



Some Themes in Chemical Crystallography Pertinent to the Indian Contribution

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Abstract | It is particularly appropriate that the *Journal of the Indian Institute of Science* is bringing out a commemorative issue to mark the International Year of Crystallography 2014 (IYCr2014). India has had a strong crystallographic tradition, and the earliest work in what may be described as structural crystallography from this country is the work of K. Banerjee on the determination of the crystal structure of naphthalene in 1930.¹ The Indian Institute of Science itself has played no small part in establishing and sustaining the subject of crystallography in this country. A large number of papers in this special issue are written by authors who have either have been trained in the Institute or who have some kind of professional association with this organization. In this article I will try to capture some unique features that characterize the intersection of the crystallographic and the chemical domains, mostly as they pertain to the Indian contribution to this subject. Crystallography is of course as old as chemistry, and some would say it is even older. The relationships between chemistry and crystallography go back to much before the discovery of diffraction of X-rays by crystals.² The discovery of polymorphism by Mitscherlich in 1822,³ Haüy's formulation of the *molecule integrante*,⁴ and the work of Fedorov⁵ and Groth⁶ on the identification of crystals from their morphology alone, are well known examples of such relationships. A very early article by Tutton speaks of "crystalline chemical analysis".⁷ In this article, I shall, however, be dealing with the interplay of chemistry and crystallography only in the post diffraction era, that is, after 1912. Much had been written and said about chemical crystallography, and even within the context of the present special issue, there is a review of chemical crystallography in India including some futuristic trends.⁸ This topic was also reviewed by Nangia in a special publication brought out by Indian Academy of Sciences in 2009,⁹ and by Desiraju in a special publication¹⁰ brought out by the Indian National Science Academy in 2010. A rather detailed account of crystallography in India appeared in 2007 in the newsletter of the International Union of Crystallography (IUCr) in which chemical crystallography was detailed.¹¹ Since all these publications are fairly recent there is little need for me to attempt a comprehensive coverage of chemical crystallography in India in this short review.

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The articles in this special issue of *J. Indian Inst. Sc.* on chemical crystallography include, in addition to the summarizing review of Sarma and Nangia,⁸ reviews by Moorthy on the use of supramolecular synthons to design host–guest compounds,¹² by Dastidar on crystal engineering principles as applied to gelation,¹³ by Mukherjee on crystal structure determination from powder X-ray data,¹⁴ by Azim on pharmaceutical solid forms,¹⁵ and by Natarajan¹⁶ and also by Maji,¹⁷ on metal organic framework solids (MOFs). These articles give a flavor of the range of cutting edge topics that are being researched in India today in the general area of structural chemistry.

Accordingly, I have chosen to be rather selective and anecdotal about the topics I have covered in this minireview. The choice of these topics may be ascribed partly to personal preference, partly to questions that I have been asked during my career and partly because of my perception of their overall significance to the further development of structural chemistry and chemical crystallography. All the topics covered here do not necessarily have an Indian connotation but since the Indian contribution is very strong in chemical crystallography as it is practiced today, some connection with research activities in India is inevitable.

1 When did Chemical Crystallography Start in India? Why did it Not Start Earlier?

Crystallography in India began with C. V. Raman and then G. N. Ramachandran both of who were physicists by training and who trained their students as physicists. The early days of structural crystallography were dominated by physicists worldwide and diffraction itself was then a novel phenomenon.¹⁸ The determination of a crystal structure of even a simple organic molecule was full of problems until the beginnings of the heavy atom method in the 1940s. Unless there was some unusual molecular symmetry (urotropin) or some other simplifying feature (phthalocyanines), crystal structures simply could not be determined. While science generally develops so that the most interesting and challenging problems get addressed one way or the other, the course of events in any particular country or region still depends very much on local circumstances and events. The emphasis of structural crystallography in the UK and USA in the 1930s and 1940s was drawn from and inspired by chemistry because principal players like L. Pauling, J. M. Robertson, R. W. G. Wyckoff and D. C. Hodgkin were chemists by training. The chemical way of thinking was applied to structural crystallography and even for

