

Organic compounds and materials science

Gautam R. Desiraju

ORGANIC substances by their very nature pose special problems in purification and in their fabrication as useful materials. The typical organic compound is low-melting, volatile and of variable purity. Further, the absence of a serious dialogue between materials scientists and organic chemists has also delayed the entry of organic compounds into the mainstream of materials science so that 'organic' materials science is far less developed than its 'inorganic' counterpart. Despite these difficulties, organic compounds, with their subtle structural variations, are capable of a much higher degree of 'fine tuning' so as to optimize a given chemical or physical property. Modern synthetic methodology is highly sophisticated and virtually any organic target molecule can be made (with a greater or lesser degree of ease). The choice of a particular target for a particular application depends in turn on a critical appreciation of weak intermolecular interactions and their role in stabilizing organic crystal structures. Accordingly, organic structures may be deliberately 'engineered' for very specific chemical or physical properties.

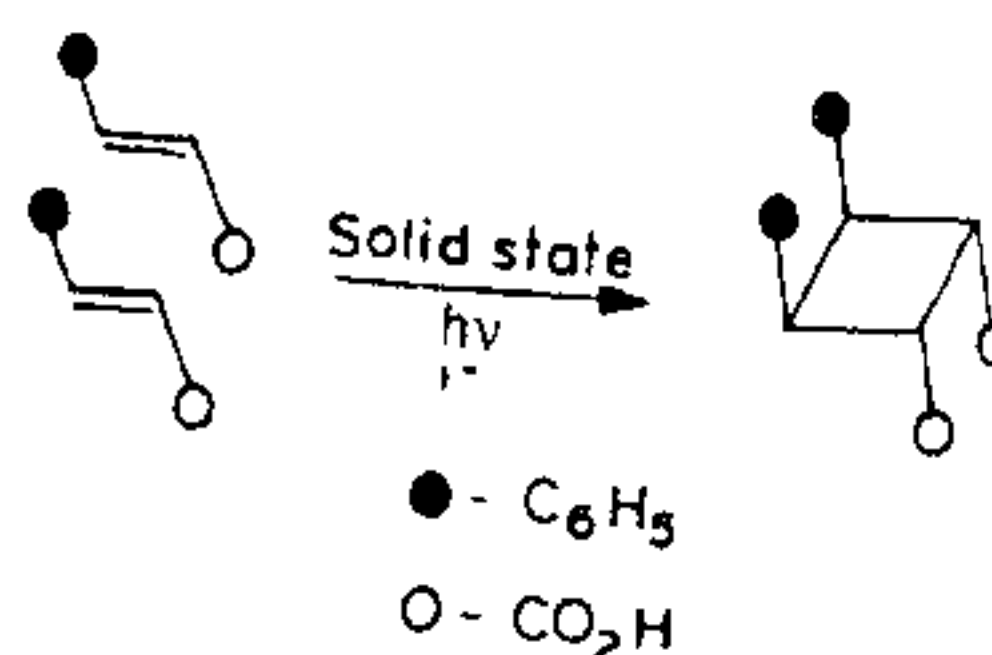
While the properties of organic molecules in solution are usually characteristic of the isolated molecule, solid-state properties of molecules are characteristic of an entire molecular assembly such as the crystal structure. Crystallization is a good example of molecular recognition and the structure of a molecular assembly in the crystal depends on the nature of this recognition and on the sometimes concurring, sometimes conflicting directional requirements of weak intermolecular forces. Such ideas have only been refined in recent times and the coining of the term 'supramolecular chemistry' by Lehn seems particularly appropriate. The construction of organic molecular and crystal structures exhibiting predesired properties has a certain deliberateness of purpose and has been likened to model-building.

Organic crystals are relevant to materials sciences in three important respects: (i) The regularity of molecular orientation in a crystal may be employed to carry out highly predictable stereoselective reactions. (ii) A certain packing arrangement in a crystal may confer predesired optical, electronic, magnetic or other physical property. (iii) Organic molecules may be included in host matrices in unusual geometries which permit only certain types of chemical reactions or such that the process of inclusion may be used to separate different molecular species.

