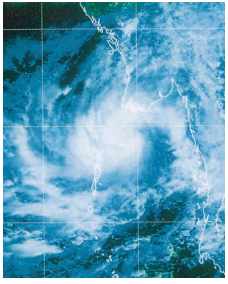


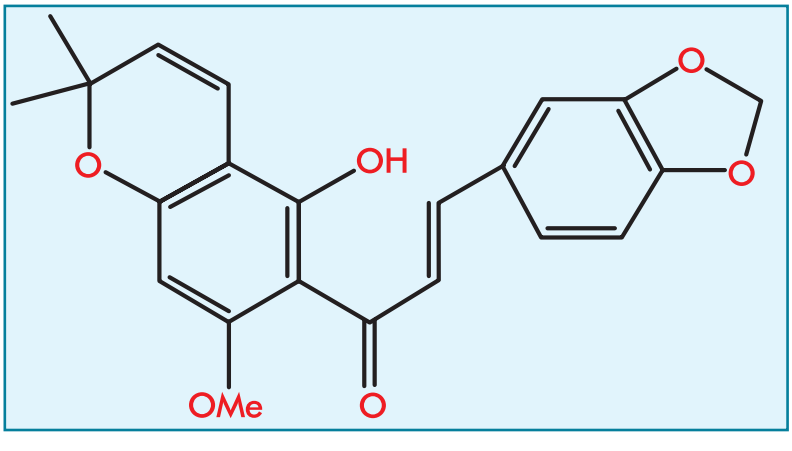
CHAPTER X

CHEMISTRY

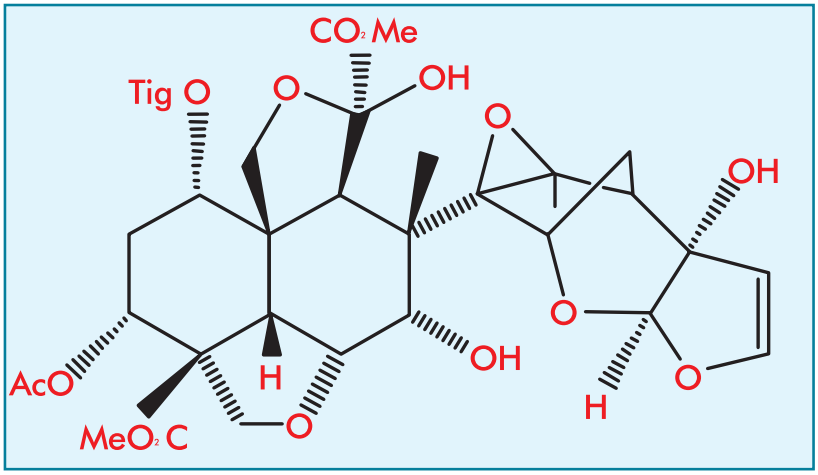
Research in chemistry has been actively pursued in the country for the past several decades. Indian chemists have made remarkable additions to basic knowledge and its applications. The number of chemists working in universities, national laboratories, other scientific establishments, and industries is very large. It is an uphill task to cover even the main achievements of chemists engaged in a wide spectrum of research pursuits. What follows is a short account that gives a glimpse into the enormous national endeavour in chemistry. The pioneering work by Acharya Prafulla Chandra Ray in the early twentieth century in Kolkata was responsible for the great turn of events in chemistry in the Indian subcontinent. The discovery of a stable mercurous nitrite composed of two relatively unstable ions, unfolding of the interesting chemistry of hyponitrite ion, synthesis of a large number of organic sulphur compounds, coordination chemistry of heavy transition metal ions, iridium, platinum and gold are some of the notable contributions of Prafulla Chandra Ray. He established the Bengal Chemical and Pharmaceutical Works in 1902 to manufacture mineral acids and pharmaceuticals through his own earnings and this forms the earliest entrepreneurial endeavour of Research and Development in the country. In the subsequent decades, the major thrust in chemistry was in organic chemistry, especially in the chemistry of natural products. In recent years, efforts have been made in several new directions in the various branches of chemistry.

