ZnP}^{+\cdot} \sim \text{Pc}^{-\cdot}$ depend on the distal and orientational parameters (Table I). An estimate of the free-energy change accompanying the excited state electron-transfers (ΔG_{et}) has been made. It is found that the ΔG_{et} values are exergonic for singlet excited state electron-transfer and endergonic for the corresponding reaction from the excited triplet state.

Table I

The decay times and quantum yields of the light-induced radical pairs of the porphyrin-acceptor systems

Compound	300 K		140 K		$\Delta G_{\text{et}}^{(c)}$ (meV)
	$\phi_{\text{EPR}}^{(a)}$	$t_{1/4}^{(b)}$ (min)	$\phi_{\text{EPR}}^{(a)}$	$t_{1/4}^{(b)}$ (h)	
ZnPpPc	0.27	3.0	0.27	1.5	-460
ZnmPPc	1.00	10.0	1.00	2.5	-440
ZnoPPc	0.30	3.8	0.80	2.5	-430
ZnPpDNB	0.10	1.5	0.18	3.0	-380
ZnmPDNB	0.16	1.5	0.30	1.5	-340
ZnoPDNB	0.66	1.5	0.64	1.0	-400

(a) Refers to relative ultimate saturation yield relative to the EPR signal intensity of $\text{ZnmP}^{+\cdot} \sim \text{Pc}^{-\cdot}$ which is taken to be 1.0.

(b) The time required for the EPR signal intensity to reduce to 25% of the original value.

(c) $-\Delta G_{\text{et}} = E_{1/2}(\text{D}/\text{D}^{+\cdot}) - E_{1/2}(\text{A}^{-\cdot}/\text{A}) - E_{0-0}^{\text{p}}$ where $E_{1/2}(\text{D}/\text{D}^{+\cdot})$ is the oxidation potential of the donor, $E_{1/2}(\text{A}^{-\cdot}/\text{A})$ is the reduction potential of the acceptor and E_{0-0}^{p} is the 0-0 spectroscopic transition energy of the porphyrin.

Noncovalent porphyrin dimers are structurally analogous to the chlorophyll dimers which are known to be the primary donors in the photosynthetic function. Extensive electrochemical, spectroscopic and magnetic resonance studies on a series of noncovalent metalloporphyrin, TCP/MTCP [M = Mg(II), VO(II), Ni(II), Cu(II), Zn(II) and Mn(III)] dimers formed upon addition of K⁺ to MTCP have been carried out. It is found that the first ring-oxidation potentials of the dimers are less anodic (70–200 mV) relative to the corresponding monomers. Moreover, the optical absorption and emission data point out the existence of exciton-coupling in these dimers. Supermolecular formalism has been proposed to account for the electrochemical and spectral features. The EPR characteristics of the mono- and di-cation radicals of the dimeric ZnTCP ($g = 2.0032$ and $\Delta H_{p,p} = 0.45$ mT) and those of monocation radical of ZnTCP ($g = 2.0034$ and $\Delta H_{p,p} = 0.45$ mT) are found to be similar. This indicates that the unpaired electron on the dimeric ZnTCP is localized on one of the porphyrin rings which is in contrast to that found in the "special-pair" chlorophylls of the reaction centre complex of the bacterial photosynthetic system².

A description of the spectral features of the Schiff-base porphyrins of Ni(II)|Cu(II)TPP and the dibenzo 18-crown-6-derivative of these porphyrins is presented in the thesis. Red-shifts in the Q-bands (~ 40 nm) and/or broadening/shift in the Soret bands of both the monomeric and dimeric Schiff bases are observed upon addition of HCl/CF₃COOH. The changes in the optical and magnetic resonance (¹H NMR and EPR) spectral features upon protonating these compounds are ascribed to the charge-localization in the vicinity of the tetrapyrrole ring. The red shifts in the absorption bands upon protonation of Schiff bases have been explained on the basis of stabilisation of $e_g(\pi^*)$ orbitals of porphyrin. The latter arises from mixing the π^* orbitals of the substituent R group of the Schiff-base with the ring orbitals of the porphyrin. A quantitative estimate of these factors has been made from electrochemical and optical data.

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Thesis Abstract (Ph.D.)

X-ray studies on the structure and interactions of analgetic fenamates by V. Dhanaraj.

Research supervisor: M. Vijayan.

Department: Molecular Biophysics Unit.