Organic solid-state reactions

Reactions between molecules in fluid media can only occur after molecules diffuse together, and because of the isotropic nature of the medium, a pair of potentially reactive molecules may approach one another in a variety of orientations. This is one of the reasons why an organic reaction in solution often results in a multitude of products. The relative yields of these products depend on, in addition to obvious chemical factors, the probability that the reactant molecules diffuse together with a certain orientation. In the crystal, this variability of intermolecular orientation is hardly significant and it may be expected that if molecules are close enough (for a 'diffusionless' reaction), they should react to yield one or a very small number of products. Accordingly, solid-state reactions may be employed in situations where a certain very specific type of reactivity is desired.

The connection between the structure of a molecular assembly and its chemical properties is a crystallographic one and was formulated by Gerhard Schmidt more than thirty years ago as the topochemical principle. Schmidt found that the solid-state reactivity of crystalline cinnamic acids, $\text{Ar}-\text{CH}=\text{CH}-\text{CO}_2\text{H}$, is completely determined by the near-neighbour relationship between molecules in the crystal. If potentially reactive molecules are sufficiently close in the crystal to undergo dimerization, a (usually) quantitative reaction occurs on irradiation to yield cyclobutanes. If molecules are too far apart in the crystal, there is no chemical result on irradiation. If the reactant molecules are related by a crystallographic centre of inversion, the product has inversion symmetry. If the reactant molecules are related by unit cell translation, the product has mirror symmetry. In other words, *the crystal symmetry of the reactant transforms as the molecular symmetry of the product*. In general, the course and outcome of these solid-state reactions are quite different from the corresponding solution processes. In this instance, cinnamic acid does not photodimerize in solution or in the melt. In many other cases, a solid-state reaction results in (usually) one product in quantita-



Gautam R. Desiraju is in the School of Chemistry, University of Hyderabad, P.O. Central University, Hyderabad 500 134.

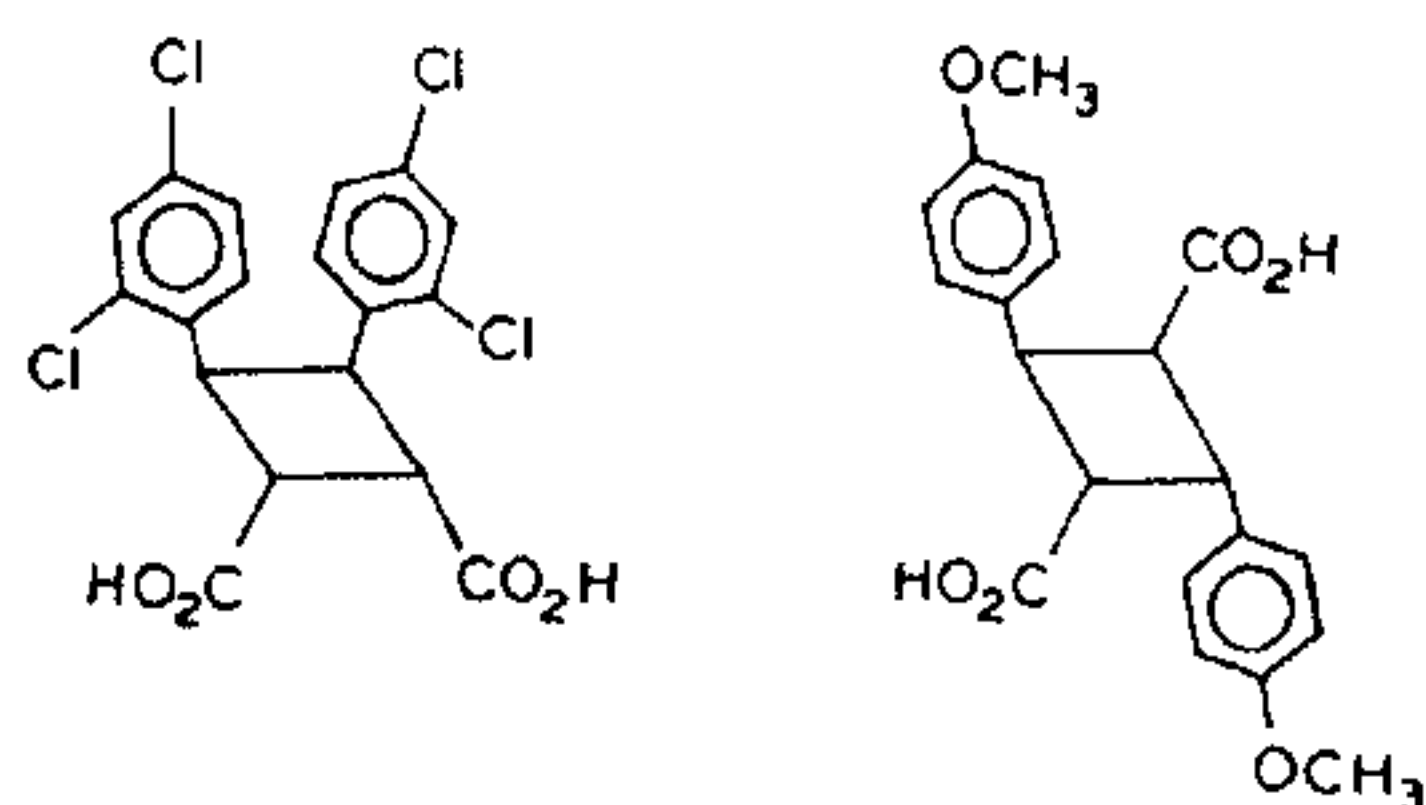
tive yield while the corresponding solution reaction is far less 'clean' and several by-products may be obtained.

