

### Jack Dunitz -- The Early Years

In this autobiographical narrative Jack D. Dunitz describes his education and early "itinerant" research at Oxford, Caltech, and the Royal Institution. After these experiences he went on to an illustrious career as Professor of Chemical Crystallography at the Swiss Federal Institute of Technology (ETH), retiring in 1990 after 33 years. Jack is a Fellow of the Royal Society of London and the American Association for the Advancement of Science; he is a Foreign Associate of the US National Academy of Sciences and a Foreign Member of the American Philosophical Society. Among his many honors are the Paracelsus Prize (Swiss Chemical Society), the Arthur C. Cope Scholar Award (American Chemical Society) and the Buerger Award (ACA). He has published more than 350 articles. He is the author of the classic "X-ray analysis and the structure of organic molecules" and the co-author with Edgar Heilbronner of "Reflections on symmetry: in chemistry-- and elsewhere".



**Jack receiving the 1991 ACA Buerger Award from Judith Flippen-Anderson.**

I have had the enormous good fortune to spend my time more or less as I liked to spend it — in inventing and solving scientific problems, mainly in structural chemistry — problems that to the best of my knowledge have had no practical relevance, either for good or for evil. The last half-century has probably been the only time in history when such a thing was possible; when a person of modest abilities could enjoy a comfortable existence doing whatever seemed interesting. I feel I have been tremendously fortunate.

I do not remember ever having made a conscious choice or decision to follow a career in science. It just happened, as in a dream. In a dream you don't do things, things happen to you. Near the beginning, during the early 1940's, I was a student of chemistry at Glasgow University, ignorant not only of chemistry but of almost everything else, an innocent in every way one can imagine. I did not choose chemistry. My mother would have liked me to study medicine, my headmaster tried to push me into the study of classics. I did not much fancy either of these possibilities. The science teacher at my school, John McLennan, chose chemistry for me by making it interesting. Likewise, I did not choose crystallography. Crystallography chose me. As a frustrated mathematician, my interests were mainly in physical chemistry. After a somewhat compressed wartime three-year crash course in chemistry, most of the Phys. Chem. students were funneled off for work about which they were not allowed to talk (now we know it was radar research), but in 1943 John Monteath Robert-

son returned to Glasgow as newly appointed Gardiner Professor and needed a few doctoral students to carry out work in x-ray crystallography and molecular structure studies. At that time and place, there was no question of a student choosing a research supervisor or a line of research. It was still wartime. "You, you and you will report for duty at such and such a locality, you, you and you will stay on here and work for Robertson" and so it was that I came to chemical crystallography. As Robertson was much away on official duties, and as there was no formal post-graduate course of study, we doctoral students taught one another what we had taught ourselves about the theory and practice of crystal structure analysis.

After my arrival as a post-doctoral researcher in Dorothy Hodgkin's laboratory at Oxford in late 1946, I practiced my skill in trial-and-error analysis by determining the crystal structure of the centrosymmetric isomer of 1,2,3,4-tetraphenylcyclobutane in projection down the short (5.77 Å) monoclinic axis and then also tested my endurance by calculating lines and sections of the three-dimensional electron density distribution, based on visual estimates of all photographically recorded reflections within the  $\text{CuK}\alpha$  sphere of reciprocal space. From today's perspective, when the measurements could be made in a few hours and the calculations in a few seconds, it is hard to imagine how much drudgery was involved in such an exploit in those days, working with paper, pencil and Beevers-Lipson strips. Why on earth did I take it on, and why did I persist? No one was pushing me. Perhaps I merely wanted to show that I could do it.

My tetraphenylcyclobutane work did not bring me fame but it did bring me to Caltech. Indirectly. From my results, the bond distances in the cyclobutane ring appeared to be longer than the standard carbon-carbon single-bond distance of 1.54 Å, while those in the phenyl groups were normal for benzene rings. However, according to the recently developed "bent bond" model, bonds in small carbocyclic rings were expected to be slightly shorter than the 1.54 Å, as had been found, indeed, for cyclopropane and spiro-pentane from gas-phase electron diffraction. Were the long bonds found in tetraphenylcyclobutane an intrinsic property of the cyclobutane ring? Or were they in some way connected

with the presence of the four phenyl substituents? Or were they merely attributable to experimental error? When I discussed this problem with Verner Schomaker during his visit to Oxford in the early summer of 1948, we decided that the problem called for a gas-phase electron diffraction study of cyclobutane itself. I was interested in learning this technique, and, through Schomaker's intervention, Pauling offered me a research fellowship to come to Caltech.



