The all-chemist

Linus Pauling set the agenda for a century of chemical research.

Gautam R. Desiraju

All of chemistry is a fugue between the statics of structure and the dynamics of reaction, and at its very core lies the covalent bond. Physics and chemistry went hand in hand until the early decades of this century, when the ionic bond followed from Niels Bohr's model of the atom. But it was only when the idea of electron sharing was accepted and quantified that the chemical bond came into its very own. Chemistry had no further need of physics for the rest of the century. This extrapolation from physics to chemistry and the articulation of chemistry as an independent subject was the handiwork of a single individual. Linus Pauling ranks with Galileo, Da Vinci, Shakespeare, Newton, Bach, Faraday, Freud and Einstein as one of the great thinkers and visionaries of the millennium. Truly he was not of this age, but for all time.

Pauling's ingenuity and awesome intuition permeated quantum mechanics, crystallography, biology, medicine and, above all, structural chemistry. He was curiously silent on organic chemistry, even after enunciating its most fundamental feature, namely that a sharing out of electrons evenly among equivalent energy states — the hybridization of bond orbitals — explains the tetrahedral valences of the saturated carbon atom. His influence on inorganic chemistry was profound. Hybrid orbitals were spectacularly successful in explaining the magnetic properties of transition-metal coordination compounds and the structural vagaries of organometallic complexes.

The late nineteenth and early twentieth centuries saw the growth of the molecular paradigm in the hands of the grandmasters. August Kekulé, Adolf von Baeyer and Richard Willstätter, among others, developed the idea of the simple molecule, and the inorganic chemist Alfred Werner took this forward to the extended molecule in his description of coordination compounds. Pauling's early work brought all of this within a common model and in so doing effected a grand unification of molecular structure.

In retrospect, it appears that chemistry was waiting for Pauling. His chapters in *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, one of the most influential books of the twentieth century, proceed almost ruthlessly through interatomic distances, electronegativity, ionic, covalent and van der Waals radii, aromaticity and the structure of benzene, multiple bonds, electron-deficient substances, the metallic bond and the hydrogen bond. They were a route map for chemical research for the rest of the century.

CALTECH

All-conquering: the next generation of chemists must escape from Pauling's shadow.

Pauling did not work directly on the dynamics of chemical reactions, but the implications of his work on the subject are all too apparent, for unless one understands the molecule at rest, one cannot begin to comprehend it as it stirs. Chemistry grew and prospered simply by proving time and again that Pauling was correct in just about all his conjectures, for he projected with unerring accuracy into the future with only about 0.01% of today's structural information.

Chemistry, then, is utterly different from physics and biology in its dependence, at a primal level, on just one scientist. This raises some awkward questions. Did Pauling's influence modify, divert or even stunt the development of other, perhaps still unexplored or unidentified, branches of the subject? Are chemists introverted and cautious because much of their research flows from a single stream of consciousness, making big imaginative leaps unnecessary? Does chemistry lack the high drama of physics and the glamour of biology because these were appropriated by one larger than life individual?

These questions are not completely frivolous. Pauling elevated the molecule to the high altar and it became the delimiter of all the important properties of a substance, to the extent that there was no world outside it. This could account for the relatively late take-off of supramolecular chemistry, nearly 70 years after Emil Fischer enunciated his lock-and-key principle and Paul Pfeiffer described the first molecular complexes. Again, the central position given to the covalent bond could account for solid-state chemistry's struggle to join the mainstream. Even today, computational chemistry is largely concerned with discrete molecular systems. As for structural chemistry, the phenomenon of hydrogen bonding did not allow for weak donors and acceptors for decades, mostly because Pauling had said that only strong donors and acceptors could form these bonds.

To paraphrase Jean-Marie Lehn, chemistry is all about diversity, whereas biology revels in complexity. Pauling's work does not fade with ever-increasing chemical diversity, for it is too fundamental with respect to structure. It is as chemistry moves from the molecule towards the study of complex systems that chemists will have to think beyond Pauling. Very short timescales, very large length and dimension scales and the intersection of chemistry with materials science and biology will hold chemists' attention. Chemistry will become a different subject as it transforms from a unitary to a diversified science. Will it ultimately delocalize and dissolve into other disciplines? Only time will tell, but if it does, it would only be because its very identity depended for so long on the contributions of a single individual. ■

Gautam R. Desiraju is in the School of Chemistry, University of Hyderabad, Hyderabad 500 046, India.