A number of significant results may be derived, given the validity of the topochemical argument in this and related systems.

Substitutional manipulation

A particular substitution pattern on the phenyl ring of the cinnamic acid molecule may promote crystallization in either the inversion (α) or translation (β) form. A knowledge of the weak intermolecular interactions may therefore permit a prediction of the crystallization pattern (and hence of the solid-state reactivity) of a new derivative. Dichlorosubstitution leads, for example, to the (β) crystal, while methoxy substitution leads to the (α) crystal, with the following dimers being produced exclusively on irradiation. These products would be very difficult to synthesize stereoselectively by solution processes.

It may be mentioned that such 2 + 2 solid-state photodimerization reactions have been suggested for applica-



tions in microlithography and for making photoresists.

Asymmetric syntheses

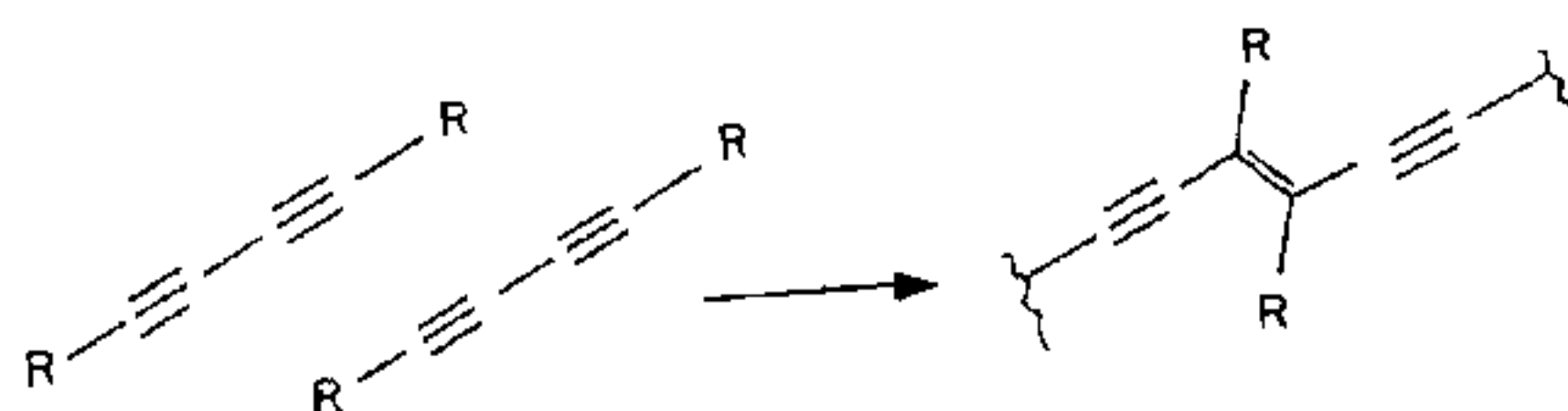
A fascinating yet unanswered question is how optical activity was generated in prebiotic conditions on our planet. In searching for an answer to this question, chemists have postulated that an early chemical reaction might have taken place under the influence of circularly polarized light leading to an enantiomeric excess of the product. A more plausible, even compelling, idea envisages that the early chemical reaction took place within a non-centrosymmetric crystal (or upon the non-centrosymmetric surface of a template crystal) and that the dissymmetry inherent in such a milieu was extended as molecular chirality of the product. Accordingly, a topochemical process in a non-centrosymmetric crystal structure which also lacks mirror and glide planes ($P2_1$, $P2_12_12_1$, $C2$) must take place in a chiral environment where the forces acting on the reactant molecules are dissymmetric. So the products formed must be chiral. In other words, *crystal chirality in the reactant is transformed to molecular chirality in the product*. Hence non-centrosymmetric organic crystals are ideal media for conducting asymmetric syntheses. Such asymmetric syntheses are not