molecules of biological interest, it went through a “chemical” route. Pauling beat W. L. Bragg to the α -helix structure, mostly because he knew that the peptide link must be planar. Watson and Crick reached the DNA structure with confidence because Donohue advised them about the correct tautomeric forms of the nucleobases. In India, however, chemistry largely meant natural products chemistry right through till the 1960s and there was a singular absence of physical organic chemistry in any organized manner. This lacuna had an implication in that a natural bridge between chemistry and crystallography could not be created. Of course why the subject of physical organic chemistry did not develop in India say in the 1940s and 1950s is another matter, and is beyond the scope of the present article. However, this having been gainsaid, the fact remained that chemistry, as such, in India meant synthetic chemistry, natural products chemistry, and the classical study of inorganic compounds. Spectroscopy appeared a little later but in the absence of a physical organic tradition, the link between spectroscopy and crystallography failed to materialize. The situation in Europe was slightly different during these decades in that there was a pervasive influence of mineralogy and diffraction physics. But mineralogy has its connections with solid state chemistry¹⁸ and so the link between chemistry and crystallography remained intact.

It is a measure of Ramachandran’s versatility that he was able to bridge the gap between a physics oriented crystallography and structural biology without (what now appears to be) a natural resting point in structural chemistry. While this was a truly ingenious feat, one of the unintended consequences that followed from his leap of faith was that macromolecular crystallographers in the country continue to be trained till today without an extensive background in chemistry. This was acceptable in earlier times, when the determination of a macromolecular crystal structure was in itself a research goal. However, today, it deprives the Indian macromolecular community of a competitive edge, when biological mechanisms are being investigated with crystallography. Here, a chemistry background is essential. Going back to yesteryear, the domination of Ramachandran and other physicists like A. R. Verma in most aspects of Indian crystallography through the 1950s and even 1960s, meant realistically that chemical crystallography could not take off during that period. I can say therefore that the beginnings of chemical crystallography in India only occurred in the late 1960s and more definitely so only by the late 1970s. The availability of advanced

neutron diffraction facilities in Bhabha Atomic Research Centre were well exploited during this period by Chidambaram, who studied hydrogen bond patterns in several amino acids and related compounds.¹⁹ This work led to the development of certain guidelines to predict hydrogen bond patterns in crystals. However, the study of these interactions was not really in the mainline interest of Indian chemists of the time. A contribution by Manohar and Ramaseshan on the crystal structure of echitamine hydrochloride was exemplary,²⁰ not only in that these authors beat Robert Robinson to the correct structure of this natural product but also because their analysis of the crystal packing provided an interesting footnote to the early history of the C–H...O hydrogen bond.²¹ By the late 1970s and early 1980s, chemical crystallography in India was far better organized. The work of Manohar on topotactic reactions²² and Venkatesan and Ramamurthy on topochemical reactions in organic solids²³ started in this period. I began my independent career in the University of Hyderabad in 1979 and initiated a formal program in chemical crystallography,²⁴ beginning with a revisit of the cinnamic acid problem of G. M. J. Schmidt. Both Manohar and Venkatesan were students of Ramaseshan and they too were trained as physicists.²⁵ It should be recorded that they also made a leap of faith but this time from physics to chemistry with their work on solid state reactions. I, however, was an organic chemist by training and perhaps one of the first crystallographers in India with a completely chemical background. To summarize therefore, it may be said that chemical crystallography in India had a relatively slow start because of various circumstantial reasons and that it had its formal beginnings sometime in the mid to late 1970s. Chemical crystallography can be most naturally practiced by physical organic chemists^{26a,26b} (as subsequent events in India and elsewhere in the world have shown). Since this species hardly existed in India until the 1970s, chemical crystallography did not start in this country till then.

2 Did G. N. Ramachandran “Discover” C–H...O Hydrogen Bonds?

When I started work on weak hydrogen bonds in the mid-1980s, a number of Indian crystallographers, notably students of Ramachandran, pointed out to me that Ramachandran had already noted the importance of this interaction in his papers on collagen²⁷ and polyglycine²⁸ two decades earlier, and that I was mostly re-discovering the wheel. Subsequent events of course have taken the entire subject of weak (or non-conventional) hydrogen bonds to a very different plane²¹ but I sometimes

recollect the old criticisms and raise this point here with the implication that perhaps Ramachandran received less credit for this “discovery” than he deserved. However, after some consideration, I can conclude that, at least on this count, the international scientific community has not been unfair to Ramachandran.