**Jack at Caltech, 1948 (from the Ava Helen and Linus Pauling Papers, Special Collections & Archives Research Center, Oregon State University).**

Our gas-phase electron-diffraction study of cyclobutane confirmed my supposition that the carbon-carbon bonds were long. Moreover, contrary to what had been generally assumed until then, the four-membered ring was not a planar square but was buckled ( $D_{2d}$  rather than  $D_{4h}$  symmetry). The reason for the striking difference between the C—C bond distances in cyclopropane (1.51 Å) and cyclobutane (1.57 Å) is that in the former there are no non-bonded 1,3-interactions, whereas the four-membered ring shows the strongest possible interactions of this type, which are, of course, strongly repulsive. It was a great experience to work with Verner Schomaker, to argue with him, and, more than anything, to share with him the writing of a scientific paper. Our cyclobutane paper took ages to write, but, as compensation, after almost 50 years, I am still pleased with the result. Among other things, that publication contained what must have been one of the earliest force-field calculations, and also a carefully qualified sentence defining what we meant by the term “bent bond”: “It appears that this argument might be expressed in terms of the significant existence of a bond line, to be distinguished from the internuclear (straight) line, which more or less follows a line of maximum density of the bonding electron distribution, and which, in the bent bond, tends to retain a fixed length, thereby possibly causing the internuclear distance to be shortened in spite of the resulting increased internuclear repulsion.”



*Model of cyclobutane showing the puckered ring - courtesy of Jeff Deschamps.*

More than thirty years later, when bent bonds had become fashionable and had showed up in Bader's theory of chemical bonding, this definition received a seal of approval when it was reproduced in one of Bader's papers. Not many sentences in the scientific literature are deemed to be worth repeating after thirty years.

Pauling had a feeling for drama. At the lecture where Pauling first publicly announced his stable hydrogen-bonded model structures for polypeptide chains, on the table in front of him stood bulky columnar objects shrouded in cloth, which naturally excited the curiosity of those in the packed auditorium. Only after describing in detail the structural principles behind the models did he turn to the table and unveil the molecular models with a characteristic theatrical gesture. There were the two structures, the three-residue and the five-residue spirals, later dubbed the  $\alpha$ - and  $\gamma$ -helices! I was immediately converted, a believer right from the start.

While my own work at Caltech had nothing to do with protein structure, Pauling used to talk to me occasionally about his models and what one could learn from them. In his lecture, he had talked about spirals. In conversation a few days later, I told him that for me the word “spiral” referred to a curve in a plane. As his polypeptide coils were three-dimensional figures, I suggested they were better described as “helices”. Pauling's erudition did not stop at the natural sciences. He answered, quite correctly, that the words “spiral” and “helix” are practically synonymous and can be used almost interchangeably, but he thanked me for my suggestion because he preferred “helix” and declared that he would always use it henceforth. Perhaps he felt that by calling his

structure a helix there would be less risk of confusion with the various other models that had been proposed earlier. There was no going back. A few years later we had the DNA double helix, not the DNA double spiral. The formulation of the  $\alpha$ -helix was the first and is still one of the greatest triumphs of speculative model building in molecular biology, and I am pleased that I helped to give it its name.



*Friends from Caltech days, Jim Ibers and Jack in Zurich (summer 1989, courtesy of Carol Brock).*

Back in Oxford in Dorothy Hodgkin's lab, I came across an astonishing proposal from a group of Harvard chemists (Wilkinson, Rosenblum, Whiting, and Woodward) for the structure of the recently obtained compound,  $C_{10}H_{10}Fe$ : two parallel cyclopentadienyl rings with the iron atom sandwiched between them. The only physico-chemical evidence offered for this unprecedented structure was the infrared absorption spectrum, which contained, in the 3-4  $\mu$  region, a single, sharp band at 3.25  $\mu$ , indicating the presence of only one type of C—H bond. It may be difficult today to appreciate just how surprising, unorthodox, even revolutionary, this structure was at the time. At any rate, my first reaction was one of extreme skepticism. On my way out of the library I met my friend Leslie Orgel, at that time holder of a research fellowship at Magdalen College, and asked if he had seen the remarkable structure proposed in the latest *JACS* number. We retrieved the journal and re-read the article together. He was as skeptical as I was. When we learned that the compound was relatively easy to prepare in crystalline form, we decided to make it and determine the crystal and molecular structure. Or rather, since neither of us had access to facilities in a synthetic laboratory, we decided to try to persuade a friendly organic chemist Hugh Cardwell to carry out the relatively straightforward synthesis.

