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Perfect chemistry

The nation would remember Prof. Rao as the champion of basic science of Independent India

BY T. PRADEEP

A great teacher, intense researcher, affectionate advisor, caring mentor, careful critic, demanding disciplinarian and visionary institution builder, Prof. C.N.R. Rao, whom the nation has selected for its highest civilian honour, the Bharat Ratna, is all these and much more. I have seen him closely in all these roles for nearly 30 years and, therefore, it is difficult to look at any one of these aspects in isolation.

When I joined him as a joint PhD student (with Prof. M.S. Hegde as my other advisor), Prof. Rao was the director of the Indian Institute of Science (IISc). Though busy, he kept his doors open, whenever I wanted to meet him, which he continues for all his students even today. Once in a while, he would peep into the lab. "Are you there?" he would ask, inviting me to join him for a walk, on his way to the director's office. The walk would take us through different footpaths of the sprawling campus and he would discuss ideas, data, papers, literature, politics and many other things. Occasionally, he would catch me in the morning, while I am rushing to the lab on my bicycle. This was his method of instruction although he never considered it that way. How memorable were those days!

I remember the day I got the first signal from a photoelectron spectrometer that I constructed. Our efforts of two years breathed life into the machine. That was the best spectrum I had ever seen for argon, usually used to check the resolution of the instrument. I

Outstanding effort

Prof. Rao is probably the most prominent materials chemist of modern times. His most important contribution is the establishment of solid state and materials chemistry as a discipline. He started his career at a time when solid state chemistry was rather unknown. He made sustained efforts to nurture the area. The first books on solid state chemistry were written by him. Soon, his research evolved into all modern areas of materials, with deep connections to the emerging frontiers of several areas of natural science, like high-temperature superconductivity. Today, most of his contributions are in the area of nanomaterials, new forms of carbon, hybrid materials and complex oxides. He conducted the best possible science in a relatively less endowed part of the world and contributed to the development of science there and the third world at large, while being part of a larger international endeavour. For this, he nurtured institutions and organisations, both national and international.

He is credited with the isolation of the phase responsible for superconductivity in the YBaCuO system, discovery of Y-junction nanotubes, universal ferromagnetism in nanomaterials, discovery of a diverse array of novel materials such as graphene analogues of BCN [boron carbon nitride], inorganic analogues of nanotubes and graphene, electronic devices of these systems, organic framework solids and many more. Advanced gas phase spectroscopy, understanding of hydrogen bonding and expansion of computational materials science as a discipline, have all been greatly influenced by his contributions.

ILLUSTRATION: JAIRAJ T.G.

placed the graph on Prof. Rao's table. I could see the joy in his eyes. He stood up and fondly stroked my hair, something that he did to convey that you had done well. The second time he did that was when I finished my thesis colloquium. It was, indeed, a fascinating set of results for a PhD thesis.

As this note is about Prof. Rao's science, I must quickly move on.

Chemistry is about molecules and their transformations. For a nonspecialist, describing molecular phenomena can be boring. Therefore, the discussion here will be in more general terms, although a few scientific terms may pop up occasionally.

Prof. Rao is a spectroscopist at heart. He probed chemistry through instrumentation, mostly spectroscopy. Spectroscopy is concerned with light-matter interactions. In a typical experiment, one interrogates matter with a radiation and looks at the changes in the radiation coming out of the specimen. There are diverse methods of spectroscopy which can tell the observer how matter is composed of and how it changes under a given situation.

His PhD problem at Purdue University was on the structure of molecules—how the atoms are arranged with chemical bonds—in the gas phase, using electron diffraction. Diffraction is a process by which particles or light undergo scattering from matter. He showed that the structure of some simple resonating molecules (an example would be carbon suboxide, C_3O_2) is linear, a work cited by Nobel laureate and legendary chemist Linus Pauling in his book, *The Nature of the Chemical Bond*.

Structures stayed with Prof. Rao all through his career. As he moved on from molecules to materials, structure was related strongly to the latter's properties and structure-property correlations became the central theme of his research.

Just after his PhD, Prof. Rao worked on the structure of titanium dioxide, which was his first important work in solid state chemistry. As an independent scientist in India, his early contributions of spectroscopy were to understand phenomena like hydrogen bonds, donor-acceptor interactions, phase transitions, catalysis and metal-insulator transitions. Those were the days of limited infrastructure, but

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unlimited energy.

The science of Prof. Rao evolved from no-infrastructure (in the 1960s) to infrastructure-limited (in the 1980s and 90s) to infrastructure-unlimited (in the 2010s) over the past 60 years. Infrastructure is always limiting for a working scientist as thought goes far beyond, and faster than instruments. Therefore, facilities can never be enough. This change in availability of resources is reflected in his science. One of the important problems he pursued in the early days, soon after he joined the faculty of the IISc, was phase transformations, and the system was decided by the limitations of the X-ray diffractometer available. The camera of the machine could 'see' only two diffractions of titanium dioxide, but that was enough to determine the transformation. Obviously, this study would have been impossible had he chosen another chemical system. He would often stress on the need to choose the problem wisely.