For a start, C–H...O hydrogen bonds occurred regularly in the literature long before Ramachandran’s references to this subject. Glasstone ascribed the association of acetone and chloroform to this interaction as far back as 1937.²⁹ Pauling ascribed the higher boiling point of acetyl chloride when compared to trifluoroacetyl chloride to weak hydrogen bond formation in 1939.³⁰ Dougill and Jeffrey related the high melting point of dimethyl oxalate to the same interaction in 1953,³¹ an observation that we revisited in 2010.³² Most importantly, Sutor postulated, formally, the repetitive nature of C–H...O hydrogen bonds in a set of related purines with chemical arguments in 1960.³³ Ramachandran’s papers came well after these developments.

Secondly, and this is more significant, Ramachandran “assumed” that a C–H...O hydrogen bond is a stabilizing interaction and likened it fully to an N–H...O or an O–H...O hydrogen bond. He used the term “C–H...O hydrogen bond” in a straightforward way and without any qualification. According to one of his students of that time, he deemed the phenomenon to be so unexceptional that he did not elaborate further on the issue³⁴ except to quote “normal” and “outer limit” (short) distance ranges for this geometry to alert crystallographers that short C...O distances need not cause alarm. All this reflects the physics background of Ramachandran, because only a chemist would appreciate that there is something significant when an atom of such low electronegativity (carbon) forms hydrogen bonds that seem to be very similar to hydrogen bonds formed by atoms of higher electronegativity (oxygen, nitrogen). This is not what is expected from Pauling’s definition of the hydrogen bond.³⁵ Much, if not all, of the controversies that surrounded the subject of the weak hydrogen bond, right down till around 2000, centered around the conjecture that carbon is not electronegative enough to form a hydrogen bond.³⁶ So if Ramachandran observed a C–H...O hydrogen bond, he did not appreciate its chemical significance, and thereby lost the chance to get credit for its “discovery”, if it can even be called that.

The matter becomes even more obvious when it is noted that Donohue,³⁷ who was the chief opponent of the idea of C–H...O hydrogen bonds

in the 1960s and 1970s, actually used Ramachandran's "normal" and "outer limit" values to affirm that the short C...O distances noted by Sutor in her study of purines needed no special explanation because Ramachandran had said that they are expected. One can hardly be said to have discovered a phenomenon if the main observation in one's work is actually used by an adversary to debunk the very idea one has suggested.

This entire matter is an interesting excursion into scientific psychology. When one makes a discovery that is significant, it is sometimes important to emphasize to the scientific community, why indeed this discovery is significant. If Ramachandran is to be faulted at all, it is to the extent that he was innocent of the chemical implications of a C-H group acting as a donor of hydrogen bonds. Therefore I have included this discussion in a review on chemical crystallography. Unless there is chemistry in the crystallographic research, it is not chemical crystallography.

3 Why did Crystal Engineering Take Off?

This question has been discussed already in a textbook on crystal engineering that I co-authored in 2010 with Vittal and Ramanan.³⁸ Crystal engineering took off internationally in the late 1980s and early 1990s for three main reasons: (i) the ready availability of single crystal diffractometers; (ii) the fact that it became relatively easy to determine crystal structures of small molecules; (iii) that there was a critical mass of work that defined crystal design as an important chemical problem; (iv) the award of a Nobel Prize for supramolecular chemistry in 1987. Each of these points may be elaborated.

Computer controlled diffractometers first appeared in the early 1970s and became standard equipment in chemistry departments by the early 1980s. The Indian Institute of Science obtained its first automatic single crystal diffractometer in 1977; the Indian Institute of Technology Madras followed a few years later. Abroad, these machines were far more common by that time. Till then, there were faculty positions to be had in what might be termed chemical crystallography. After the appearance of these machines, crystallographers who determined small molecule crystal structures gradually morphed into service crystallographers, who were attached to chemistry departments, or changed their interests to problems of greater chemical or biological interest. Among the topics of a chemical nature that could be tackled with crystallography, crystal engineering was one of

the most attractive, because there was already an interesting body of work on solid state organic reactions and topochemistry. This provided a link between organic chemistry and solid state chemistry.