restricted to alkene 2 + 2 cycloaddition reactions.

Solid-state polymerization

If a reactant monomer molecule has two reacting centres, it is in principle capable of topochemical conversion to give stereoregular polymeric products. This type of solid-state polymerization has been realized in the well-known diacetylene system. Diacetylene polymerization is exemplified in the following schematic diagram and proceeds not only in a topochemical but, more remarkably, in a topotactic fashion. The main strategy in designing a polymerizable monomer is to ensure that sufficient attraction exists between the substituents, R, on adjacent molecules to bring the reactive centres close enough together.

The unique feature of the diacetylene polymerization reaction is that, in many cases, it can be carried out as a single-phase process. There are not many methods of making



such perfectly oriented macromolecules and polydiacetylene chemistry has therefore been the subject of extensive investigation. The commercial importance of these materials has also been recognized. With their highly conjugated framework, ease of oxidation (and therefore their capacity to be doped) and optical nonlinearity, these substances could be very significant for electro-optical applications.

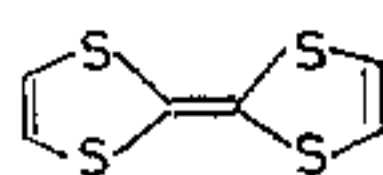
Physical properties of organic crystals

The notable advantage in using organic materials to achieve certain predesired physical properties is that these properties may be fine-tuned to a much greater degree in molecular structure than is possible with inorganic solids. The earliest attempts to design organic solids for materials research were in the area of molecular semiconductivity. The discovery of metallic conductivity in the tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) complex in 1973 was the starting point of research on molecular conductors. Research on conducting charge-transfer salts ultimately led, in the early eighties, to the discovery of the first ambient-pressure organic superconductors. It is pertinent to note that molecular semiconductors have already been incorporated in a commercial product; an organic photoconducting thiapyriliun dye is a vital component of a rather successful photocopying machine. While an organic conductor or superconductor is yet to be exploited commercially, the vast crystallographic literature that now exists on these substances has greatly helped in refining our ideas about their structural chem-

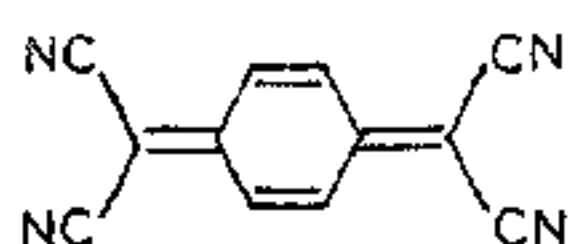
istry.

The study of electrical conductivity in organic compounds was initiated in the 1940s with the study of two groups of compounds: polycyclic aromatic compounds, phthalocyanines and dyestuffs on the one hand and addition compounds of the donor – acceptor type on the other. Polymer semiconductors appeared in the late fifties, while polyacetylene and other highly conjugated polymers were synthesized in the form of thin films. Polypyrrole has also been the object of much study on account of its electronic properties.