1. Introduction

Non-steroidal anti-inflammatory drugs (NSAID) encompass a broad spectrum of compounds with varying degrees of analgetic, anti-inflammatory and antipyretic activities. In spite of the diversity

in their chemical nature, their biological activity is believed to be mainly due to their ability to inhibit the biosynthesis of prostaglandins¹. Inasmuch as these drugs are known to be enzyme inhibitors, a prerequisite for elucidating the molecular mechanism of their action is a thorough understanding of their molecular geometry, the non-covalent interactions they are likely to be involved in, and the geometric and electronic consequences of these interactions. This is sought to be achieved in this laboratory through the X-ray analysis of the drug molecules and their crystalline complexes with other suitable molecules². This ongoing programme has so far been concerned primarily with analgetic pyrazole derivatives. The previous work on fenamates (fig. 1), which is the common name for mefenamic acid, meclofenamic acid, flufenamic acid and niflumic acid, has been confined to the X-ray analysis of the individual free compounds³⁻⁷. The fenamate molecules essentially consist of three planar groupings, namely, two six-membered rings interconnected by an imino group and an *ortho* carboxyl group attached to one of the rings. The substituents on the other ring differentiate one fenamate from the other. A striking feature common to all the fenamate crystal structures is the near coplanarity of the carboxyl group with the ring bearing it and the imino nitrogen atom. Another interesting feature invariably found in these structures is the internal N-H...O hydrogen bond between the imino nitrogen and the adjacent carboxyl oxygen.

Having delineated the structural features of free fenamates, the obvious next step was the preparation and the X-ray analysis of their complexes. A major part of the thesis is concerned with this step.

2. Methods

Several attempts, made to prepare crystalline complexes of fenamates with basic amino acids, were not successful. Subsequent experiments were carried out with ethanolamine and choline, two basic molecules with considerable biological importance. These experiments led to the preparation of good single crystals of three 1 : 1 complexes, namely, (a) ethanolamine niflumate monohydrate, (b) choline meclofenamate monohydrate and (c) ethanolamine meclofenamate. The ethanolamine complexes are triclinic whereas the choline complex is orthorhombic. The niflumate crystals have one set of molecules in the asymmetric unit while two sets of crystallographically independent molecules are present in the crystals of the meclofenamates. The X-ray structure determination of the crystals was carried out^{8,9} using counter data employing the direct methods and the least squares technique.

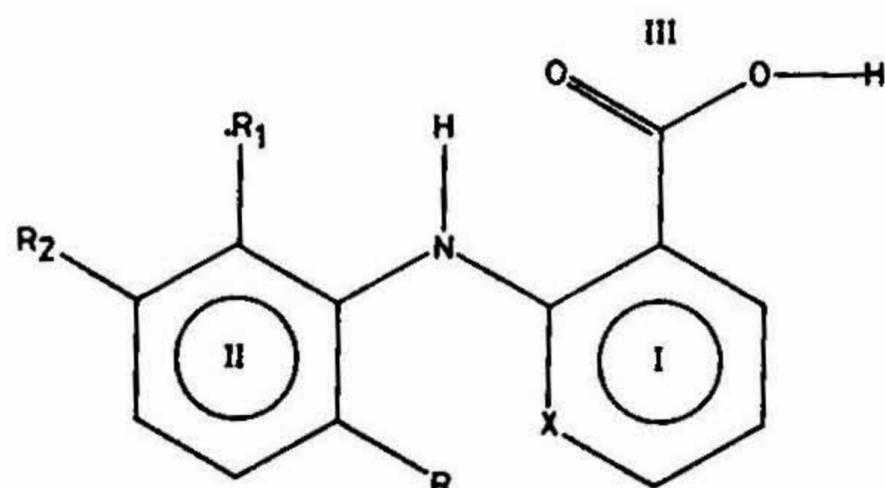


FIG 1. The general formula of fenamates. The Roman numerals indicate the designation of the planar groups in the molecule.

	R	R ₁	R ₂	X
Mefenamic acid	H	CH ₃	CH ₃	CH
Meclofenamic acid	Cl	Cl	CH ₃	CH
Flufenamic acid	H	H	CF ₃	CH
Niflumic acid	H	H	CF ₃	N

As indicated earlier, the fenamate molecules are essentially made up of three reasonably rigid planar groups connected by single bonds. The conformational flexibility of the molecule arising from possible rotations about these bonds was explored by conformational energy calculations employing semi-empirical methods. The calculations were performed for all the fenamate molecules in both the ionisation states.