It became increasingly easy to determine crystal structures of small organic molecules by the mid-1980s. The Nobel Prize for direct methods was awarded to Karle and Hauptmann in 1985 and provided an "official" sanction for this default method of crystal structure determination. It is said that after this event, chemical crystallographers became crystallographic chemists. Slowly but surely, chemists without fully rigorous backgrounds in structural crystallography were able to collect X-ray single crystal data and solve crystal structures. What remained was to identify a sufficiently interesting chemical problem that depended on obtaining crystal structures easily. Crystal engineering became such a research problem, facilitated in part by contributions from Robson, Etter and myself.

Etter's papers in 1990 and 1991, described the importance of the hydrogen bond as a design element.^{39a,39b} She termed this interaction as both strong and specific. While a number of these ideas had already been outlined by Robertson in the 1950s,⁴⁰ they found a ready relevance and application only after structure determination became easy—an idea is accepted only when its time comes. My contribution, described in the book I wrote in 1989,³⁵ brought together the concepts of intermolecular interactions and close packing, in modern parlance the kinetic and thermodynamic influences on crystallization.⁴¹ Robson, in 1990, showed that the principles of structure design could be applied to a new category of substances, the metal-organic coordination compounds.⁴² He may be credited with distinguishing between coordination compounds and coordination polymers. The use of retrosynthesis, and of the definition of a target crystal structure as a network, was also outlined by him for coordination polymers. The definition of the crystal as a retrosynthetic target and the identification of crystal engineering as a form of supramolecular synthesis were described by me in a review in 1995.⁴³ The supramolecular concept itself had received a tremendous fillip in 1987 with the award of a Nobel Prize to Pedersen, Cram and Lehn, facilitating the ready acceptance of the ideas outlined in my review, in particular of the term *supramolecular synthon* (Figure 1). All these developments provided a sufficiently strong chemical underpinning for the whole exercise of crystal engineering and the

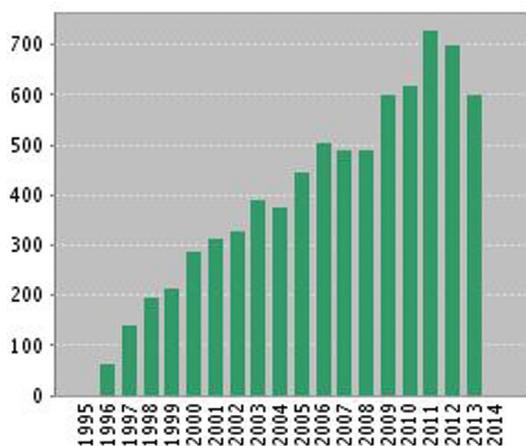


Figure 1. Numbers of citations to papers that contain the term *supramolecular synthon(s)* in their titles (From Web of Science).

subject may be said to have reached the take-off stage by 1995.

4 Is the Study of Metal Organic Framework Compounds (MOFs) a Part of Crystal Engineering?

This is a question that I have been asked often and it seems to me that the answer is obvious. MOFs to my mind constitute an integral part of crystal engineering because there is little conceptual difference in terms of design strategies for MOFs and pure organics. In part, there was a great deal of unnecessary confusion as to whether coordination polymers and MOFs are the same or whether they are different.^{44a,44b} This resulted in an impression that MOFs are some special category of compound quite unlike anything else in chemistry. This is patently untrue. There were also some attempts to link the definition of a MOF to a property rather to a structural feature. This line of argument also has its limitations. Nomenclature becomes a contentious issue in an evolving subject because it is linked to the apportioning of credit. The other point is that the energy of the linking interactions is different for MOFs and organics. Therefore the course of crystallization events and the success or otherwise of a design strategy is somewhat different in these two categories of substance. The applications of MOFs and organics are also often very different—MOFs became closely associated with gas absorption. Generally, MOFs are studied by inorganic chemists and molecular organics by organic chemists. This results in other different perception issues. All this gainsaid, both MOFs and molecular organics conform to the definition of crystal engineering that I provided in my

1989 book,³⁵ a definition that has stood the test of time till the present. There, I stated that *crystal engineering is the understanding of intermolecular interactions in the context of crystal packing and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties*. Accordingly, I have no problem in identifying the study of MOFs as a part of crystal engineering, and the topic is so described in one of the chapters of our 2010 textbook of crystal engineering, referred to earlier.