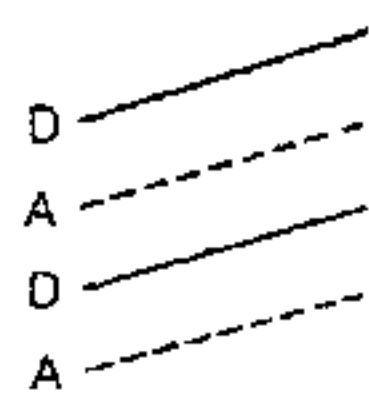
Organic metals are typically 4-Å short-axis donor-acceptor complexes with segregated stacks of planar aromatic π -donors (D) and π -acceptors (A). These D and A



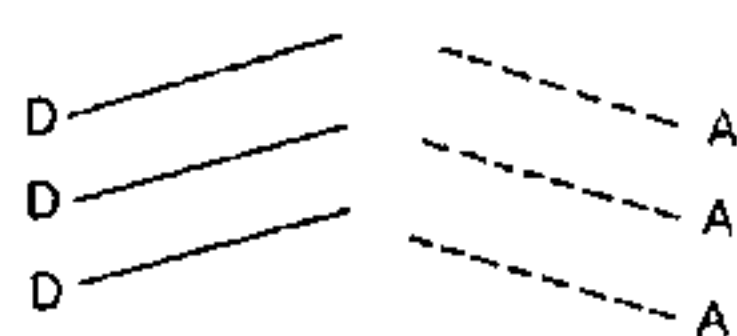
Tetrathiafulvalene (D)



7,7,8,8-tetracyanoquinodimethane (A)



Mixed stack (insulator)

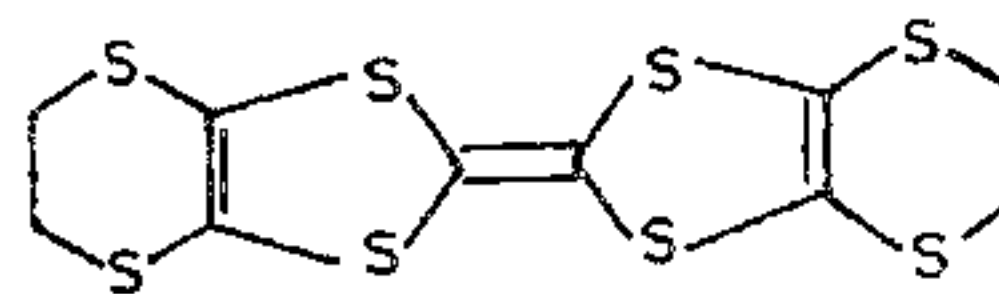


Segregated stack (conductor)

molecules are arranged in segregated stacks DDD...AAA..., with the D and A bearing fractional charges. This segregated arrangement is uncommon. Small changes in the molecular structure of donor or acceptor moieties usually result in the common mixed-stack arrangement DADADA.... However, this seemingly unlikely organization of all negatively charged ions into one set of stacks and the positively charged ions into another set is generally agreed to be an essential prerequisite for high electrical conductivity. The largely unanswered structural question concerning these complexes is just what molecular features in the donor and acceptor molecules favour a segregated-stack structure as opposed to a mixed-stack structure.

The dominant interactions in TTF-TCNQ are the interstack D-D and A-A forces. This quasi-one-dimensional structure readily undergoes a metal-insulator transition at low temperatures (~70 K). In order to increase the dimensionality of these solids and suppress the Peierls transition, molecules have been designed, in which, in addition to the intrastack π --- π interactions, interstack (lateral) heteroatom interactions are also important. An extreme situation where interstack interactions dominate the packing at the expense of the intrastack interactions is found in the donor – acceptor complexes of BEDT-TTF this ethylenedithiotetrathiafulvalene ('ET') with inorganic anions such as I^- , ReO_4^- and ClO_4^- .

The unique feature of ET complexes is that donor molecules do not stack face-to-face like in TTF-TCNQ but rather



BEDT-TTF (ET)

adopt a lateral or side-by-side arrangement where the organic species are separated by inorganic anions. Many of these ET salts are metallic or superconduct at low temperatures (<10 K). The conductivity within the two-dimensional sheet is about 100 to 1000 times higher than along the perpendicular stack direction.

Non-linear optics

The invention of lasers and the consequent availability of powerful coherent light sources has rendered possible the observation of previously predicted nonlinear optical effects in crystals. Materials with nonlinear optical properties can be used in devices that process information efficiently. It has been recognized that such devices will become the standard vehicle for future communications systems. An important nonlinear effect is second harmonic generation (SHG), which is used in frequency doubling of infrared and other electromagnetic radiation. Early developments of nonlinear optics grew around inorganic materials like $LiNbO_3$ and KH_2PO_4 but it was realized that organic materials have SHG efficiencies that are greater by several orders of magnitude. This is offset by their poor mechanical properties but it is well accepted that organic compounds offer much more scope for the deliberate tailoring of both electronic and crystallographic properties.