3. Results and discussion

In each of the crystal structures containing fenamates analysed so far, half the molecules are related to the other half by a crystallographic or non-crystallographic inversion centre. The centrosymmetrically-related molecules are, however, not superimposable and are, therefore enantiomorphous in the solid state. Thus the molecules are formally asymmetric and the crystals contain a racemic mixture. However, it is not known whether rapid inter-conversion between the two isomers is possible in solution.

Interestingly, the invariant features of fenamate geometry, namely, the rigid coplanar geometry of the six-membered ring carrying the carboxyl group, the carboxyl group and the imino nitrogen atom, and also the internal hydrogen bond connecting the imino and the carboxyl groups, are retained even when the molecules interact strongly with other molecules, as in the complexes. The limited conformational differences between molecules and crystal structures result from the changes in the orientation of the second six-membered ring with respect to the rigid coplanar moiety. The results of conformational calculations also indicate that the flexibility of the fenamate molecules is restricted to a limited region of conformational space. The observed minimum regions largely correspond to a coplanar arrangement of the carboxyl group with the ring to which it is attached. This arrangement facilitates the formation of an internal hydrogen bond between the imino nitrogen and a carboxylate oxygen. Thus conformational calculations provide a theoretical rationale for the occurrence of the observed invariant features. The theoretical calculations are indeed in complete accord with the results of the crystallographic studies.

In all the three crystal structures, complexation is achieved primarily through ionic and hydrogen bonded interactions involving the deprotonated carboxylate group of the fenamate molecule. In the crystals of the complexes, the carboxylate groups, the ethanolamine or the choline molecules and water molecules, when present, form hydrophilic columns. The bridging imino nitrogen atoms occur at the periphery of the columns. The hydrophilic columns are surrounded and separated by hydrophobic regions made up of the two six-membered rings and the substituents on the second ring. This mode of packing is presumably a consequence of the amphipathic nature of the fenamate molecules.

The crystal structures and the results of energy calculations provide a basis for informed speculations on structure-activity relationships in fenamates. The repeated occurrence of the invariant features, referred to earlier, in all the available fenamate structures, including complexes, leads one to believe that they are a structural requirement for the pharmacological action of the drugs. The crystal structures conclusively show that the carboxyl group is the main, and almost the only, specific site of interaction of fenamates with other molecules. The X-ray results and the conformational calculations appear to indicate that mefenamic, meclofenamic, and flufenamic acids probably assume the same conformations when they bind to the appropriate enzyme in the prostaglandin synthetase system. They also provide a structural and conformational rationale for the somewhat different activity profile of niflumic acid.

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Thesis Abstract (Ph.D.)

Pathways in aromatic oxidation mechanistic studies on the reactions of aromatic substrates with periodic acid by B. M. Hosur.

Research supervisor: T. R. Kasturi.

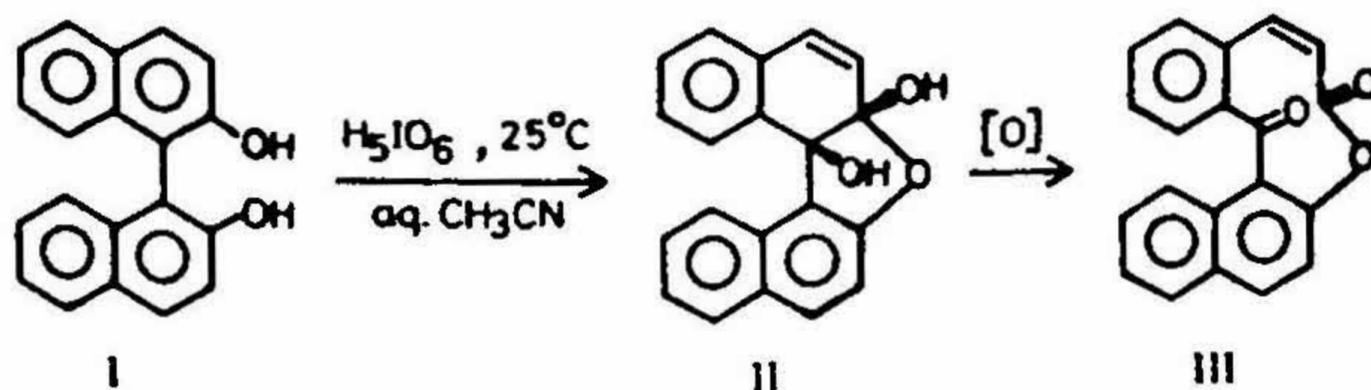
Department: Organic Chemistry.