5 What are the Circumstances in India that Favor the Present Position of Crystal Engineering in India?

Crystal engineering is doing very well in India at the present time. There are a large number of independent research groups who are working in many areas of the subject. Indian researchers (working in India) account for 10–20% of the papers in the two important subject journals, *Crystal Growth & Design* and *CrystEngComm*, and these are among the highest percentages for chemistry journals. A number of these researchers have served or are serving in editorial positions in these and other journals devoted to structural chemistry and chemical crystallography. A special issue on *Structural Chemistry in India* was brought out by *Cryst. Growth Des.* in 2011.⁴⁵ A similar special issue is being brought out by *CrystEngComm* in 2014 to commemorate IYCr2014. There have been several reasons for these developments. The availability of single crystal diffractometers in chemistry departments saw a sharp increase after 2000, when the funding policies for the acquisition of such machines were changed. A number of coordination chemists modified their interests towards a study of coordination polymers and MOFs, along the lines seen elsewhere in the world. The rise of the generic pharmaceutical industry in India post-2005 has resulted in an upsurge of interest in solid forms of active pharmaceutical ingredients, and topics such as polymorphism, cocrystal generation and solvation/hydration began to be investigated in depth. It is to be recorded that a paper in *Cryst. Growth Des.* in 2012 was authored by 35 or so Indian and American researchers⁴⁶ who had gathered for an Indo-US symposium on pharmaceutical solids in Manesar, and that it provided clarifying definitions for the term *pharmaceutical cocrystal* and suggested modifications in FDA guidelines that had been proposed. The Indian contribution to crystal engineering, both of pure organics and of MOFs, is now well established and influential.

6 What is the Future of Chemical Crystallography in India?

Several important papers have appeared in recent times that seem to augur well for the future of chemical crystallography in India. I would like to mention papers that advance new ideas. A recent paper by Guru Row provides good evidence with charge density data for the so-called “carbon bond”,⁴⁷ a concept that was introduced, also recently, by Arunan,⁴⁸ in analogy with the hydrogen bond and a halogen bond.⁴⁹ Nangia has published reviews on solubility of amorphous forms,⁵⁰ and on eutectics⁵¹ formed by organic molecules, both novel approaches, while Natarajan⁵² has written about high throughput screening methods for metal-organic compounds. The link between structure and property is well brought out in papers by Biradha,⁵³ Banerjee⁵⁴ and Reddy.⁵⁵

Traditionally, the Indian contribution has been strong in idea-based research and falls short in equipment intensive research. This has always been our failing, and also in other branches of crystallography, through the decades. The present scenario in crystallography is one where the ready availability of synchrotron radiation has become quite important in many areas of the subject. Chemical crystallography is no exception. For example, any breakthrough in crystal structure determination from X-ray powder data will depend on obtaining high resolution synchrotron powder data. High throughput crystallography and even crystallization studies are influenced by the availability of synchrotrons. In this country, the situation is a truly unfortunate one because after nearly four decades of planning, Indian crystallographers and structural scientists still do not have a ready access to synchrotrons *within the country*. The examples of South America and Australia are relevant. The embryonic crystallographic community in South America is growing rapidly because of the synchrotron facility in Campinas, Brazil which has transformed Latin American crystallography completely. The investment by Australia to have its own synchrotron has kept that country at the academic forefront in several areas of crystallography. Even small countries like Thailand and Singapore seem to have better access to synchrotrons than India. I need not even mention China which has very advanced synchrotron facilities. Much is said in public forums by Indian scientists with decision making ability that more money needs to be put into science. However, these utterances do not seem to have been translated into real things at the ground level. The reasons for these shortcomings have to do with politicians, bureaucrats

and above all, scientists themselves. The lack of a proper and state-of-the-art synchrotron facility in India is a shortcoming that will have the gravest of repercussions in the future. It will affect all areas of structural science. More than the cost, it is now a question of the time required to get a facility like this going and operating in a smooth manner with little to no down time. Without appearing to be unduly pessimistic, I predict that without a coherent policy for synchrotron radiation facilities in India, the present favorable picture with regard to chemical crystallography in India may soon be a forgotten phase.

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