I made optical measurements on crystals of the new compound on June 9th, 1952 and began to make preliminary x-ray photographs the following day. I soon found that the crystals slowly sublimed in the atmosphere at room temperature and had to be sealed into glass capillary tubes. From the space group alone it was evident that the molecule must sit at a crystallographic center of symmetry. By the end of the following week, I had made enough intensity measurements to produce two electron-density projections down mutually perpendicular directions. This was possible because, fortunately for me, there was a slack period in the laboratory so that not only one but two x-ray Weissenberg cameras were free for my use. Of course, to get all this done on my own, I had to work long hours, during the evenings and over the weekend too. As the structure began to emerge from the electron-density maps, calculated with Beevers-Lipson strips with the aid of an adding machine, I was becoming so excited that I was working through most of the night as well. By the end

of the following week, the structure was solved. Extraordinary as it seemed to me, the Harvard proposal was correct. The rings were parallel, with the iron atom sandwiched between them at a crystallographic center of symmetry. There was no doubt about it. That was the marvelous thing about crystal structure analysis. When it worked, the result had a satisfying definiteness about it. Even though this aura of definiteness could sometimes be misleading! The crystalline structure of ferrocene occupied me, on and off, for more than thirty years. Later, the apparently staggered orientation of the cyclopentadienyl rings was revealed to be an artifact resulting from crystal disorder. Ferrocene turned out to be trimorphic — at least — and the ring orientation in the low-temperature stable polymorph is eclipsed not staggered.

Back to 1952; there was still the question of how to account for the new kind of bonding in this extraordinary molecular structure. How can the iron atom simultaneously make ten Fe—C bonds? How could the tenfold symmetry be reconciled with the well known tendency of  $\text{Fe}^{2+}$  to form 4- or 6-coordinated complexes? Faced with this challenge, within a few days Leslie developed an explanation based on orbital symmetry properties, on the relationships between the symmetry properties of the d-orbitals of the metal atom and the  $\pi$ -molecular orbitals of the cyclopentadienyl rings. This was new terrain. This new type of molecule required a new type of description of its bonding, and Leslie's model, formal and over-simplified as it was, expressed the essence of this. When it was first explained to me I did not understand a word, but by the end of the week I had picked up enough of the group theoretical background of this new language to construct simple statements on my own. In particular, I could see that the model was a generalization of the standard molecular orbital (MO) model of benzene and other aromatic systems. So we wrote a paper, covering both the structure determination and the new theoretical model, and sent it off to *Nature* on July 2nd, less than a month after we had the crystals, under the provocative title, "Bis-cyclopentadienyl Iron: a Molecular Sandwich". That was the first time, I believe, that this gastronomic epithet had been used in the title of a chemical publication. The name certainly stuck.

Since the same symmetry arguments as we applied to ferrocene could be applied *mutatis mutandis* to the then still unknown and scarcely imagined molecules dibenzene chromium and dicyclobutadiene nickel, Orgel wanted to include in our paper his prediction that these molecules would turn out to be stable species. I argued that it would be a pity to spoil a good, solid paper by what could be regarded as risky speculation and managed to persuade him to omit the additional paragraphs. As Leslie later ruefully remarked, one characteristic of our collaboration was that we sometimes succeeded in shooting down each other's best ideas.



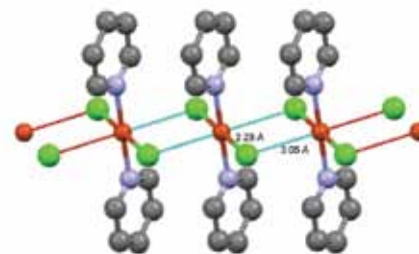
*Jack and Barbara Steuer were married in 1953 (summer 1985, courtesy of Carol Brock).*

Besides our work on ferrocene, Orgel and I wrote a paper about hydrogen bonds. It was then generally considered that O—H...O hydrogen bonds were unsymmetrical, with the hydrogen atom closer to one oxygen atom than to the other. We proposed that the acid maleate anion should have an unusually strong, symmetrical hydrogen bond, and backed this up with spectroscopic observations on crystalline potassium hydrogen maleate. Our proposal was subsequently confirmed by neutron diffraction studies. This may be the first example of what came to be known much later as a low barrier hydrogen bond.