For him, any material in the solid state, anything which has a structure, has been fascinating. The concept of materials itself has evolved in the course of his research life of 60 years. While they were inanimate inorganic objects then—as one would find on a road or on a barren land—today the field of materials encompasses everything that can be seen around us. We ourselves, the biological matter, are now considered part of materials science. From bricks and concrete to plastics, clay and porous catalysts to gels, nanoscale wires to molecular conductors, the field has exploded. Prof. Rao contributed to most of these evolving interfaces of the area. He has stayed at the expanding horizon of the subject. In each one of the giant explosions in this field, such as high-temperature superconductivity, fullerenes and nanotubes, nanomaterials and, recently, graphene, he has made seminal contributions so that the field itself evolved with his science. In many of the other materials, such as open framework solids, he has explored new avenues of applications. In each of them his quest has always been on the changes in properties, as change in itself is the cornerstone of chemistry.

Nation's pride: Prof. Rao with his wife after he was presented with a Mysore peta by Karnataka Chief Minister Siddaramaiah; (left) the author with Prof. Rao

In solid state materials, a big event happened in 1986 with the discovery of high-temperature superconductivity in an oxide system, $La_{2-x}Ba_xCuO_4$, belonging to a family of oxides related to perovskites [a calcium titanium oxide mineral species]. Till then, no one thought that superconductivity, generally associated with metals, is possible with oxides, which are ceramic powders. However, this indeed happened and became one of the most fascinating areas of physics, materials science and solid state chemistry.

The parent chemical system La_2CuO_4 was studied by Prof. Rao earlier. He had, in fact, shown that the system is antiferromagnetic, a property

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Pinnacle of glory

Prof. Chintamani Nagesa Ramachandra Rao
Born: June 30, 1934
Chairman, Scientific Advisory Council to the Prime Minister

Education
MSc, BHU (1953)
PhD, Purdue University (1958)
DSc, Mysore University (1960)

Research interests
Solid state and materials chemistry, structural chemistry
Honorary doctorate from 51 universities
Author of nearly 1,500 research papers
Author/editor/co-editor of 48 books

Awards
Third scientist to win Bharat Ratna
Padma Shri (1974)
Padma Vibhushan (1985)
India Science Prize (2004)
Legion of Honour, France (2005)
Order of Friendship, Russia (2009)
The Queen's Medal by the Royal Society, London (2009)
Award for International Science Cooperation, China (2012)

of the oxide. However, infrastructure allowed him to pursue the properties only down to liquid nitrogen temperatures, while superconductivity was discovered at much lower temperatures. However, the Bangalore team identified the superconducting phase $YBa_2Cu_3O_7$, which showed superconductivity at liquid nitrogen temperature. This was published in *Nature* dated April 30, 1987.

The materials science wave expanded into fullerenes [a family of carbon allotropes, named after Buckminster Fuller]. They were made in Bangalore within one month of the publication of the original paper, using a new apparatus. The very first N[nitrogen]-doped fullerenes were discovered in Bangalore. The research soon expanded to carbon nanotubes, where a unique Y-junction was found by a simple reaction during the growth process, which turned out to be the smallest device to achieve rectification. The research on one-dimensional nanostructures expanded to inorganic nanotubes and several modifications of one-dimensional systems.

A natural extension of nanotubes was graphene, the planar one-atom thick sheets of carbon, which was the subject of the Nobel Prize of 2010, wherein several surprises were found in Bangalore. One such surprise was a large synergy in mechanical properties when graphene was combined with nano-diamonds.

Prof. Rao's recent interests extend to areas such as splitting of water using solar energy, problems of environmental remediation such as carbon dioxide sequestration, unusual chemical processes at nanomaterials and chemistry at interfaces.

When we observe Prof. Rao's work from a distance, it is evident that he entered into an area while it was nascent and he expanded it to an established discipline and then left it for others to explore further. Though he found several phenomena in his research career, they were not pursued for industrial exploitation, possibly because, either industry was not ready in most cases, or an application could not be made market-ready in the time normally expected by the industry. Significantly, in each of those areas, he produced a talent pool which expanded and established the subject far and wide. While infrastructure was created in his lab, he allowed the establishment of similar facilities all over the country so that advanced research could be conducted by all. As excellence disappeared in the universities, he nurtured new institutions. Prof. Rao as an individual is inseparable from the institutions he built. They remind us of the vision of the founder. While he built his own science, with equal or more passion, he built science of others through such institutions. The institutions he built were not only physical entities, they were also virtual. He also founded several professional societies and all of them are doing well.

Prof. Rao guided a large number of PhD students—155 of them in all. He has the largest number of scientific collaborators, explored the widest variety of problems and, of course, established the largest array of tools for the investigation of materials. His students built their groups and the chain continues.

The nation would remember him as the champion of basic science of Independent India.

The writer is a professor at the Indian Institute of Technology Madras.