In earlier years the chemistry of alkaloids, terpenes and steroids engaged the attention of Indian chemists. Synthetic drugs such as antimalarials, contraceptives, sulfonamides and sulfones received serious consideration. Synthesis of long chain fatty acids leading to partial synthesis of natural products was achieved. Noteworthy work was carried out in the country on terpenes especially those occurring in Indian plants. Extensive investigations were made on natural colouring compounds related to benzopyrones and anthroquinones. A large number of plant alkaloids and flavonoids were isolated and their structure determined. Several novel natural products characterized by unique carbocyclic skeletons and

Glabrachnomene, a furanoflavonoid isolated from Derris indica (formerly called Pongamia glabra).



intricate stereochemical features have been synthesized, particularly noteworthy being the diverse sesquiterpenes. In recent years, research in natural products has assumed immense importance from the point of view of drug discovery and bioassay-guided fractionation of extracts to identify lead molecules. A coordinated activity in the area of drug discovery has been initiated by the CSIR in various laboratories and institutions.



Structure of azadirachtin, a potent insect antifeedent compound and inhibitor of ecdysis, isolated from the seeds of the neem plant Azadirachta indica.

Synthetic organic chemistry has been pursued by many researchers. Synthetic design of novel polyhydranes is a major area in which substantial achievements have been made. Synthetic work on the platonic hydrocarbon, dodecahydrane, attracted the attention of the international scientific community. A number of new reactions and organometallic reagents based on silicon, chromium, boron, palladium and phosphorus. have been developed. One of the important aspects of research in organic chemistry has been the synthesis of several organic intermediates for the pharmaceutical industries in the country. This has directly benefitted the industries; the speciality chemicals and pharmaceutical industries have registered an export market of US $ 3.5 billion accounting for 11% of the total exports from India.

Among the accomplishments in organic photochemistry, the unravelling of the mechanism of photochemical reactions such as photoperoxidation, photomerization and photocycloaddition reactions are notable. A novel 'photothermal' metathesis strategy turned out to be a key element in the synthesis of complex organic molecules. Many important achievements have been made in the area of polymer chemistry. Synthesis of novel precursors for polymeric materials, polymer binders, hypergolic polymers and so on have been carried out. In addition to the synthesis of thermally stable polymers, several oligoesters were synthesized which when added to the plasticized PVC drastically reduced its inflammability. Research on speciality polymers with desired properties has been initiated in many laboratories.

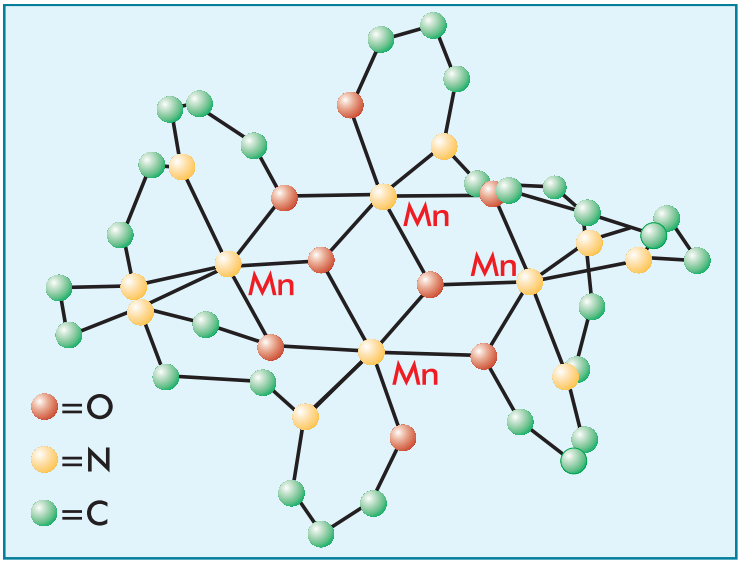
Studies on the synthesis of C_{60}-fullerene and its precursors by rational design resulted in the development of newer methods of making carbon-carbon bonds. Total synthesis of carbasugars having interesting biological activity has been pursued with vigour.