Research on organic nonlinear materials has focused on compounds such as 3-methyl-4-nitroaniline and 3-methyl-4-nitropyridine-*N*-oxide, both of which are more efficient than $LiNbO_3$ by an order of magnitude. It is convenient to conceptually divide the design strategy for a new organic material for SHG into two steps: molecular engineering, wherein the electronic properties of the molecule are optimized, and crystal engineering, wherein crystallization in a non-centrosymmetric space group is achieved. However, the main problem is that these two steps are not generally independent of one another. For instance, a compound whose molecular structure has been optimized for SHG by including a delocalized π -system (high molecular polarizability) may tend towards centrosymmetry because of dipole-dipole stabilization. A number of other factors such as noncritical phase matching capability, low molecular weight, infrared and visible transparency, thermal stability and mechanical ruggedness have to be taken into account. All this renders the search for the ideal organic frequency doubler a complex and difficult task.

Other useful physical properties that depend on the lack of an inversion centre in an organic crystal are ferroelec-

tricity, piezoelectricity, pyroelectricity and triboluminescence. Organic compounds such as Rochelle salt and triglycine sulphate are well-known ferroelectrics. Pyroelectrics could find applications as heat sensors. Much effort is also being expended in the design of a molecular ferromagnet.

Separations and catalysis

Geometrical attributes of organic molecules such as shape and size may be utilized in separation of mixtures and in catalysis. Such applications of organic materials are still novel and uncommon. However, with the growth and development of supramolecular chemistry, it is possible and even likely that ingenious uses will be found for organic compounds in the synthesis and processing of new compounds.

An early example of organic separation which depends on variability of intermolecular interaction is the resolution of a racemic mixture of compounds with a so-called 'resolving agent'. These latter compounds are typically optically active natural products such as brucine, quinine, tartaric and mandelic acids. The patterns of interactions in pairs of diastereomeric salts have been found to be remarkably different, accounting for the ease of separation of the corresponding racemic mixture. More subtle are resolutions that employ a chiral clathrating compound. The internal cavities of compounds such as cyclodextrins and tri-orthothymotide are chiral. Therefore these substances can discriminate between enantiomers in their complexing abilities and accordingly effect a separation. It has been suggested that cyclodextrins may be used in the food packaging industry; the active principle in many spices are volatile, optically active substances that are gradually lost on

standing. These substances may be encapsulated in cyclodextrins and stored as such without loss of freshness till used.

Conclusions

Organic materials are only now coming of age but it is clear that the materials scientist will consider these substances more seriously in the future. These substances would be most useful in situations where inorganic materials cannot, for some reason or other, be used. Factors that further tend to increase their availability and applicability are ease of synthesis and structural variety. For instance, it is not inconceivable that a molecular computer and a high-temperature organic superconductor will be developed in the future. Theories of molecular packing are becoming increasingly sound and should pave the way for systematic design or engineering of molecular materials for a multitude of uses.

1. Schmidt, G. M. J. *et al.*, *Solid State Photochemistry* (ed. Ginsburg, D.), Verlag Chemie, Weinheim, 1976.
2. Kitaigorodskii, A. I. (ed.), *Molecular Crystals and Molecules*, Academic Press, New York, 1973.
3. Wright, J. D. (ed.), *Molecular Crystals*, Cambridge University Press, Cambridge, 1987.
4. Desiraju, G. R. (ed.), *Organic Solid-State Chemistry*, Elsevier, Amsterdam, 1987.
5. Scheffer, J. R., Ramamurthy, V. and Turro, N. J. (eds.), *Organic Chemistry in Anisotropic Media*, Tetrahedron Symposium-in print, No. 29, Tetrahedron, 43, 1197-1737, 1987.
6. Desiraju, G. R. (ed.), *Crystal Engineering - The Design of Organic Solids*, Elsevier, Amsterdam, 1989.

ACKNOWLEDGEMENT. I thank Prof. S. Ramaseshan for his encouragement during the preparation of this article and for a critical reading of the manuscript.