In April 1955, Sir Lawrence Bragg offered me a five-year appointment as Senior Research Fellow at the Davy-Faraday Research Laboratory at the Royal Institution. There I decided to study the crystal structures of cobalt dipyridine dichloride,  $\text{CoPy}_2\text{Cl}_2$  and its copper analogue  $\text{CuPy}_2\text{Cl}_2$ . There were two known forms of the cobalt compound, one violet colored, the other blue. The blue form was known to contain discrete molecules with tetrahedral bonds at the cobalt atom, while the violet form was believed to contain polymeric chains with octahedral bonds at the cobalt atom, each chloride ion linked to two cobalts, each cobalt to four equidistant chloride ions and to the pyridines. Indeed, this turned out to be the case. The copper compound was found to have a very similar structure, except that the four chloride ions were not equidistant from the metal atom; instead, there were two short Cu—Cl bonds and two long ones.

This result led to another collaboration with Leslie Orgel, who, a couple of years earlier, had suggested that such distortions of octahedral complexes could be interpreted in terms of crystal-field theory as structural expressions of the Jahn-Teller effect. The differences between the octahedral coordination in the cobalt compound and the distorted octahedral coordination in the copper compound seemed a perfect illustration of this, and I soon found that similar differences between other pairs of structurally related compounds occurred according to a quite regular pattern. We also saw that crystal field theory could be applied to minerals with the spinel structure. Spinel is a mineral with composition  $\text{MgAl}_2\text{O}_4$ , built from a cubic close-packed arrangement of oxygen atoms with the  $\text{Mg}^{2+}$  ions at tetrahedral cavity sites and the  $\text{Al}^{3+}$  ions at octahedral ones. There are many other  $\text{AB}_2\text{O}_4$  minerals with essentially the same structure, with the  $\text{A}^{3+}$  ions in tetrahedral sites and  $\text{B}^{3+}$  ions in octahedral ones. However, in "inverted" spinels the tetrahedral sites are occupied by  $\text{B}^{3+}$  ions, with the  $\text{A}^{2+}$  ions and the remaining  $\text{B}^{3+}$  ions distributed at random over octahedral sites. We found we could explain all the known experimental evidence on the metal ion distributions in the normal and inverted spinels.

Moreover, the existence of tetragonally deformed spinels could also be explained by our theory in terms of the Jahn-Teller distortions expected to occur when certain metal ions were present. When I told Bragg about these results he



*The structure of  $\text{CuPy}_2\text{Cl}_2$  showing two Cu—Cl distances (drawn by Jeff Deschamps from CSD PYRCUC01).*



was delighted. He was just then working on a new edition of his classic *The Crystal Structures of Minerals* and could now include an explanation of the problem of the inverted and tetragonally distorted spinels.



*Jack with A.I. Kitaigorodskii and Olga Kennard, 1970s (from the Jack Dunitz Papers, Special Collections & Archives Research Center, Oregon State University).*

In December 1956 Edgar Heilbronner telephoned out of the blue to ask if I could come to Zurich to talk to Professor Leopold Ruzicka about the possibility of my starting a crystal structure analysis group at the Swiss Federal Institute of Technology (ETH Zurich). Ruzicka was due to retire the following October from his position as Professor of Organic Chemistry. Impressed by Dorothy Hodgkin's success in deciphering the structure of vitamin B<sub>12</sub>, he saw that a strong organic chemistry team would be incomplete without this new method. Ruzicka offered me a post

as associate professor and gave me fourteen days to decide. A few days before the end of the year I sent a telegram to Ruzicka to accept the offer. Thus, after only a year and a half in London, I landed in 1957 at the Organic Chemistry Laboratory of the ETH in Zurich, to join an illustrious group of natural philosophers there, my friends and colleagues for the last fifty years and more, during which we have argued and discussed and learned together about chemistry and molecular structure and about everything else under the sun.



*Jenny Glusker, Jack, and Carol Brock at the 40th anniversary celebration of CCDC (2005, courtesy of Carol Brock).*

*Editor's note: An extended version of this narrative appeared recently in *Helvetica Chimica Acta* (2013, **96**, 545). Also see [scarc.library.oregonstate.edu/coll/dunitz/primavera/page1.html](http://scarc.library.oregonstate.edu/coll/dunitz/primavera/page1.html). The complete version of Jack's narrative for ACA will be deposited at the Niels Bohr Library & Archives and will also appear on the planned ACA History website.*