The importance of interface areas between chemistry and biology has been recognized. Attempts have been directed towards development of expertise in techniques for the cultivation of bacteria, isolation of bacteriorhodopsin and rhodopsin and synthesis of a few model retenoids.

Interesting work has been carried out by a few groups in peptide chemistry and several peptides of biological interest have been synthesized. Isolation and characterization of myobacillin, a new polypeptide containing 13 amino acids was accomplished. Nucleic acid research initiated in a few laboratories essentially focused attention on the understanding of the functions of DNA at the

molecular level and to generate nucleotides and novel reagents for site-specific modification of biomacro-molecules. Several studies have been initiated in the areas of biomembranes and metal ion interaction with biomolecules.

Green chemistry has gained great importance today. Several research groups have taken up this challenge and have been engaged in the synthesis of biologically active molecules. A large body of work has been generated in asymmetric synthesis in which a number of optically active naturally occurring terpenes and amino acids have been used as building blocks to get enantiomers of pure biologically active molecules.



Photosynthetic manganese --Modelling the assembly tetranuclear manganese -- Structure of a manganese salicylaldimine dication complex.

Work in the emerging area of supramolecular chemistry, molecular recognition systems, and design of multifunctional catalysts have become the focal point in some laboratories. The preparation of novel materials to perform specially designed functions has become a key feature. Significant advancements have been made in respect of nonlinear optical materials and precursors of MOCVD.

Analytical chemistry using organic chemicals as reagents has been a matter of special interest to many chemists in the country. Solvent extraction, development of sophisticated electroanalytical methods, pollution abatement in industrial workers, and water clarification are some of the important subjects in which research has been pursued. Several laboratories/centres providing analytical facilities have been established in the country.

Research in inorganic chemistry in the country in the last few decades has been considerable. Noteworthy contributions have emerged in the areas of coordination chemistry, bioinorganic chemistry, organometallic chemistry, chemistry of main group elements, spectroscopy and structural inorganic chemistry. The directions of research have been on the synthesis of novel systems for studies on multiple bonded metal-metal clusters, stabilization of low and high valent transition metal ions, homogenous catalysis, metal ion binding in macrocyclic and macropolycyclic ligand systems bearing several donor atoms such as oxygen, nitrogen, sulphur, selenium, tellurium and others. The development of model systems for mimicking the active sites of metalloenzymes and metalloproteins, metal-nucleic acid interactions, photosynthetic functions are some of the fields in which notable progress has been made. Studies on solution equilibria involving several metal ions with ligand systems of biological interest have been pursued vigorously. These have a direct bearing on the role of metal ions in biology and medicine.

Ingenious approaches have been made in the design and synthesis of organometallic systems for small molecular activation. The inorganic ring systems containing phosphorous, nitrogen, boron and silicon have been probed to elucidate the nature of multiple bonds in these systems. Considerable work has been carried out on organo tin and phosphorous compounds in view of their importance as insecticides and pesticides. Extensive

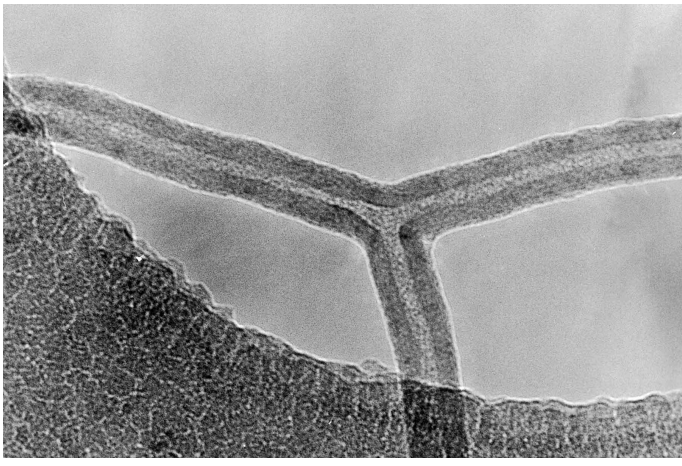
work has been carried out on metal alkoxides which are precursors of novel ceramics. Research in inorganic chemistry in the country is increasingly employing sophisticated spectroscopy (multi-nuclear NMR, EPR, and laser flash photolyser), structural (single crystal X-ray diffractometry) and electrochemical techniques.