1. Introduction

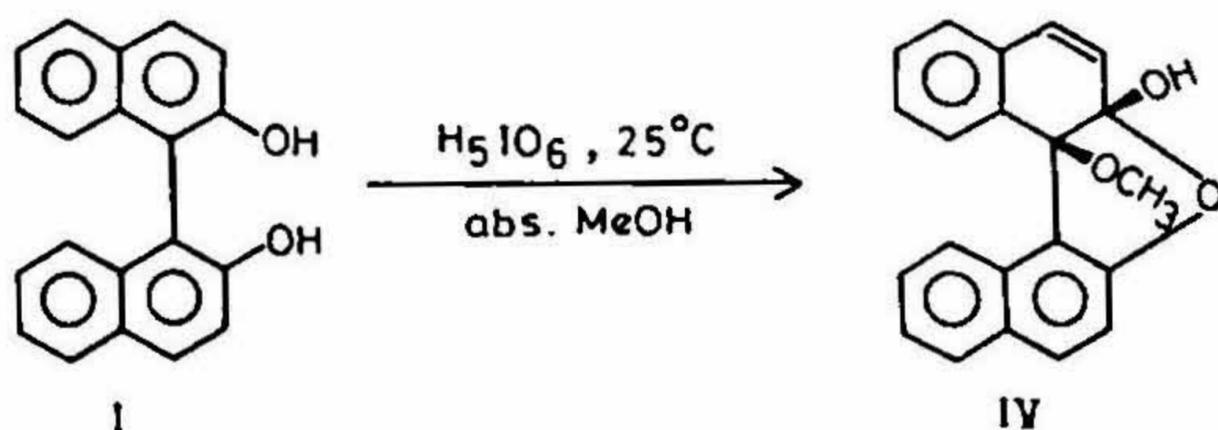
Periodic acid has been widely used as oxidising agent in degradative and synthetic organic chemistry. When Malaprade¹ introduced it for the cleavage of *cis*-glycols in 1928, it made much impact. The mechanism of cleavage of *cis*-glycols and related compounds by the involvement of a cyclic periodate ester intermediate is generally accepted^{2,3}. The mechanisms of oxidation of aromatic substrates (phenols, polycyclic aromatic hydrocarbons, aromatic ethers and aryl alcohols) is the subject matter of present thesis.

2. Main results and discussion

Oxidation of 2,2'-dihydroxy-1,1'-dinaphthyl (I) in aqueous acetonitrile medium produced a nine-membered ketolactone (III). An intermediate (II) has been isolated in the oxidation of (I) to (III).



Oxidation of (I) with periodic acid in absolute methanol medium formed a product IV. The structure (IV) is assigned to this product based on the spectral properties and is further confirmed by single crystal X-ray diffraction studies (carried out by K. Venkatesan and D. Kanagapushpam).



Electron spin resonance (e.s.r.) experiments on the reactions of phenols with periodic acid showed a one line e.s.r. signals. On the basis of these results a general single electron transfer mechanism involving the aromatic cation radicals is postulated. The literature data is fully consistent with this view⁴⁻⁶.

The products of oxidation of these phenols by periodic acid and a typical one-electron oxidant like ceric ammonium nitrate (CAN) are found to be the same. It is concluded that reactive intermediates in the oxidation of phenols by periodic acid and ceric ammonium nitrate are the same.

The oxidation of aromatic ethers by periodic acid in absolute methanol medium is carried out. Most of the aromatic ethers formed iodinated products in moderate to good yields. The aromatic ethers having methyl substituents in the ring were oxidised in the side chain to the corresponding aldehydes when two moles of periodic acid was used. From the results of e.s.r. experiments on the reactions of aromatic ethers with periodic acid, a single electron transfer mechanism, involving formation of aromatic cation radicals is put forward.

The oxidation of polycyclic aromatic hydrocarbons like naphthalene, anthracene and phenanthrene is carried out. The results of e.s.r. experiments of these aromatic hydrocarbons in aqueous trifluoroacetic acid medium, suggested the intermediacy of aromatic cation radicals. On the basis of these data and by an analysis of the product pattern, a general single-electron transfer mechanism as a pathway in the reaction of polynuclear hydrocarbons is proposed.

Oxidation of benzyl alcohol produced a mixture of benzaldehyde and 4-iodobenzaldehyde. Similarly phenethylalcohol formed the mixture of benzaldehyde, 4-iodobenzaldehyde and 4-iodophenethyl alcohol. A single-electron transfer mechanism which operates in the case of phenols, aromatic ethers and polycyclic aromatic hydrocarbon is now proposed.