Reaction mechanisms of both organic and inorganic systems have been pursued by several groups. Special mention should be made of the following: photochemical transformations, photoperoxidation, dimerization, quenching of fluorescence, emission spectroscopy of dyes, rare-earth complexes, conversion of solar energy, laser spectroscopy, photoisomerization, photocyclo-addition and others. Research centres are being established in different parts of the country for the investigation of ultra-fast processes in chemical systems. Pioneering investigations have been made in the evaluation of rate constants of diverse reactions in free-radical polymerizations. There have been other significant achievements in polymer chemistry, kinetics and mechanism of photopolymerization, redox polymerization, crystallization of polymers, novel synthesis of polymers and polymer alloys and polymer fuels.

The application of quantum mechanics to chemistry started in India around 1950. Theoretical methods are being widely used to understand the structures, stabilities and reactivities of organic and inorganic molecules. New concepts, sophisticated formulations, mathematical theories (or models) in statistical and quantum mechanics, computational methods and strategies have been and are being developed for various static and dynamic properties of small and large systems both in ground and excited states. These include coupled cluster calculations, density functional methods, molecular modelling methods and theories of ultrafast processes.

A number of researchers are studying chemical thermodynamics, especially on equilibrium property measurements. Work on non-equilibrium thermodynamics is also being pursued by some chemists. The various aspects of electrochemical investigations include electrochemical energy systems, electrode kinetics, surface modified electrode systems, electroplating, and corrosion problems among others. Physical measurements on solid catalysts as well as studies of catalytic reactions have been carried out in several centres. The design and development of zeolite-based catalysts for industrial applications (especially for xylene separation) is one of the most significant achievements by Indian chemists.

Research in solid state chemistry, surface science and materials chemistry are being actively pursued. Notable contributions have emerged in the study of phenomena, structure-property relations and materials design. The materials include transition metal oxides, novel forms of carbon (fullerenes and carbon nanotubes), supramolecular assemblies, micro- and macro-porous solids, nanoparticles and thin films and clusters. Special mention is made of the discovery of a simple method for fashioning aligned nanotube bundles and Y-junction nanotubes, which has received international acclaim in view of its application in electronic circuitry in the nano-



Y-junction carbon nanotube synthesized by direct chemical route. At the junction, the nanotube exhibits characteristics of a dioxide, thereby suggesting the potential of Y-junction nanotubes in nanoelectronics.

technology regime. The various aspects of solid state chemistry investigated include superconductivity, porous solids, structural and electrical properties, colossal magnetoresistance and charge density wave propagation. Many interesting findings emanating from research in these areas have made a significant impact in the international scene. The efforts have put India on the map of nanoscience research in the world.

Nuclear chemistry is mainly concentrated in the Bhabha Atomic Research Centre, but several groups in the country use tracer techniques. There has been considerable effort in radiation chemistry as well.

Techniques of magnetic resonance spectroscopy, electronic absorption and emission spectroscopy, Mo¨ ssbauer spectroscopy and electron spectroscopy provide support to organic, inorganic and solid state chemists and are engaging the attention of many physical chemists. Lasers have come to play a major role in research in the country. Mention must of made of areas, such as time-resolved spectroscopy of transitory intermediates, isotope separation, two photon spectroscopy, electron spectroscopy of surfaces, circular dichroism, resonance Raman, FT-IR, 300-5000 MHz NMR, solid state two-dimensional NMR, and photoacoustic spectroscopy which are being actively pursued at various centres in India.