3. Conclusions

In the literature, oxidation of phenols by periodic acid has been described by the mechanism involving the periodate ester of phenol and its heterolytic cleavage to form phenoxenium ion. Oxidation of aromatic hydrocarbon is rationalised by a mechanism which involves an electrophilic attack of periodic acid on the aromatic ring. The results of the present work are inconsistent with these mechanisms. A common mechanism involving a single electron transfer from aromatic substrate to periodic acid leading to the formation of aromatic cation radicals is proposed.

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Thesis Abstract (Ph.D.)

The structural state of plagioclases and petrogenesis of anorthosites, Holenarasipur belt, Karnataka Craton, South India by S. N. Gananath.

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1. Introduction

A petrogenetic model for the anorthosites of Holenarasipur Supracrustal belt, based on geological relations, petrography, mineral chemistry and geochemical criteria is proposed.

The Peninsular Gneiss Complex, the older Sargur Group, the younger Dharwar Supergroup and the younger granitoids are the major crustal components of the Archaean Karnataka Craton in the southern Indian shield. The older Sargur Group is preserved under the younger Dharwar Supergroup in the unique trident-shaped Holenarasipur Supracrustal belt (HNSB) which is surrounded by the Peninsular Gneisses¹.

The gabbro-anorthosite suite of rocks confined to the Sargur Group in the Holenarasipur belt has yielded an emplacement age of 3095 my by Rb-Sr systematics² while the amphibolites of the Dharwar Supergroup yield an age of 2600 my³. The Peninsular Gneiss surrounding the HNSB has recorded an age of about 3071 my⁴. The similar age relations and low Sr-isotope ratios of anorthosites (0.7016) and gneisses (0.7008 to 0.7020) suggest that they are contemporaneous and may be comagmatic.

2. Mineral chemistry

Petrographic studies of the Holenarasipur anorthosites reveal relict primary igneous texture and the predominance of C-twins in plagioclases characteristic of magmatic rocks. The amphibole compositions of HNSB anorthosites are predominantly Mg-horn-blends extending into the tschermakite field unlike those observed in the associated ultramafic rocks which are tremolitic or actinolitic. The mineral and whole rock chemical trends are clearly brought out in the AFM diagram. The calcalkaline nature of the magma that gave rise to the anorthosite suite is indicated.

The plagioclases of HNSB anorthosites range in composition from An₆₃ to An₈₃. The structural state of plagioclases has been determined by X-ray powder diffraction method. Unlike the low temperature plagioclases observed in the layered Archaean anorthosites, high temperature plagioclases are predominant in the Holenarasipur anorthosites. It is interpreted that the disordered structural state of plagioclases is most probably due to elevated temperatures and water pressures attained during deformation and metamorphic recrystallization. Further, electron paramagnetic resonance (EPR) spectral studies reveal that the high structural state is due to the occupancy of Fe³⁺ ions in the distorted tetrahedral sites in the plagioclase structure⁵. The absence of Ti³⁺ signals in the EPR spectra of plagioclases indicates that the plagioclase crystals were formed under oxidising environment unlike those of lunar plagioclases.

3. Petrogenesis

Field relations imply that the anorthosite suite has genetic relations with the gneisses and the ultramafic rocks in HNSB. However, mineral chemistry rules out the genetic relationship between the anorthosites and the ultramafic rocks. In the CaO : MgO : (Fe₂O₃ + FeO + MnO) ternary variation diagram the anorthosite suite displays a vertical trend whereas the ultramafic rocks define an oblique trend. There is an obvious gap between the two trends suggesting that the ultramafic rocks and the anorthosite suite are not genetically related.

The low initial Sr-isotope compositions of the anorthosite suite (0.7016) and the gneisses in the vicinity (0.7008 to 0.7020) indicate the comagmatic character of the two. The whole-rock Rb-Sr ages of both the suites are also almost similar (*i.e.* about 3100 my). An examination of chondrite-normalized REE abundance levels shows that the anorthosites with low abundances exhibit positive Eu-anomaly while the gneisses with high abundance levels show negative Eu-anomaly. Thus, the REE data highlight the profound geochemical and petrogenetic differences between the anorthosites and the gneisses. Assuming basaltic andesite to be the most likely parent magma, it can be interpreted that the anorthosite suite formed an early cumulate sequence and the silicic gneisses formed out of the residual liquid.

Computer analogs of graphical tests (R-mode cluster analysis, Q- and R-mode factor analyses) have also been presented to show the genetic relation of anorthosites with the gneisses.

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